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PAPER #1

LITHOGEOCHEMICAL AND MINERALOGICAL METHODS FOR BASE METAL AND GOLD EXPLORATION

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GEOLOGICAL SURVEY OF CANADA
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Abstract

Specific criteria used for exploration for new ore may be derived from genetic models. These might include specific lithological assemblages, fractionation trends, alteration assemblages and ore-controlling structures, for example. Three "lithogeochemical" methods of use in exploration include: diagnostic petrogenetic trends, obtained from geographical or statistical analyses of major and minor element data; diagnostic mineral assemblages, obtained through petrographic and XRD analyses; and specific elemental signatures (gains, losses, and isotopic shifts), also obtained from analytical data.

Volcanogenic massive sulfide deposits formed from high-temperature metalliferous fluids generated in the sub-seafloor through heating (from a subvolcanic intrusion) of down-welling seawater. Both the subvolcanic intrusions and related volcanic rocks have somewhat aberrant petrochemical trends, caused by unusually rapid heat removal to the hydrothermal, system; extensive fractionation is evident in both major element and REE trends. Alteration includes lower semi-conformable horizons, albite-epidote-actinolite-quartz zones, and under some deposits, broad carbonatized zones. Alteration pipes vary from those with cores of Fe-chorite and silica and rims of Mg-chlorite (after smectite), through Mg-chlorite core and sericite-rim pipes, to silica-sericite^{+}/-Fe-carbonate pipes. All are Na-, Ca- and Sr-depleted.

Lode-gold deposits are associated with major transgressive (typically high-angle reverse) fault zones. Vein systems typically occur either in dilational jogs, near fault terminations, or at contacts between units with high ductility contrast. Regional alteration is dominated by CO_2 addition. Fe-dolomite and/or ankerite are most common near the deposits, but dolomite or calcite form the regionally-developed alteration assemblage. Sphene occurs distally, but rutile is common near vein systems. Sericite and albite or K-spar occur within a few 10's of metres or less of the deposits.

Magmatic sulphide deposits formed by segregation of immiscible sulphide liquid from a parent mafic or ultramafic magma. Deposits occur in intrusions and flows with unusually high Mg/Fe ratios. Ni is depleted relative to Mg in fertile intrusions. Olivine in "barren" intrusions is rich in Ni, compared with "fertile" intrusions. Because sulphur saturation is promoted by assimilation of sulphur from an external source, Se/S ratios are higher in ore-bearing intrusions. Sulphur isotopes may deviate strongly from mantle compositions because of assimilation, particularly in post-Archean intrusions.

Résumé

Certains critères utilisés pour l'exploration de nouveaux minerais peuvent être tirés de modèles génétiques. Ceux-ci peuvent être, entre autres, des assemblages lithologiques spécifiques, des tendances de fractionnement, des assemblages d'altération et des structures de contrôle du minerai. Les trois méthodes "lithogéochimiques" suivantes sont utilisées en exploration: les tendances pétrogénétiques diagnostiques, obtenues à partir d'analyses graphiques ou statistiques de données des éléments dominants et secondaires; les assemblages de minéraux d'altération diagnostiques, obtenus par des analyses pétrographiques et de diffraction des rayons X; et les signatures spécifiques d'éléments (gains, pertes et déplacements isotopiques), également obtenus à partir de données analytiques.

Les gisements de sulfures massifs d'origine volcanique se sont formés à partir de fluides métallifères à haute température produits par chauffage dans des couches suboéaniques (à partir d'une intrusion hypovolcanique) d'eau de mer descendante. Les intrusions hypovolcaniques et les roches volcaniques associées présentent des tendances pétrochimiques quelque peu aberrantes, causées par une élimination inhabituellement rapide de la chaleur dans le système hydrothermal; on observe un fractionnement poussé dans les tendances des éléments principaux et des terres rares. L'altération se traduit par des horizons inférieurs semi-concordants, des zones d'albite-épidote-actinote-quartz et, dans certains dépôts, par de grandes zones carbonatées. Les cheminées d'altération varient en composition: les unes ont des noyaux de chlorite ferrugineuse et de silice et des bordures de chlorite magnésienne (après smectite). D'autres ont des noyaux de chlorite magnésienne avec des bordures de séricite et, enfin, certaines sont formées de silice-séricite avec plus ou moins de carbonate de fer. Elles sont toutes appauvries en Na, Ca et Sr.

Les gisements aurifères filoniens sont associés à d'importantes zones de failles de transpression (en général, des failles inverses à angle élevé). Les filons sont habituellement présents soit dans des ressauts de dilatation, près de l'extrémité des failles, ou aux contacts entre les unités à fort contraste de ductilité. L'altération générale est caractérisée par un supplément de CO_2. La teneur en dolomie ferrugineuse et/ou en ankérite est plus élevée près des gisements, mais la dolomie et la calcite forment l'assemblage d'altération régionale. Le sphène est présent à distance mais le rutile se retrouve près des systèmes filoniens. La

séricite et l'albite ou le feldspath potassique sont présents à moins de quelques dizaines de mètres des gisements.

Les gisements de sulfures magmatiques se sont formés par la ségrégation d'un liquide de sulfures non miscible à partir d'un magma mafique ou ultramafique. Les gisements sont localisés dans des intrusions et des coulées ayant les rapports Mg/Fe inhabituellement élevés. Le Ni est appauvri par rapport au Mg dans les intrusions fertiles. L'olivine, dans les intrusions "stériles", est riche en Ni, comparativement aux intrusions "fertiles". Étant donné que la saturation du soufre est favorisée par l'assimilation de soufre par une source externe, les rapports Se/S sont plus élevés dans les intrusions minéralisées. Les isotopes de soufre peuvent dévier fortement en composition de ceux du manteau en raison de leur assimilation, en particulier dans les intrusions post-archéennes.

INTRODUCTION

The ease of discovery of new orebodies is decreasing as the limits of "conventional" technology are reached. Conventional prospecting and airborne geophysical surveying will continue to assist in finding new ore, but with the need to look beneath deep overburden, or to find resources within the upper two kilometres of the crust, a multi-disciplinary approach to exploration is imperative.

The search for new ore must start with an exhaustive application of geological principles. Effective ore deposits research has always had a firm underpinning of good mapping. Exploration companies rely on accurate maps as the basis for selection of prospective areas. Mappers should be aware of the principal geological attributes of ore-bearing areas, and specifically record these on their maps, if these maps are to be of maximum use to the exploration industry. Identification of these attributes usually results from ore-deposits research. For some deposit types, the best tools at our disposal are the critical geological attributes. For example, knowledge of the sedimentological characteristics of paleoplacer-associated (Elliot Lake-type) uranium and gold deposits has been widely applied in finding additional deposits. Mapping that includes analysis of sedimentary facies as well as close attention to stratigraphic detail is essential in exploration for additional deposits of the paleoplacer type.

Today, a multitude of research techniques, including intensive petrochemical, mineralogical and isotopic techniques are usually brought to bear on an ore-genesis problem. The results of research are to produce a geological model for the formation of any ore deposit type. These models are continually evolving, and occasionally take a major evolutionary leap. They are only useful if they identify specific geological attributes that can be used in determining areas of high ore potential. Critical lithological assemblages, specific fractionation trends, and diagnostic alteration assemblages are examples of attributes that were originally documented during the quest for genetic models, but have important application in exploration for new ore.

This review can only touch on a few deposit types. The applicability of lithogeochemical and mineralogical methods to exploration is highly dependant on deposit type. For example, the well-documented mineralogical and chemical characteristics of alteration associated with both porphyry copper/molybdenum and volcanogenic massive sulphide deposits have been used very effectively as an exploration tool for many years. Unique fractionation trends, the presence of magmatic sulphide minerals, and anomalous Se/S ratios can be applied in the search for magmatic sulphide ores. Alteration associated with vein-gold deposits, however, has more limited application. For the latter deposit type, a good understanding of structural control has proven to be the most useful tool in finding new resources, particularly in established districts.

The deposit types to be reviewed here are those specific to the Canadian Shield, and primarily those associated with greenstone belts.

VOLCANOGENIC MASSIVE SULPHIDE DEPOSITS

Volcanic-associated deposits occur in terrains dominated by volcanic rocks; the deposits are typically in volcanic strata, but may also be in or near sedimentary strata that are an integral part of a volcanic complex. Volcanic-associated deposits contain variable amounts of economically-recoverable copper, zinc, lead, silver and gold. Their close spatial (and probably genetic) association with volcanic rocks has prompted the use of the classification term "Volcanogenic Massive Sulphide deposits", or "VMS deposits" as their most common acronym.

VMS deposits occur as two compositional classes, the copper-zinc and zinc-lead-copper groups (Franklin et al., 1981). Archean deposits of the copper-zinc group have been further divided into two types (Morton and Franklin, 1987): one typified by the deposits in the Sturgeon Lake area ("Mattabi-type"); and, the other by deposits at Noranda and Mattagami Lake, P.Q. ("Noranda type"). Although this subdivision is subject to revision, each of its types displays distinctive compositional and alteration aspects. Consequently, mineralogical and petrochemical criteria used as exploration guides must be sufficiently extensive to include both sub-types of deposits.

Some of the geological attributes (Figure 1) that are of use in exploring for VMS deposits include :

1. Presence of submarine volcanic strata; paleo-water depth controls some variations in volcanic morphology, as well as alteration assemblages and ore composition. Volcanological studies provide useful information to help determine which assemblages and compositions to expect.

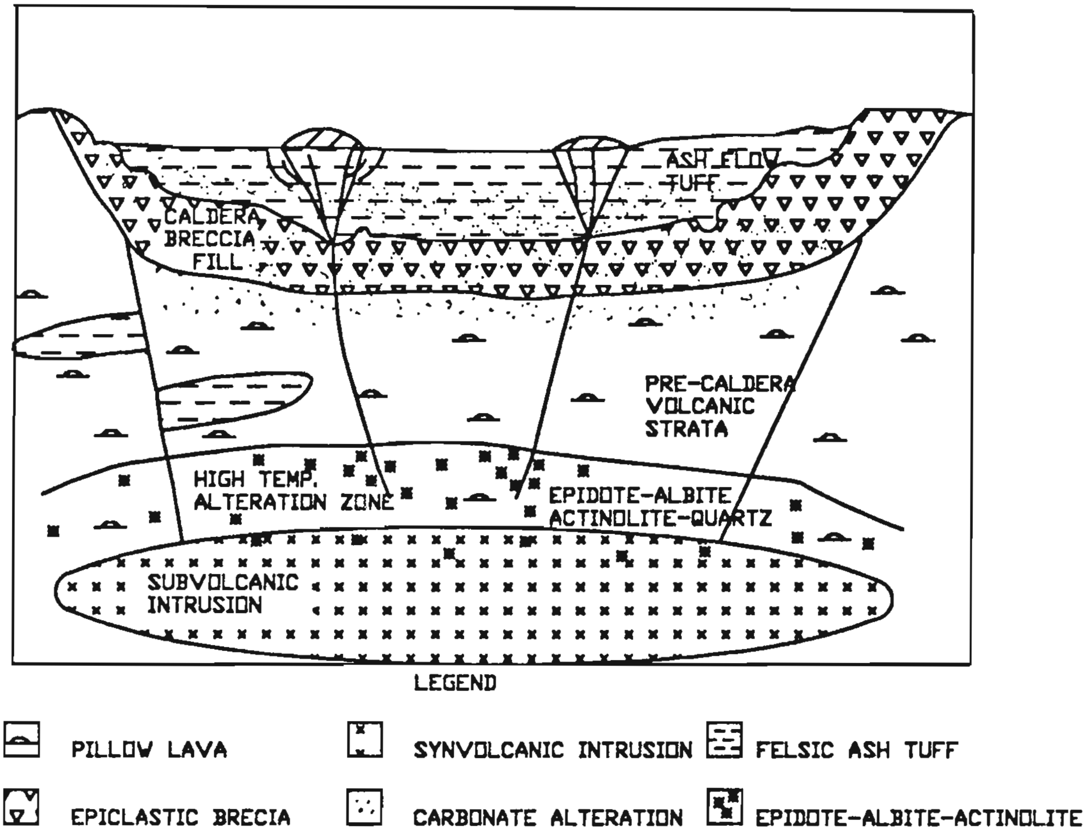

Figure 1. *Composite section through a volcanogenic massive sulphide system. Note locally advecting seawater near the deposit, which could form a Na-depleted, Mg-enriched alteration zone. The scale of this alteration depends on the longevity of the system, as well as the physical nature of the footwall rocks.*

2. Presence of a sub-volcanic magma chamber at shallow crustal levels (ca. 2 km). These can be any composition represented in the overlying volcanic rocks, and are: a) sill-like, but locally transect stratigraphy; b) texturally variable, composite intrusions, formed through multiple recharges of the magma chamber; c) highly fractionated, with "reverse zonation" common in felsic intrusions; mafic portions are more abundant along their top (as irregular pods) and ends; d) devoid of a significant metamorphic halo relative to intrusions emplaced at deeper, drier crustal levels; e) potential hosts to very low grade porphyry-copper zones that are superimposed on all rock types.

3. Presence of high-temperature reaction zones (one form of semi-conformable alteration) within about 1.5 km of the subvolcanic intrusions. Quartz-epidote-albite alteration, commonly mistakenly mapped as intermediate to felsic rocks, is prevalent under many copper-zinc deposits.

4. Presence of laterally extensive carbonatized volcanic strata that are depleted in sodium near deposits that formed in relatively shallow water (accompanied by explosion breccia, debris flows, some subaerial volcanic products). These possibly represent the zone where ambient seawater reacted with the upper part of the hydrothermal reservoir.

5. Syn-volcanic faults that are recognizable because: a) they do not extend far into the hangingwall of most deposits; b) they are commonly altered, with pipe-like distribution of mineral assemblages, in their stratigraphically highest portions; c) they may have asymmetric zones of growth-fault-induced talus; and, d) they may be locally occupied by syn-volcanic dykes.

Virtually all of these formed in tensional tectonic regimes, and may be listric. Some may be related to caldera margins, and thus curvilinear; others may be margins of elongate axial summit depressions (grabens), and sub-parallel to the axis of spreading (Kappel and Franklin, 1989).

6. Alteration pipes may have sufficient vertical stratigraphic extent to be mappable. The volcanic rocks in virtually all pipes are sodium depleted, but mineralogical characteristics vary. Most commonly, rocks are silicified near the deposits, sericitized less locally, and have variable amounts of both Mg- and Fe-rich chlorite or smectite. Less commonly, but important in many Cu-Zn districts, the pipes may have intensely chloritized cores, with sericitic rims. Peripheral to the distinctive pipes, there is commonly a broad zone of more subtly altered rock; smectite and zeolite minerals may be important. Chemical changes in these latter alteration zones may be very subtle, requiring mineralogical or isotopic studies to detect them.

Metamorphosed pipe assemblages are usually relatively easy to recognize. Typically, rocks in Mg-enriched pipes have been recrystallized to anthophyllite and cordierite. Adjacent, less intensely altered rocks may contain staurolite. Gahnite and Mn-rich garnets may be important accessories. The relatively high ductility of altered volcanic rocks compared with their hosts resulted in exceptional deformation in some districts. They may have become detached completely from their related orebodies.

7. Strata immediately above deposits may contain indications of mineralization. Hanging-wall volcanic rocks may contain alteration pipe assemblages, or at least zeolite-smectite assemblages similar to the peripheral alteration associated with the pipes.

More importantly, hydrothermal precipitates, such as ferruginous chert, sulphidic tuff, and products of oxidation of sulphide mounds may be sufficiently laterally extensive to be detected. Base metal contents within these, although of sub-ore grade, may increase towards the deposits.

Petrochemical Trends

Recent studies of hydrothermally active sites on the modern seafloor (Embley et al., 1989) as well as research on subvolcanic and related volcanic rocks associated with ancient deposits (Campbell et al.; 1982) have demonstrated the presence of very specific, and possibly unique petrochemical trends that are related to the ore-forming process. As described above, an important constituent of the hydrothermal system is the heat source, commonly represented by a sub-volcanic intrusion. Compositional variations within these intrusions can be affected by the presence of a hydrothermal system in two ways: the rapid removal of heat can cause exceptional fractionation to occur within the subvolcanic intrusion, and secondly, hydrothermal fluid may enter into the melt.

The presence of anomalously fractionated basaltic sequences has been documented on the Galapagos ridge (Embley et al., 1988) and at Cyprus (Schminke et al., 1983). In both cases, fractionation has proceeded from N-MORB through ferrobasalt, Fe-Ti basalt to andesite (Figure 2). Sulphur and the volatile contents increase with amount of fractionation, although sulphur decreases remarkably in the end-member andesite. Efficient removal of olivine and immiscible-sulphide droplets into the base of shallow magma chambers has occurred during fractionation.

Fractionation has also occurred in shallow-level felsic subvolcanic magma chambers, as at Sturgeon Lake (Beidelman Bay intrusion) and Noranda (Flavrian intrusion). Again, rapid removal of heat has forced disequilibrium crystallization, and caused early formation of anonmalous amounts of Ca-plagioclase and ferromagnesian minerals. Irregularly-disposed mafic portions of these intrusions are common near their stratigraphic top and lateral terminations. Removal of feldspar from the melt has resulted in depletion of the melt in europium relative to other REE's, forming a distinctive REE pattern (Figure 3) in the residual melt (i.e. in the felsic part of the subvolcanic intrusion and related felsic volcanic products) (Campbell et al., 1982).

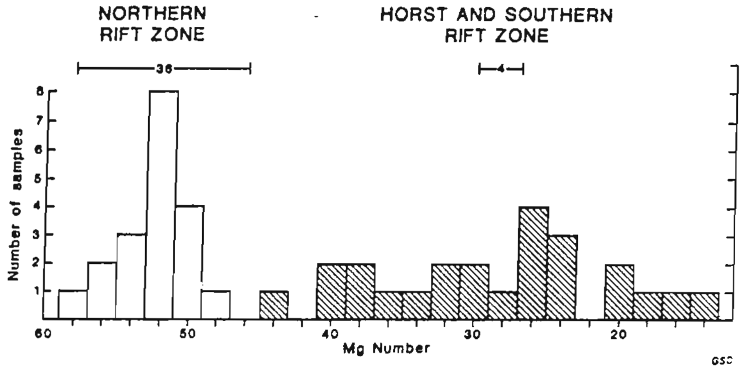

Figure 2. *Fractionation index of seafloor basalt near active spreading ridges. Note the high values and relatively narrow range of Mg numbers (Mg/Mg + Fe) for basalts not associated with VMS deposits (Northern Rift Zone), compared with the large range and low values for those rocks associated with deposits (Horst and southern rift zone).*

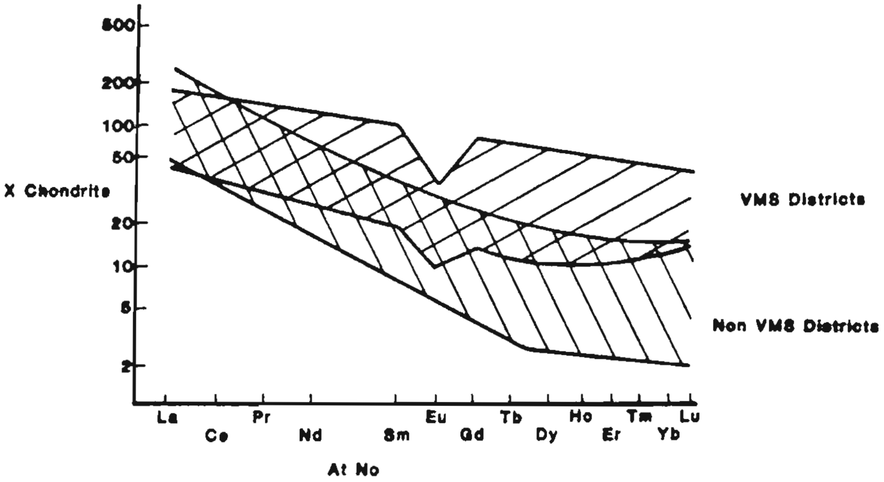

Figure 3. *Composite REE patterns for felsic rocks in Archean sequences. Note that the range of patterns displaying a prominent negative Eu** *anolmaly is associated with massive sulphide deposits, the relatively flat pattern with "barren" areas.*

Caution must be exercised in using incompatible elements as indicators of ore potential. The primary distribution of these elements in the juvenile melt (prior to any potential fractionation) should be determined. Also, chemical alteration can mask primary rock types, causing misleading comparisons. Incompatible element studies should be conducted at a district-scale, and based on extensive study in well-mapped mining camps.

Although virtually no data exist on the Cl contents of ancient sequences, these data may be useful indicators of the potential for hydrothermal activity to have occurred in an area.

Recent data on the Sr isotope and Cl contents of the various members of the fractionated suite at Galapagos indicates that this melt was progressively contaminated by seawater. This could have been caused either by assimilation of old crust or ingress of hydrothermal fluid into the melt. Cathles (1990) suggested that the latter process may be important in forming large hydrothermal systems.

Alteration beneath Cu-Zn massive sulphide deposits

Alteration has been studied more extensively than most attributes of these deposits. Alteration mineral assemblages and associated chemical changes have been very useful exploration guides. Alteration occurs in two distinct zones beneath these deposits (see Figure 1). 1) **Alteration pipes** occur immediately below the massive sulphide zones; here a complex interaction has occurred among the immediate sub-strata to the deposits, ore-forming (hydrothermal) fluids and locally-advecting sea water; and, 2) **Lower, semi-conformable alteration zones** (Franklin et al., 1981) occur several hundreds of metres or more below the massive sulphide deposits, and may represent in part the "reservoir zone" (Hodgson and Lydon, 1977) where the metals and sulphur were leached (Spooner and Fyfe, 1973) prior to their ascent to and expulsion onto the seafloor.

Under Precambrian deposits formed in deep water (Noranda-type), alteration pipes typically have a chloritic core, surrounded by a sericitic rim (Figure 4). Some, such as at Matagami Lake, contain talc, magnetite and phlogopite. The pipes usually taper downwards within a few tens to hundreds of metres below the deposits to a fault-controlled zone less than a metre in diameter.

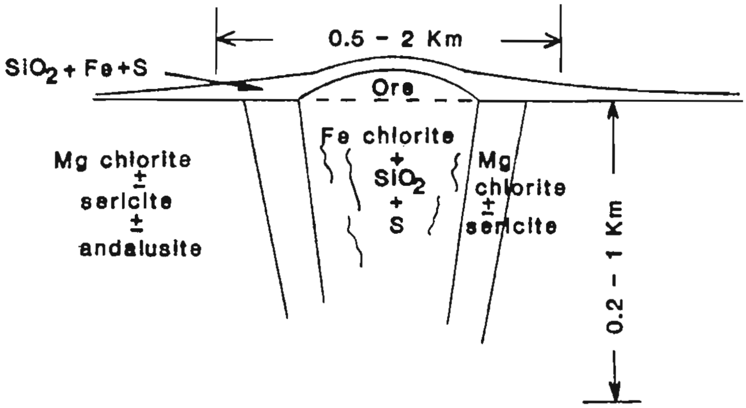

Figure 4. *Composite characteristics of a "Noranda-type" alteration pipe.*

Beneath deposits formed in shallow water (Mattabi-type), the pipes are silicified and sericitized; chlorite is subordinate and is most abundant on the periphery of the pipes. Aluminosilicate minerals, such as pyrophyllite and andalusite, are prominent (Figure 5).

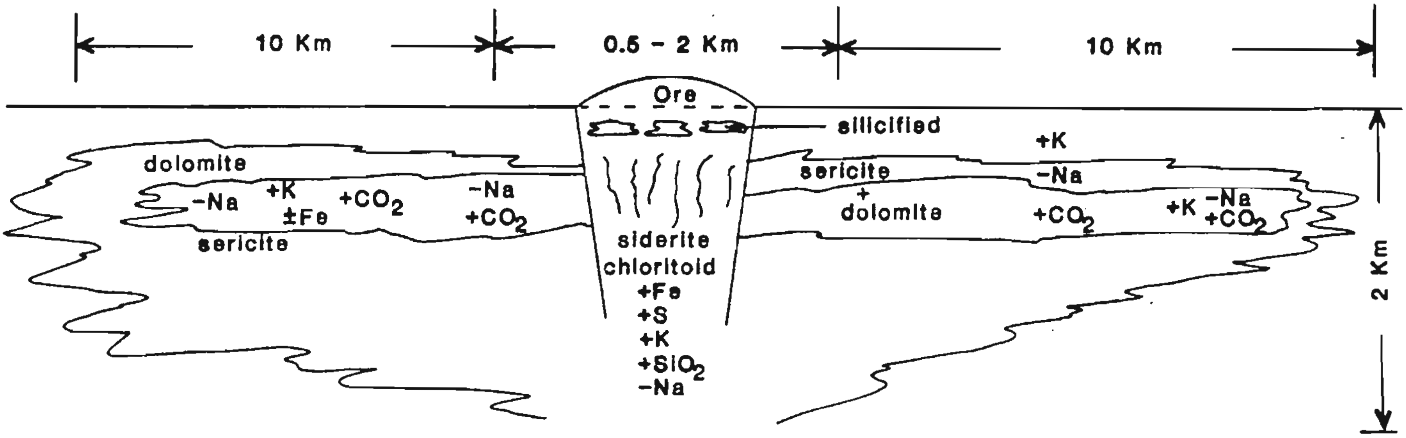

Figure 5. *Composite characteristics of local and regional alteration associated with massive sulphide deposits formed in shallow-water (< 2 km).*

Alteration pipes under Phanerozoic Cu-Zn deposits are similar to, but more variable than those under their Precambrian counterparts. For example, Aggarwal and Nesbitt (1984) described a talc-enriched alteration core, surrounded by a silica-pyrite alteration halo, beneath the Chu Chua deposit in B.C. The Newfoundland, Cyprus, Oman and Galapagos Ridge deposits have Mg-chlorite in the peripheral parts of their pipes, together with illite. Fe-chlorite, quartz and pyrite typify the central parts of the pipes.

Virtually all alteration pipes are characterized by Na depletion. Base metal additions are also ubiquitous, although highly variable in scale. The alteration pipes under deposits such as Millenbach and Ansil extend stratigraphically downwards for hundreds of metres, and contain abundant chalcopyrite. Under Mattabi, however, only a few metres of the footwall contain abundant chalcopyrite. As noted above, chlorite species varies considerably; the well-known Mg addition under some deposits is by no means a common feature under many other deposits. At Mattabi, for example, Mg is depleted in the footwall (Franklin et al., 1975), but Fe and Mn are enriched. Enrichment in Mn occurs only where syn-depositional carbonate alteration is prominent in the footwall.

The **lower semiconformable alteration zones** have been recognized under deposits in several massive sulphide districts. These include laterally extensive (several kilometres of strike length) quartz-epidote zones, several hundred metres thick, that extend downwards a few hundred metres stratigraphically below the Noranda, Matagami, and Snow Lake deposits of the Canadian Shield. Zones containing epidote, actinolite and quartz in the lower pillow lavas and sheeted dykes of the ophiolite sequences at Cyprus (Gass and Smewing, 1973) and in East Liguria, Italy, were explained by Spooner and Fyfe (1973) to be due to increased heat flow as a result of convective heat transfer away from the cooling intrusions at the base of these sequences. All of the epidote-quartz zones are depleted in copper, zinc and sulphur. They represent the zone of high temperature hydrothermal reaction (ca. 400°C), under low water-rock ratio conditions, where the metals and sulphur entered into the ore-forming solution (Richards et al., 1989; Spooner, 1977; Spooner et al.,1977a; Spooner et al., 1977b).

The albite-epidote-quartz alteration zones are generally metal-depleted. Skirrow and Franklin (in prep) show that virtually all of the copper has been removed from the albite-epidote-quartz zone in the footwall to the Snow Lake (Manitoba) deposits. Only about one-third of the zinc has been removed. Silica and calcium have been added, and magnesium has been lost. MacGeehan and MacLean (1980) illustrate similar changes for the footwall sequence at Matagami Lake, P.Q.

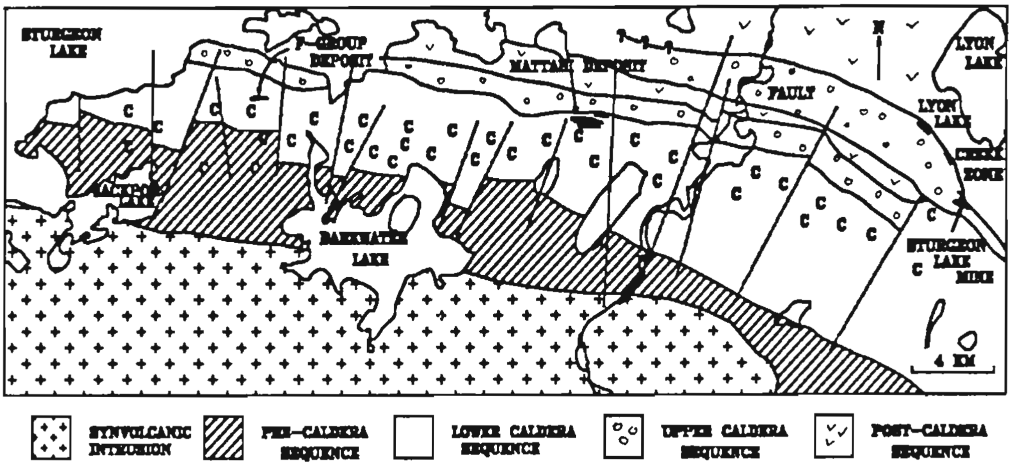

Figure 6. *Regional distribution of carbonate alteration in the Sturgeon lake district, Ontario. Carbonate is shown with "C" symbols. The carbonate-bearing rocks are usually Na-depleted.*

Zones of alkali-depleted, variably carbonatized strata occur directly beneath some deposits in sedimentary rocks, and under the Mattabi-type deposits. These may extend for as much as tens of kilometres along strike, and occur in the upper few hundred metres of the footwall (Figure 6). These zones probably represent a sealed cap to the hydrothermal reservoir, and formed through progressive heating of downward percolating seawater, with some possible input CO_2 from an underlying magma chamber, or by pyrolysis of organic compounds in the footwall.

The distinctive change in carbonate species provides a very important exploration guide. Franklin et al. (1975) and Morton et al (1990) have shown that on a regional basis, calcite has been added to the felsic strata, and Fe-dolomite to mafic strata (see Figure 5) in the Sturgeon Lake, Ontario, area. Siderite is the carbonate species that occurs immediatley below and within a few hundred metres of deposits, whereas Fe-dolomite and calcite occur farther away from the deposits. Although the total CO_2 content of the rocks remains essentially unchanged (about 5-10 % of the rock), the high Fe content of the mineralizing fluid that passed through these rocks converted the earlier-formed Ca and Fe-Mg-Ca carbonates to siderite. Concomitantly, Mn was incorporated into the siderite. Data on carbonate nodules that are presently forming under the deposits at Middle Valley and Escanaba Trough confirm this transition.

The alkali depletion that is common in many alteration zones is manifest as abundant aluminosilicate minerals (andalusite and, less commonly, kyanite) in areas of abundant carbonate alteration. In the absence of carbonate, margarite (at Snow lake; Zaleski, 1989) and chlorite replace the feldspar.

Amphibolite-grade metamorphism significantly changes the alteration assemblages under VMS deposits. At upper greenschist facies, chloritoid forms in the carbonatized alteration zones. Although Mg-chlorite remains stable well into amphibolite facies, Fe-chlorite has changed to staurolite in districts such as Snow Lake, Manitoba (Walford and Franklin, 1982) and Manitouwadge (Friesen et al., 1982). In very Fe-rich rocks (and in the absence of potassium) anthophyllite is abundant (Froese, 1969).

The mica species in alteration pipes are poorly documented. At Mattabi, although sericite is the most abundant mica, paragonite is common, even in Na-depleted rocks.

Alteration beneath Zn-Pb-Cu deposits

Alteration associated with Zn-Pb-Cu deposits is typified by that in the Hokuroku district of Japan (Figure 7). Canadian deposits, such as those at Buchans, Nfld. and the Buttle Lake, B.C. districts, have similar alteration patterns to Hokuroku deposits and those in the Tasman Geosyncline, Australia. The "lower semiconformable" alteration zones, such as those which underlie the Cu-Zn deposits, are unknown under these deposits. However, the lower strata are difficult to access in Japan, and structural complexities at Buchans, Buttle Lake and Tasmania may have removed these parts of their sequences.

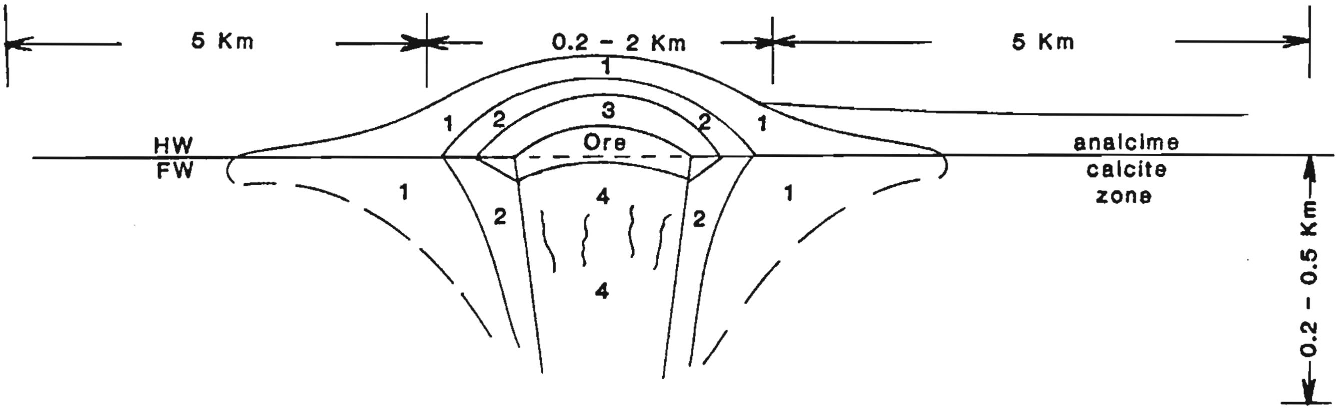

Figure 7. *Mineral zonation associated with Zn-Pb-Cu deposits (Kuroko type). After Iijima, 1974.* **For descriptions of zones see text.**

Four alteration zones (Figure 7) in the Hokuroku district have been described by Shirozu (1974), Ijima (1974), Date et al., (1983). The most intense zone of alteration, zone four, is immediately below the deposits, and consists of silicified, sericitized rock, with a small amount of chlorite. Zone three contains sericite, Mg-chlorite, and montmorillonite, and is not silicified. Feldspar is absent from zones three and four. Zone two consists of sericite, mixed-layer smectite minerals, and feldspar. Zone one contains zeolite (typically analcime) as an essential mineral, with montmorillonite. Outside these four zones, the volcanic rocks have been affected by deuteric alteration, which formed clinoptilolite and mordenite. Metamorphism and deformation obscure the alteration minerals associated with zones 1 to 3. At Buttle Lake, for example, zone four alteration is most prominent; carbonate is also present, and is also present distal to the the Hokuroku deposits. Although chlorite is much less abundant under Zn-Pb-Cu deposits than under Cu-Zn deposits, the alteration pipe under the Woodlawn deposit (Tasmania) is very chloritic (Petersen and Lambert, 1979). Alteration under the sediment-associated deposits of this group consists of locally distributed sericite-quartz; many deposits do not have obvious alteration zones.

Syn-depositional indicators of ore potential

Many massive sulphide districts have "sedimentary" or distal, syn-depositional strata that reflect the ore-forming process. For example, the various sulphidic tuff horizons at Noranda (Kalogeropoulos and Scott, 1983,1989), the Key Tuffite horizon at Matagami Lake (Davidson, 1977), the ochres at Cyprus (Herzig et al., in press), and the shale beds associated with several deposits (Kidd Creek, Uchi, West Arm) were all deposited penecontemporaneously with VMS deposits. Modern seafloor hydrothermal sites also have hydrothermal sediments surrounding them (Hannington et al., 1990). Finally, many VMS deposits have thin, laterally extensive "tails" leading away from the economic sulphide deposits; these may extend for hundreds of metres or more. They usually contain sub-economic metal contents; most are composed of "barren" pyrite.

The "near-field" sedimentary strata may be divided into two groups; those that contain sulphide as at least an accessory mineral, and those that contain oxide minerals. The origin of each of these is somewhat complex. Sulphidic sediments may have incorporated fallout particles from hydrothermal plumes. They may also have formed from the discharge of poorly-focussed low-temperature hydrothermal fluids in areas surrounding the high temperature vents. The oxide zones may be formed from the oxidation of sulphides (Hannington et al., 1990; Kalogerlopolous and Scott, 1983), or by direct precipitation of oxide minerals (i.e. iron formation).

The geochemical aspects of these two types of deposits that pertain to exploration have only been examined in a few districts. Some preliminary findings are as follows.

For sulphidic sediments:

1) Base metal contents increase towards the ore zone, although rather irregularly (Kalogeropoulos and Scott, 1989).

2) The silver contents of disseminated sulphides in any type of VMS-related sedimentary rock are higher than in those in pyrite from strata where the sulphide was generated biogenically (Elliot, 1984). At Kidd Creek, for example, disseminated sulphide in the hangingwall graphitic shale unit contains 60 ppm Ag, in comparison with the silver content of pyrite from unmineralized black shale of 18 ppm. Pyrite from VMS-related sedimentary rocks

also has lower Ni and Co contents(200 and 120 ppm, respectively) than the abundances in biogenically-generated pyrite(2000 and 650 ppm).

3) The sulphur isotopic composition of sulphides in sediments that are associated with Archean or Proterozoic VMS mineralization typically have a very narrow range ($^+/_-$ 1 $^o/_{oo}$), clustered around 0 $^o/_{oo}$, in contrast to sulphides in shales not associated with VMS deposits, which are probably biogenically generated (Goodwin et al. 1976), and have very wide ranges (typically -8 to +8 $^o/_{oo}$).

For oxide-rich sediments derived through degradation of VMS sulphides, only a few indicators are noteworthy.

1) Hannington et al. (1988) have demonstrated that gold is enriched by a factor of 10 to 100, by a secondary process in the oxidized sulphidic sediments at the TAG field (Mid Atlantic Ridge) and in the ochres at Cyprus (Herzig et al., in press). This enrichment may only be present where bottom water was oxidizing, i.e. in Phanerozoic open-ocean areas.

2) The lead isotope composition of oxidized sulphide material is conserved from the primary deposit composition, and is much less radiogenic than the lead in oxides generated by weathering of ferruginous (non-sulphide) rocks, or from iron formation (Gulson and Mizon, 1979).

LODE-GOLD DEPOSITS

Lode gold deposits occur in close association with major deformation zones, and can occur in virtually any rock type (Keays et al., 1989). The general characteristics of Archean examples of this deposit type have been summarized by Kerrich (1983), Colvine et al. (1988) and Card et al. (1989). This deposit type occurs in sequences of all ages, although they may be more plentiful in Archean rocks; Superior Province has produced 142 million ounces of gold, only surpassed by the paleoplacer deposits of the Witwatersrand (Card et al., 1989). Otherwise their geological characteristics are similar regardless of age.

The lode-gold group of deposits includes both vein- and disseminated (or sulphidic schist)-types. These two types account for the majority of the gold produced in Canada. They are associated with major fault zones, and are themselves structurally controlled. They appear to form very late in the geological history of their regions, typically after the peak of metamorphism.

Some geological attributes useful for exploring for this deposit type (after Poulsen, in press; Robert, in press) are:

1) Areas containing significant volumes of mafic volcanic rocks and a major fault zone, especially near the edge of a volcanic domain are most favorable. Shear zones or faults demonstrating high-angle reverse to reverse oblique motion contain the largest deposits (Sibson et al., 1988).

2) Gold deposits do not normally occur in the first-order fault or shear system, but in subsidiary fault and shear zones.

3) Favourable segments of fault or shear zones are those intersecting favorable host rocks such as small felsic intrusions, iron-formations, and iron-rich rocks. Also, portions of a shear or fault system where splays or deviations from the overall trend are evident are more productive.

4) Rocks surrounding the deposits are commonly (but not ubiquitously) carbonatized.

Petrochemical Trends

As gold deposits formed well after nearly all of their host rocks, little, if any information on the petrogenesis of these rocks has relevance to the deposits. A hypothesis has been presented (e.g. Callan and Spooner, 1989) for a genetic relationship between the tonalite - trondhjemite - granodiorite magmatic assemblage and gold deposits. The isotopic data used in their argument do not provide a unique resolution of this hypothesis. Although the common association of small albitic porphyry intrusions with gold deposits also provides some possibility for a genetic relationship, age data (Anglin et al., 1988; Marmot and Corfu, 1989), as well as petrogenetic arguments (the porphyry bodies usually pre-date the metamorphic peak, the veins post-date it; Robert, in press) make any genetic relationship virtually impossible.

Rock et al. (1989) and Wyman and Kerrich (1989) noted the association of gold deposits with shoshonitic (typically lamprophyric) intrusions. Although no direct genetic (or temporal) connection with this magmatic suite has been confirmed, the age of these intrusions is similar to ages determined for some gold veins (Bell et al, 1989). This similarity may reflect some common source attributes for gold-bearing fluids and alkaline rocks, but no more direct genetic relationship has been established.

Alteration

Alteration associated with gold deposits has a very complex genesis. Only a few "diagnostic" features have been observed, and these must be treated with some caution (Fryer and Franklin, 1982).

Alteration is caused by two processes.

1) Dynamo-thermal alteration, usually on a regional scale, accompanied the formation of most major shear and fault zones. Feldspar destruction (yielding a mica) was commonly accompanied by dissolution of some components, leading to volume loss within a shear zone (Beach, 1976). Alkali elements may have been gained, through mica formation, or lost, through feldspar destruction. Typically, ferromagnesian components are conserved. Fluid movement through shear zones caused hydration, and possible re-setting of isotopic systems. All of these alteration processes can combine to yield a geochemical signature with no relevance to the ore-forming process. Almost any shear zone will be mineralogically and chemically modified; caution must be exercised in using these changes to determine ore potential.

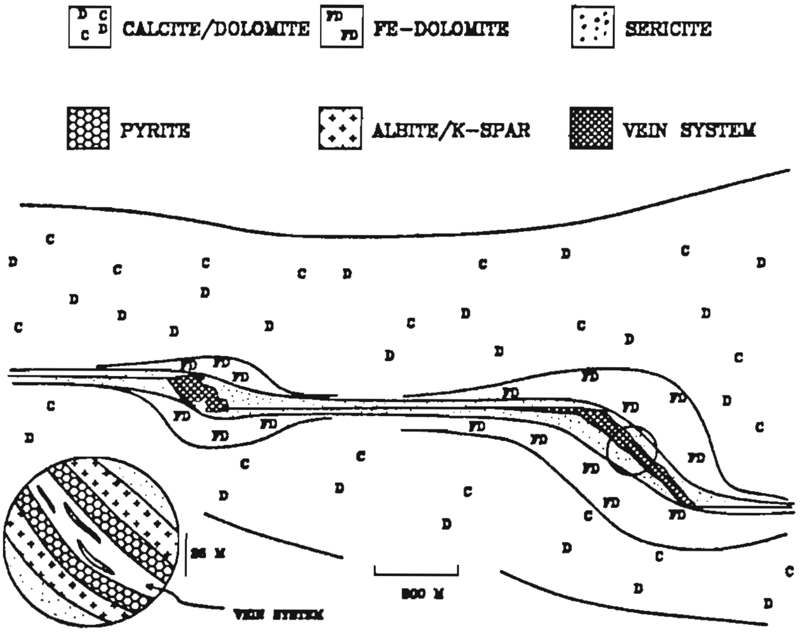

Figure 8. *Schematic illustration of alteration associated with lode-gold deposits.*

2) Ore-related fluid movement through the area of gold mineralization imparted mineralogical and geochemical change at two scales (Figure 8). Many aspects of alteration associated with gold deposits are reviewed by Colvine et al. (1988).

At a local scale, sulphidation, alkali metasomatism (either K or Na), boron enrichment, hydration and carbonatization are very common. The scale of alteration is typically from a few centimetres to a few metres adjacent to veins. The area affected by alteration is controlled by the fracture-induced permeability of the rocks. Pervasive alteration is present in schistose deformation zones, but much more defined (and possibly equally extensive) alteration is observed adjacent to extensional veins. For example, at the Doyon Mine (Guha et al., 1982) vein and disseminated gold mineralization occurs within a broad envelope of highly sheared, sericitized volcanic rocks. In contrast, Robert and Brown (1986) documented very well defined alteration zones, typically a few metres wide, adjacent to the veins at the Sigma Mine.

Mass balance studies (Robert and Brown, 1986; Ames et al., 1991; Dube, 1990; Clark et al., 1989; Kerrich, 1983) yielded results that demonstrate a lack of consistency in alteration styles for lode gold deposits. A few generalities can be drawn.

1) The complexity of chemical gains and losses increases as the ore-bearing veins are approached.

2) Alteration mineral assemblages, as well as chemical gains and losses, are furthermore a function of pre-alteration mineral assemblages. The latter generally reflect the primary rock type, but metamorphic modification of the pre-ore mineral assemblage can significantly affect the final alteration assemblage. For example, an ultramafic rock that was already converted to a talc-chlorite assemblage will react quite differently during alteration in comparison with a rock composed of olivine, pyroxene and plagioclase.

3) Either Na_2O and K_2O (but rarely both) are the most extensively added components. K_2O addition is most common. Sericite and biotite are common alteration minerals, particularly, but not exclusively in disseminated-type deposits. Paragonite may also be present (Ames et al., in press). Albite or K-feldspar is more common adjacent to veins which occupy brittle fractures. At Hemlo, however, K-feldspar (microcline) is extensively developed around the ore (Kuhns, 1986), with sericite alteration peripheral to the microcline zones.

Elemental additions most diagnostic of gold mineralization are (in approximate order of importance) Au, S, CO_2, K, Rb, SiO_2, Na, As, Sb, W, B, Mo and Pb (Davies et al., 1982;

Andrews et al., 1986 and references therein). A few elements, notably Ca and Sr, may be depleted, due to feldspar destruction. Given that volume reduction may have occurred during deformation, some immobile elements (e.g. Al_2O_3, TiO_2, Zr) display **apparent** increase, but mass balance calculations may confirm that such changes occur through volume or mass change, rather than real gain or loss. The size of geochemically anomalous zones of these elements is variable, from centimetres to hundreds of metres away from ore. Typically, the zones of geochemically measurable alteration are about the same width as the ore deposits themselves, and are symmetrical to the ore zone.

4) Sulphide minerals (commonly pyrite) typically have overgrown and replaced ferromagnesian minerals. Iron was added at the Victory Mine (Clark et al., 1989), but sulphidization was prominent at the San Antonio and Norbeau deposits (Ames, 1991; Dube, 1990). Sulphidization is probably a particularly important indicator of gold mineralization, as reduction in the sulphur content of the gold bearing fluid probably de-stabilized the Au-bisulphide complex, inducing very efficient deposition of gold.

Pyrite (or, less commonly pyrrhotite) is most abundant where gold-bearing fluids have interacted with iron-rich rocks. Sulphidized iron formation (e.g. Geraldton; Anglin and Franklin, 1986) and sulphidized Fe-basalt are important hosts to gold mineralization. As noted by Kerrich et al., 1977), the Fe^{2+}/Fe^{3+} ratio increases towards gold veins, largely in response to pyrite formation.

5) Alumina appears to have been mobile on a very local scale. Silicification is most common in broad shear zones, where silica-sericite-pyrite alteration assemblage typifies many disseminated-type deposits.

6) Tourmaline, scheelite, and arsenopyrite are all locally abundant in some deposits. In addition, very minor amounts of base-metal sulphides occur in some veins; molybdenite and chalcopyrite seem most common, but sphalerite and galena are recorded at several deposits (Hodgson and MacGeehan, 1982). Virtually none of these minerals are sufficiently abundant to provide an indication of ore potential, although all may occur as weathered and transported products in overburden.

Regional scale alteration is well developed in some districts, such as Timmins (Davies and Whitehead, 1982), Red Lake (MacGeehan and Hodgson, 1982), and Geraldton (Anglin and Franklin, 1986), less well developed at Bissett (Ames et al., 1991), and not prominent or even absent at others, such as Hemlo, and the Thompson Bousquet - Doyon (Malartic) group of deposits. Apart from shear-related mica alteration that may be widely distributed, depending on the breadth of any particular shear zone, the principal alteration type is carbonatization.

Carbonate alteration has been intensively examined at the Victory Mine area in Western Australia (Clark et al. 1989), the Timmins district (Davies et al., 1982), the Chibougamau area (Dube, 1990), Red Lake (Andrews et al., 1986) and Bissett, Manitoba (Ames et al., 1991). Summarizing their work, the principal changes at a regional scale are as follows:

i) Virtually all rock types are affected by addition of CO_2 only. Other components of the carbonate minerals are derived through metasomatic alteration of the host rock.

ii) The species of carbonate mineral present is a function of both the mole fraction of CO_2 (X CO_2)of fluids and the pre-alteration mineral assemblage. Clark et al. (1986) demonstrated at the Victory mine that close to the mineralization, ferruginous dolomite/ankerite is the prevalent carbonate species, whereas further from the deposit, calcite predominates. Significantly, silicate and oxide assemblages also reflect varying amounts of alteration. The equations presented by Clark et al. (1986) and Ames et al. (1991) are instructive. These represent a progressive set of reactions, describing the effect of an H_2O-CO_2 fluid on a meta-gabbro or meta-basalt. They are written here in generalized form:

In meta-gabbro, the reactions are (Ames et al., in press):

1) At a scale of tens of metres or more away from the vein systems, two reactions describe the principal changes:

actinolite + epidote + CO_2 + H_2O --> chlorite + **calcite** + quartz.

The specific reaction affecting titanite to form leucoxene produces a mineral assemblage that is readily visible:

titanite + CO_2 --> **calcite + rutile** + quartz

2) At a scale of 2-5m away from the veins, ankerite appears in the alteration asemblage:

chlorite + calcite + CO_2 + albite --> **ankerite** + paragonite + quartz

3) Immediately adjacent to the veins (~0.5 m), K is added:

paragonite + quartz + K^+ --> **muscovite** + albite

In gabbroic rocks where potassium was added (either from the altering fluid or prior to carbonatization), the reactions described by Clark et al. (1986) pertain:
On a regional scale (10's or more metres):

1) amphibole + epidote + H_2O + CO_2 + K_2O --> **biotite** + chlorite + **calcite** + quartz
2) **sphene** + CO_2 -- **rutile** + **calcite** + quartz

With increasing X CO_2 (i.e. closer to the veins):

3) biotite + chlorite + **calcite** + CO_2 --> **dolomite** + muscovite + quartz + H_2O

The important aspects to note are the presence of rutile (rather than sphene) as a result of CO_2 metasomatism, and that with increased X CO_2, and that the biotite - chlorite - calcite assemblage produced in reaction 1) changes to dolomite - muscovite - quartz. Knowledge of the titanium mineral species, as well as the mica species and carbonate composition can provide some estimate of "closeness" to a gold-bearing (hopefully !) system of conduits (i.e. faults/shear zones). This type of mineral determinative work can be done by X-ray diffraction, an inexpensive and rapid method. The carbonate species can effectively be determined by staining methods.

MAGMATIC SULPHIDE DEPOSITS

Magmatic sulphide deposits form by the segregation of an immiscible sulphide liquid from a parent silicate magma. The magma is generally of mafic or ultramafic composition and the elements of economic interest which concentrate in the molten sulphide include nickel, copper, cobalt and the platinum-group elements. The most important examples of this category in Canada are the world class deposits at Sudbury, Ontario and in the Thompson Nickel Belt in Manitoba. Other significant deposits occur at Shebandowan and Timmins in Ontario, Lynn

Lake in Manitoba, and the Ungava belt in Quebec.

A number of lithogeochemical approaches have been suggested for the exploration for magmatic sulphide deposits but few of these have found wide application. Probably the most useful application of lithogeochemistry has been in the delineation of the stratigraphy within igneous intrusions or sequences of volcanic rocks. Lithogeochemistry can also be used as a direct indicator of the presence of magmatic sulphides but these methods require more research and development before they can be used routinely.

Delineation of Igneous Stratigraphy

Magmatic sulphide deposits are, by definition, syngenetic with the igneous bodies in which they occur. Sulphides segregate at specific times during magmatic differentiation and are therefore associated with particular phases or stratigraphic units within an intrusion or volcanic succession. While these units are normally defined on petrographic criteria including mineralogy and texture, their chemical compositions are often more distinctive than subtle petrographic differences. Moreover, petrographically homogeneous units commonly display significant compositional variations (i.e., cryptic variation). Finally, ultramafic rocks in particular are very susceptible to alteration which may completely obliterate any primary minerals and texture leaving lithogeochemistry as a the primary means of identifying the protolith.

For these reasons alone, lithogeochemistry should form part of any exploration program for magmatic sulphide deposits. The compositional parameters which will be most useful will depend on the circumstances in each case. However, as a general rule, some attention should be given to defining a "differentiation index". For example, in mafic and ultramafic rocks where fractional crystallization of olivine and pyroxene is a dominant differentiation process, the magnesium number[1] is frequently used for this purpose. In the case of ultramafic volcanics (komatiites), the absolute MgO content, recalculated on a volatile-free basis, serves as a practical differentiation index.

Komatiite-associated nickel sulphide deposits provide one of the best examples of the use lithogeochemistry for this purpose. These deposits are associated with extrusive komatiites in Archean greenstone terranes in Australia, Canada and Zimbabwe. Gresham and Loftus-Hills

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[1] The magnesium number, sometimes abbreviated as Mg# or *mg*, is simply the atomic ratio Mg/(Mg+Fe).

(1981) give an excellent review of the characteristics of deposits in the type area of Kambalda, Western Australia. The sulphide accumulations occur in the lower parts of thick komatiite sequences with the bulk of the ore occurring at the base of the lowermost flow-unit. The ore-bearing units average 50 m but may exceed 100 m in thickness whereas flows in the lower part of the sequence but remote from ore are typically 15 to 20 m thick. The ore-bearing and barren flow units are also compositionally distinct. The thick basal flows are richer in magnesium, averaging 40 to 45% MgO as compared with 36 to 40% in the barren flows (Figure 9). The fine-grained, flowtop spinifex-textured peridotites in these units tend to contain from 28 to 32% MgO whereas elsewhere they have less than 26%. This provides a very useful exploration guideline.

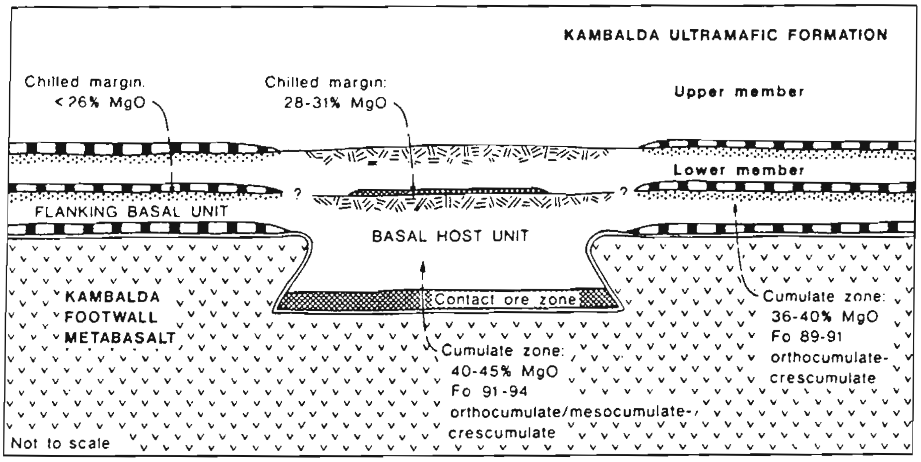

Figure 9. *Schematic cross section of a typical Kambalda "ore shoot" showing the MgO contents of the ore-bearing and barren komatiite units (after Lesher and Groves, 1984).*

<u>Presence of Magmatic Sulphide</u>

The formation of a magmatic sulphide deposit requires that the parent magma be at least locally saturated with sulphide for a finite period of time. Saturation leads to the segregation of droplets of immiscible sulphide liquid which then must accumulate to some degree if economic concentrations are to be formed. Since it is virtually impossible for the accumulation process to operate with anything approaching 100% efficiency, some significant proportion of immiscible sulphide will remain dispersed and ultimately become trapped in the silicate host rocks. The presence of magmatic sulphide grains in an igneous rock is thus an indication of a potentially "fertile" magma.

Magmatic sulphide grains can sometimes be recognized in mafic and ultramafic rocks which are not too badly altered. Such grains are commonly minute and may not be readily distinguished from secondary sulphides without microscopic examination. They are characterized by a polymineralic composition (commonly pyrrhotite-chalcopyrite-pentlandite) and their textural relationship to primary silicate minerals (globular or cuspate appearance where they are moulded around silicates). Duke and Naldrett (1976) give some of these criteria in their description of magmatic and secondary sulphides in the Main Irruptive at Sudbury.

Cameron et al. (1971) applied a lithogeochemical approach to detect the presence of small quantities of such "residual" magmatic sulphide in ultramafic rocks. They determined the concentrations of S and of sulphide-bound Ni, Cu and Co, and found that all four elements were enriched in ore-bearing as compared with barren rock suites. Copper and sulphur were the most significant factors in the discriminant function which distinguished the two populations. A practical consideration here is that Cu and particularly S tend to be mobile during alteration of ultramafic rocks. This means that a relatively large number of samples from each body should be analysed.

Sulphur Isotopes and Se/S Ratios

It is widely believed that a significant component of the sulphur in most massive accumulations of magmatic sulphides is of crustal rather than mantle derivation. The parent magma from which these accumlations segregated presumably became saturated with sulphide by assimilation of crustal sulphur. This applies to komatiite-associated nickel sulphides (i.e., Kambalda-type deposits), deposits in intrusions of continental flood basalt affinity (e.g., Noril'sk, Duluth Complex, Insizwa), and the ores of the Thompson Nickel Belt, among others. It is important to note, however, that the sulphur in many disseminated magmatic sulphide deposits (e.g., the stratabound platinum "reefs") is largely of mantle origin.

These observations suggest another lithogeochemical approach to the exploration for massive Ni-Cu sulphide ores. It was noted above that the presence of minute quantities of magmatic sulphides in an igneous rock is indicative of a "fertile" intrusion or lava sequence. Taking this one step further, geochemical parameters may be used to determine the likely source of the sulphur in these magmatic sulphide grains. A strong supracrustal signature would indicate that the parent magma had assimilated sulphur, which in turn suggests that the body in question would have some potential to host a massive sulphide accumulation.

Two parameters which are indicative of the source of sulphur are the sulphur isotopic composition and the Se/S ratio. The quantity dδ^{34} is close to zero in sulphur of mantle origin but often very different from zero in supracrustal sulphur (at least in post-Archean rocks). Similarly, rocks of mantle derivation typically have lower Se/S ratios in the range of 250 to 350 x 10^{-6} whereas the ratio in supracrustal rocks is typically less than 100 x 10^{-6} (e.g., Eckstrand et al. (1990).

Chalcophile Element Depletion

Chalcophile elements (Cu, Ni, Co, PGE, etc.) partition strongly into molten sulphide in preference to silicate liquid, and magmas from which sulphide has segregated will be depleted in these elements. Chalcophile element depletion, as revealed by lithogeochemistry, is therefore a potentially useful indicator of igneous bodies which have crystallized from sulphide-saturated magmas (Naldrett et al., 1984).

The magnitude of this depletion will depend upon a number of factors including the partition coefficient of the element, the relative masses of sulphide and silicate melts, and the mechanism by which the two liquids equilibrate. Komatiitic sequences provide an ideal situation in which to apply the chalcophile element depletion approach to exploration because they usually include spinifex-textured peridotites which have compositions equivalent to magmatic liquids. Duke and Naldrett (1978) quantitatively modelled the depletion patterns of Ni, Cu, and Co in komatiitic magmas, and predicted that these could be used as an exploration guide for Kambalda-type deposits. Subsequent studies have shown that the spinifex-textured peridotites at Kambalda (Lesher et al., 1981) and Scotia (Stolz, 1981) are indeed depleted in Ni. In each case, the entire komatiite sequence shows evidence of depletion (Figure 10) which means that this lithogeochemical approach would be useful in identifying fertile komatiite successions but not in detailed exploration within these sequences. In applying this approach, it is important to sample the fine-grained spinifex in the flow-top which will most closely approximate the initial liquid composition.

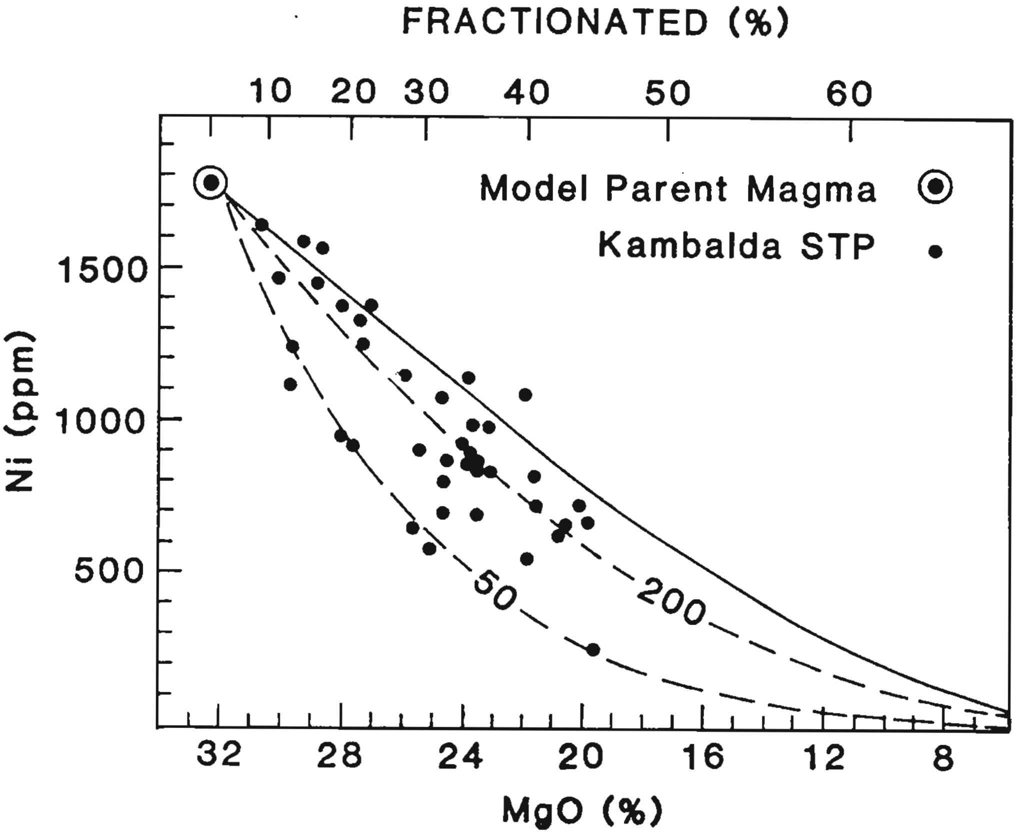

Figure 10. *Ni-depletion in the ore-bearing komatiite succession at Kambalda, Western Australia. The solid line represents the model compositional trend produced by fractional crystallization of olivine; the dashed lines show the effect of removal of olivine and sulphide in 200:1 and 50:1 ratios (Duke, 1979). The dots give the compositions of spinifex-textured peridotites (STP) from Lesher et al. (1981).*

In dealing with plutonic rocks, it is only rarely possible to identify rocks which have "liquid-equivalent" compositions. However, the chalcophile element depletion concept also applies to minerals which crystallized from sulphide-saturated magmas. Olivine is the most useful mineral in this respect because it normally contains readily detectable concentrations of Ni. Naldrett et al. (1984) have described a number of examples of nickel depletion in olivine from mineralized intrusions including the Insizwa Complex of South Africa, the Moxie and Katahdin intrusions in Maine, and the Dumont Sill in Quebec. Paktunc (1989) has documented Ni-depleted olivines in the St. Stephen intrusion in New Brunswick which hosts a number of zones of magmatic Ni-Cu mineralization.

Chromite Compositions

Lesher and Groves (1984) reported that chromites from mineralized komatiite sequences at Kambalda contain significantly higher levels of Zn than those from unmineralized sequences, specifically, 0.6 to 2.2 atomic % as compared to less than 0.6 atomic %. Chromites from ultramafic host rocks to ore at Thompson, Manitoba were found to contain similar high levels. The suggestion of Lesher and Groves (1984) that this enrichment is due to concentration of Zn in the silicate liquid during sulphide segregation is inconsistent with the inferred silicate/sulphide mass ratio[2]. A more likely explanation may lie in the fact that the magmas from which the sulphides segregated almost certainly assimilated significant quantities of sulphidic sediments which were also Zn-rich. Whatever the explanation, however, the elevated Zn content of chromites from some mineralized sequences may be a useful indicator.

SUMMARY

Alteration associated with both lode - gold and volcanogenic massive sulphide deposits results from interaction of high-temperature fluid with wall rocks. The fluids responsible for both deposit types probably had about the same range of temperatures (ca. 300-400°C). Judging from their respective products, lode-gold related fluids had very low base metal contents relative to VMS-forming fluids. Major districts containing either of these deposit types had fluids associated with them that contained high CO_2 contents; these CO_2-rich fluids may not have been the actual ore-forming fluid in either case, although these relationships have not been clarified.

Precipitation mechanisms of the ore contituents (and certainly depositional environments) were very different. Gold deposits formed through cooling on expansion of the fluid (e.g. in dilational structures; Sibson et al., 1988) or through reduction of the sulphur content of the fluid, by reaction with iron in the wallrocks to form pyrite. The latter reaction effectively reduces the solubility of gold if it was being transported in a bisulphide complex. Deposition probably occurred about 4 km below the erosional surface of the time (Robert, in press). Precipitation of metals from a VMS-forming fluid occurred primarily through cooling, either on contact with cold seawater at the seafloor or by heat-conduction in the immediate footwall.

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[2] See Duke (1990) for a discussion of the silicate/sulphide ratio which may have prevailed at Kambalda.

In the case of gold deposits, water, sulphur and CO_2 are the primary constituents added to the wall rocks. K and Na were also added, but the "reservoir" of these elements is presumed to be the hydrothermal fluid responsible for mineralization; this fluid had limited amounts of these alkali elements. In contrast, much of the alteration associated with VMS deposits was formed from locally advecting (and progressively heated) seawater. Retrograde solubility of Mg, and the virtually unlimited reservoir of Mg and K, provided the opportunity for much more extensive addition of these elements to the footwall. Iron, sulphur and silica are derived from the ore-forming fluid, however, and usually are added only in the immediate footwall area.

One of the more important aspects of alteration associated with these two deposit types is carbonatization at a regional scale. How can carbonatization related to gold deposits be discriminated from that related to VMS deposits ? Some guidelines are:

1) Carbonatization associated with gold deposits typically post-dated the peak of metamorphism. Also, the carbonatized rocks were not subjected to alkali-depletion, as was the case of the footwall sequences associated with VMS deposits. Consequently, the carbonate alteration associated with gold deposits was not metamorphosed, or if it was, this metamorphism occurred in rocks with "normal" alkali contents; metamorphosed alteration might contain diopside (or even secondary olivine, if temperatures were high enough). Metamorphosed carbonate alteration associated with VMS deposits probably contains chloritoid (Lockwood and Franklin, 1986) or staurolite, due to the alkali-deficient nature of the rocks. Also, the latter rocks are strongly per-aluminous, and typically contain andalusite (or sillimanite at higher metamorphic grades).

2) Mass balance studies of each alteration type should indicate that Ca, Mg, Fe and CO_2 were added in VMS-related carbonate alteration, but only CO_2 (and locally, possibly some K or Na) was added during gold-related alteration.

3) The "local" alteration assemblages associated with gold mineralization (e.g. ankerite and paragonite) may be much more regionally developed under VMS deposits. Although little is known about the source of CO_2 associated with VMS deposits (it could either be part of the hydrothermal fluid, a degassing product of an underlying sub-volcanic magma chamber, or formed from downward-advecting, progressively heated seawater), there is no indication of X CO_2 gradients associated with its formation.

RECOMMENDATIONS

A few admonitions may be worth considering:

1) Geological models for ore deposition are based primarily on empirical field observations, and refined using laboratory data. The field observations typically include some recurring, somewhat extraordinary assemblage of rocks, alteration patterns, or structures, for example. Careful examination of geological information, or preferably, mapping, should be the most powerful exploration tool. Where outcrop is sparse, geophysical or geochemical remote sensing methods, if applied with the full knowledge of the characteristics of ore deposits and their alteration assemblages, should provide guidance.

2) Petrochemical trends can be useful indicators of ore potential for magmatic and seafloor-hydrothermal deposits, but are of little use for most types of vein deposits. Good-quality analytical data are needed if reliable petrogenetic indicators are to be used. These data should include determination of the volatile (CO_2 and S) and halogen elements and compounds. Indiscriminate determination of a large suite of volatile and trace elements could be expensive. Where possible, sampling should be done with the best geological knowledge at hand.

3) Alteration mineral assemblages provide excellent exploration guides for VMS and lode gold deposits. Some of these can be determined in the field, others with a petrographic microscope, and only a few require x-ray diffraction analyses. All of these techniques are inexpensive, readily available, and usually unambiguous. Mineral assemblages as exploration guides are under-used as techniques in the exploration arsenal. Some useful staining methods are available for determining the composition of carbonate minerals in the field. In the case of magmatic sulphides, on the other hand, alteration often obscures primary trends making the interpretation of lithogeochemistry more difficult.

4) Lithogeochemistry as an exploration technique has been used widely, and, unfortunately, indiscriminately. The exploration geologist armed with some knowledge of alteration processes could use subtle variations in the chemical composition of a rock to good advantage. For example, Na is lost where the water/rock ratio was high in an alteration zone (i.e. near a VMS deposit), but gained where this ratio was low (i.e. in the high temperature reaction zone, 1-2 km below the deposits). Both types of anomaly can be useful guides to ore, but must be applied with full consideration of stratigraphic implications. Analysis of the mineral assemblages in such rocks will yield much more information than the chemical data alone.

"Cook-book" applications of lithogeochemical prospecting methods are potentially very misleading.

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PAPER #2

PRINCIPLES OF GLACIAL DISPERSAL AND SEDIMENTATION

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Abstract

Glacial dispersal is a term describing the processes through which debris is created and picked up by glaciers, transported in, on or under them, and ultimately released from them some distance from its origin. This size distribution of mineral or rock grains in glacial sediments and, therefore, the geochemical characteristics of different size fractions is dictated by the physical properties of the various components, properties which govern how effectively the components will be comminuted by the crushing and abrasive processes that accompany glacial erosion and transport. Because each pass of a glacier erodes unweathered bedrock and adds it to the lightly weathered debris produced during earlier glaciations, glacial sediment tends to be rich in labile components (sulphides, carbonates, etc.), which are particularly susceptible to weathering in the near-surface environment. To be able to interpret the patterns of geochemical dispersal effectively in glaciated terrain, it is imperative that the geochemist/glacial geologist recognize the possible geochemical effects of chemical partitioning by grain size and the effects of weathering on labile components. Sample populations and analytical techniques must be appropriate for depicting glacial dispersal so that they do not produce results that merely represent artifacts of sample-to-sample inconsistency in textural variation or weathering status. Along with the precautions mentioned above, samples must ensure that sediment facies are properly identified and that the stratigraphic position of the unit sampled is understood. If the above criteria can be fulfilled satisfactorily, areal patterns of geochemical dispersal from specified source areas will be seen to have characteristic ribbon or fan shapes with the apices at or near the sources. Geochemical concentration profiles in drift within dispersal trains are ideally exponential, high concentrations of a component near its source (<u>head</u> of dispersal) declining exponentially to concentrations just above background (<u>tail</u> of dispersal) for some distance down ice. Recently, large-scale dispersal trains with uniformly high, non-declining concentrations of debris from easily eroded source areas, thought to be related to ice streaming within continental ice sheets, have been observed to obscure local geochemical signatures in drift over significant areas. Local drift at the base of these exotic sediments, which often can be sampled only by drilling, generally has provenance characteristics that reflect dispersal from local sources. Finally, the composition of any sample may be the integrated geochemical signal of overlapping or superimposed dispersal trains at a variety of scales from continental (100s of km in length) to regional (10s of km in length) to local (km in length) to small-scale (100s of metres in length). It is the task of the explorationist to determine and distinguish, considering all the *caveats* and principles mentioned above, what the economic significance of a sample is within the context of the vertical or areal geochemical pattern of which it is a component.

Résumé

Le terme dispersion glaciaire désigne l'ensemble des processus par lesquels les débris arrachés et entraînés par les glaciers (soit sur le dessus, à l'intérieur ou à la base de ceux-ci), sont relâchés à une certaine distance de leur point d'origine. La granulométrie des particules de minéraux ou de roches dans les sédiments glaciaires et, par conséquent, les caractéristiques géochimiques des différentes fractions granulométriques, sont fonction des propriétés physiques des différentes composantes, propriétés qui déterminent la façon dont ces composantes sont réduites par les processus de broyage et d'abrasion qui accompagnent l'érosion et le transport glaciaires. Étant donné qu'à chaque passage d'un glacier, la roche en place non altérée est érodée et que les sédiments produits sont ajoutés aux débris légèrement altérés déposés par les glaciations antérieures, les sédiments glaciaires ont tendance à être riches en matériaux facilement altérable (sulfures, carbonates, etc.) qui sont particulièrement susceptibles d'être lixiviés s'ils sont situés près de la surface. Pour être en mesure d'interpréter les dispersion géochimique en terrain glaciaire, il est essentiel que le géochimiste ou le géologue spécialisé en glaciologie connaisse les effets géochimiques possibles du fractionnement chimique entre les différentes fractions granulométriques ainsi que les effets des intempéries sur ces matériaux facilement altérables. Le choix des échantillons et les techniques d'analyse utilisées doivent permettre de décrire la dispersion glaciaire pour que les résultats produits ne représentent pas que de simples incohérences entre échantillons dues à des variations texturales ou au degré d'altération. En plus de prendre les précautions ci-dessus, il faut s'assurer lors de l'échantillonnage que les faciès sédimentaires soient correctement identifiés et que la position stratigraphique de l'unité échantillonnée soient connue. Si tous ces critères sont satisfaits, les patrons de dispersion géochimique à partir de zones sources spécifiques seront caractérisées par des formes rubanées ou coniques dont la pointe se trouve à la source ou près de celle-ci. Les profils montrant les concentrations géochimiques dans les dépôts glaciaires à l'intérieur des traînées de dispersion suivent idéalement une répartition exponentielle: concentrations élevées près

de la source (tête de dispersion) diminuant exponentiellement pour atteindre des concentrations légèrement supérieures au fond (queue de dispersion) à une certaine distance en aval glaciaire. On a observé récemment que des traînées de dispersion à grande échelle, formées de débris de roches-sources facilement érodées et qui n'ont pas tendance à diminuer d'intensité avec la distance, et qui sont probablement liées à des zones d'écoulement rapide au sein d'un inlandsis, brouillaient les signatures géochimiques des dépôts glaciaires locaux sur d'assez grandes superficies. Les débris locaux à la base de ces sédiments exotiques, qui souvent ne peuvent être échantillonnés que par forage, présentent en général des caractéristiques de provenance qui reflètent une dispersion à partir de sources locales. Enfin, la composition de tout échantillon peut refléter le signal géochimique intégré d'un ensemble de traînées de dispersion à différentes échelles allant de continentale (centaines de kilomètres de longueur) à régionale (dizaines de kilomètres) à locale (quelques kilomètres) à zonale (centaines de mètres). Il relève du géologue de terrain de déterminer et de distinguer, en tenant compte de toutes les mises en garde et les principes donnés ci-dessus, l'importance d'un échantillon dans un contexte économique, selon la configuration géochimique verticale ou horizontale dont il est une composante.

INTRODUCTION

The composition of glacial sediments has long been of interest in wholly or partially glaciated countries with bedrock geology favourable for mineralization. In Fennoscandia, the tradition of tracing glacially displaced mineralized boulders back to their sources has been practised intensely in the 20th century but is based on observations of boulder transport that predate the general acceptance of glacial theory by a century and a half (Tilas, 1740). In the latter part of the twentieth century, the mapping and interpretation of glacially dispersed mineralized debris increasingly has involved the application of new analytical technologies to measuring the compositions of the finest fractions of glacial sediments and of the proglacial sediments derived from them (Shilts, 1976). As a consequence of the applications of these new technologies, explorationists now rely heavily on geochemical analyses to provide objective data on patterns of dispersal of glacially eroded detritus from bedrock sources of possible economic interest. In addition to or in place of traditional geochemical analyses of sieved fine fractions of glacial sediments, increasingly sophisticated techniques are now used to concentrate clay-sized minerals or coarser minerals with high specific gravities. Separates produced by various concentrating techniques are analyzed geochemically and examined microscopically or by various modern instruments, such as the microprobe or scanning electron microscope with backscattering or energy dispersive capabilities (for example, Peuraniemi, 1987; Saarnisto and Tamminen, 1987; DiLabio, 1990).

The purposes of this paper are (1) to discuss some of the sedimentological and diagenetic processes that are unique to the glacial and postglacial environment, and (2) to indicate the present thinking on how to interpret the compositional signals commonly derived from drift. Only after mastering fundamental concepts behind these two aspects of glacial deposition may the explorationist be able to interpret geochemical data with confidence and efficiency.

SOME CONSTRAINING PRINCIPLES AND CONCEPTS

In 95% of Canada, in northern Europe, throughout the north-central and northeastern United States, in Antarctica, and in glaciated terrains elsewhere in the world, the chemical and physical signature of bedrock on soils and surficial sediments has been distorted by glacial dispersal. Glacial dispersal is a term that describes the processes through which debris is entrained in ice, transported, and deposited some distance away.

Glacial origin imparts several important differences to the composition of sediments and soils of glaciated landscapes, when compared to unglaciated landscapes where unconsolidated overburden is formed by chemical (soil forming), aeolian, or fluvial processes:

(1) In glaciated terrain, enrichment of a mineralogical or chemical component is not confined just to the area where that element is enriched in bedrock; glacial transport may disperse components over wide areas, areas several times larger than the outcrop areas of their sources.

(2) Dispersal by glaciers is usually independent of drainage divides, except in mountainous areas where valley glaciers are often confined to ancestral valley systems. Thus, with the exception of some valley glaciers, detritus from a given source can be distributed throughout several drainage basins.

(3) Because glacial sediments at any given location are composites of detritus eroded from several, often genetically diverse bedrock sources, minerals and, therefore, chemical components of several origins may be found together in one sample. Such seemingly geochemically incompatible groupings as uranium - zinc - chromium may occur, for instance, where a glacier has traversed bedrock including acid, basic, and ultrabasic igneous strata in close proximity, a lithologic assemblage that is not uncommon in geologically complex terranes such as the Canadian Shield.

(4) The finest portions of glacial sediments, particularly the chemically reactive clay ($<2\ \mu m$) sizes, are composed predominantly of easily crushed bedrock detritus, such as phyllosilicate (micaceous) minerals, hematite, serpentine, etc. These components are glacially abraded to clay sizes by virtue of their soft or easily cleavable nature, have relatively low exchange capacities, and generally are not the products of weathering, in contrast to fine fractions of soils in unglaciated areas. That is not to say, however, that some true clay minerals and other products of preglacial, interglacial, or interstadial weathering are not eroded and mixed with clay-sized detritus produced by glacial grinding of fresh bedrock or clast surfaces.

(5) In glaciated carbonate terrains, and in areas where the bedrock contains sulphides, olivine-serpentine, or other minerals that are broken down during the first stages of

weathering, unweathered glacial sediments can contain these components in abundance. In contrast to unglaciated areas, which are mantled by overburden comprising chemically produced regolith with a relatively simple assemblage of stable primary and secondary minerals, the mineral assemblages of glacial overburden are complex in direct relationship to the complexity of the bedrock terrane eroded by their depositing glacier. Selective chemical removal of the labile components by weathering processes has occurred only in and just below the thin postglacial solum formed on glacial sediments, and there has been little post-depositional concentration of those secondary weathering products characterized by enhanced exchange capacities, such as Fe-Mn hydroxides or oxides, true clay minerals, etc.

For mineral exploration, the implication of a composition that reflects unaltered, but mixed, mineralogies of eroded bedrock is that even the most labile minerals of economic interest, such as sulphides, are preserved in unweathered glacial deposits. Therefore, if unweathered samples can be obtained, visual examination or geochemical analysis of the sediment can reveal primary mineralogy of source outcrops. Likewise, glacial sediment can be traced directly to its source without having to account for the effects of the low-temperature geochemical alteration of primary minerals that accompanies weathering. In weathered glacial sediments and in regolith derived by chemical degradation of bedrock in unglaciated areas, cations are redistributed by adsorption on or absorption into a variety of secondary mineral phases with high exchange capacity, such as hydrous iron or manganese oxides or clay minerals.

GEOCHEMICAL PATTERNS ON GLACIATED LANDSCAPES

The ribbon of compositionally distinct debris trailing down-ice from a particular source, once deposited, is called a dispersal train. Because glaciers in general and continental glaciers in particular traverse so many different lithologies from their flow centres to points of deposition, each sample of glacial drift can be regarded as having a composition reflecting the overlapping of many dispersal trains (Figure 1). It is the task of the glacial geologist to sort out the signatures of the various overlapping trains and, in the case of mineral exploration, to determine a method by which the components of one particular train can be differentiated, mapped, and traced back to their source.

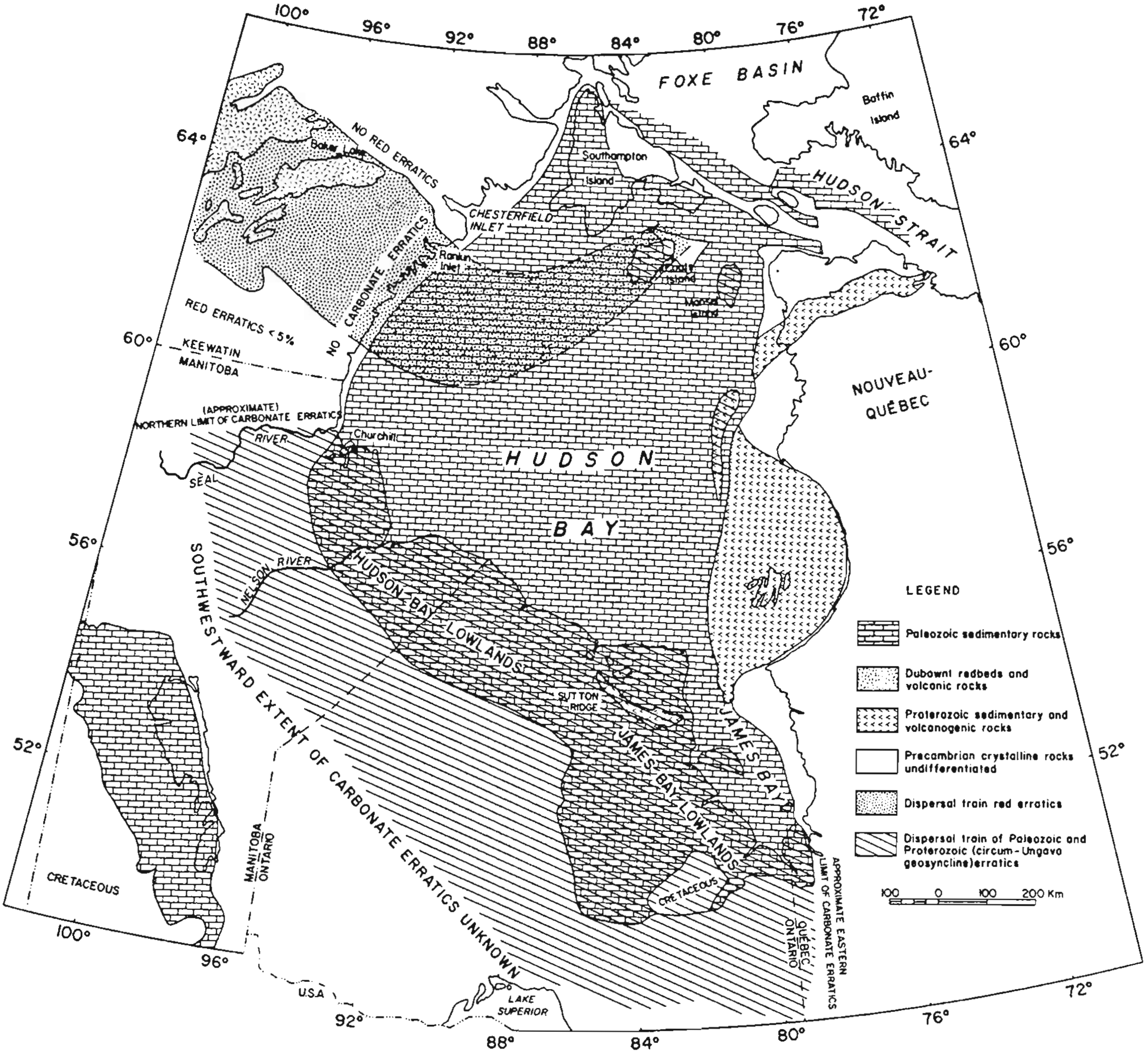


Figure 1. *Major continental-scale dispersal trains in central Canada. Proterozoic erratics and Paleozoic erratics from southeastern Hudson Bay and from the southern part of the Hudson Bay Platform are intimately mixed in trains southwest of Hudson Bay Lowlands.*

If boulders of mineralized bedrock are found, the task of tracing them to their source, while often not easy, is more straightforward than tracking down the source of a geochemical anomaly. Boulders reveal the "personality" of their source outcrops – the enclosing lithologies, mineralogy, and chemistry of the economic occurrence are often preserved together in a boulder. A geochemical anomaly, on the other hand, has little "personality", comprising usually an elemental enrichment above background, which usually can tell the geochemist little about the minerals responsible for the enrichment, much less about the nature of the unmineralized host rocks. By looking at its association with different trace and minor elements, however (modern analytical techniques make it increasingly inexpensive to do rapid analyses of a wide range of elements), it is often possible to make an 'educated guess' about the significance of an anomaly, and thereby to determine something about the geochemical and petrological "personality" of the source outcrops.

To use geochemistry of drift for determining patterns of dispersal of cations from their original outcrops and the nature of the outcrops themselves, it is necessary to understand how they and their host mineral phases are distributed in various facies of glacial sediment. Also, even a single till sample may yield a wide range of apparent concentrations of a single chemical component, depending on which size or specific gravity fractions are subjected to analysis. In order to construct a map that truly represents drift provenance, it is necessary to understand the non-provenance-related factors that influence analytical results. In addition to the obvious need to determine the sedimentological nature and stratigraphic position of material sampled for quantitative analysis, there are two major factors, chemical partitioning and post depositional weathering, which must be evaluated before analytical results can be related to provenance.

CHEMICAL PARTITIONING

Glacial sediments, regardless of the sedimentary processes by which they are ultimately deposited, are generated predominantly by abrasive or crushing processes associated with clast-to-clast or clast-to-bedrock impacts of particles held rigidly in glacier ice. For this reason, each sample of glacial or derived sediment represents a melange of crushed bedrock from outcrops up-ice from where it is collected. Samples of proglacial or postglacial water or wind-deposited sediments may be further transported in a variety of directions, depending on the topographic gradient before and after isostatic rebound and on prevailing wind direction. Till, the ultimate glacial sediment sample, represents closely the load actually suspended in glacial ice. It is composed of rock and mineral fragments with a potential grain size range from the largest fragments broken off source outcrops to the finest 'dust' created by clasts scraping against outcrops or against each other while in transport within the glacier.

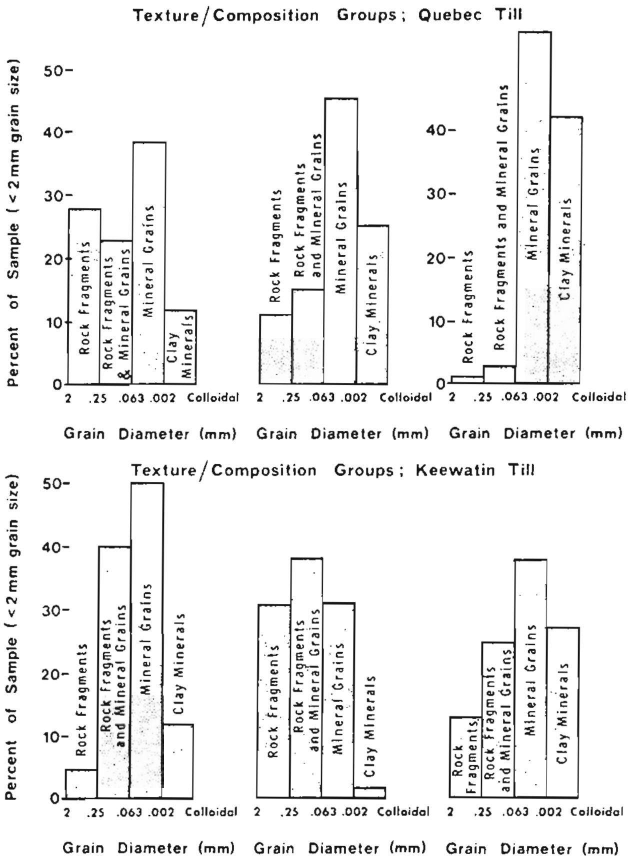


Figure 2. *Histograms showing typical variation in amount of material in various size fractions and mineralogical partitioning in till (from Shilts, 1971).*

The mineralogical/petrological composition of the various sizes of particles in till is primarily a function of their <u>physical</u> properties – micas and other soft or cleavable minerals predominante in the finest fractions; quartz, pyrite, and other hard, noncleavable minerals dominate the sand fractions. Thus, there is a marked mineralogical partitioning in the glacial load, in till formed from it, and in water (and wind)-lain sediments derived from it either before or after its deposition (Figure 2). This physical, mineralogical partitioning translates geochemically into chemical partitioning for the obvious reason that size fractions dominated by certain mineral phases will reflect the chemical make-up of those phases.

Studies of partitioning in glacial sediments are designed to determine how and where metal is held as well as the optimum grain-size range for providing geochemical analyses that accurately reflect provenance. Although many geochemical partitioning experiments have been carried out on glacial or postglacial sediments, very few have dealt with the reactive, clay-sized (<2 μm) fraction. In slightly weathered or unweathered till, this fraction, although commonly referred to as the "clay" fraction, is actually composed largely of minerals that were easily reduced to clay size by the physical processes of glacial grinding and abrasion. Although quartz, feldspars, carbonates, and other minerals can be present in the clay-sized fraction, it is commonly dominated by well crystallized phyllosilicates (mainly chlorite and micas). Locally, it may contain significant amounts of less common "soft" minerals, such as kaolinite and other true clay minerals, serpentine, graphite, and hematite.

Nikkarinen, et al. (1984) and Shilts (1984) both demonstrated that analyses based on total leaches of a wide range of grain sizes revealed copper and zinc to be significantly enriched in clay-sized fractions, particularly in anomalous samples known to be related to massive sulphide mineralization. Furthermore, selective, weak laboratory leaches applied to the clay-sized fractions of till usually removed only a small percentage of the total metal available, suggesting that the metal is held largely in the structures of primary phyllosilicate minerals and is not adsorbed appreciably or incorporated into secondary mineral phases. Selective leaches caused most oxidized samples to yield significant percentages of Fe and Mn from secondary oxide-hydroxide phases, but usually little other metal, suggesting either that the secondary phases generally have not been efficient scavengers of cations or that little metal was released during weathering.

The implications of these results are significant in evaluating geochemical data from till or other glacial or derived sediment (Table 1). They suggest that concentrations of many cations in separates containing a wide range of grain sizes are strongly skewed by the amount of <2 μm material, the coarser sand and silt-sized fractions often acting as diluents for some cations of economic interest.

Table 1 – Examples of Partitioning

Tills rich in ultramafic debris: (A) Basal till near an Archaean komatiite, central District of Keewatin; (B) Basal till near Paleozoic ophiolite complex, Quebec Appalachian Mountains; (C) Flow till forming lateral moraine of modern glacier; on Mesozoic ophiolite complex, Swiss Alps, near Zermatt.

Size fraction/element	Cr (ppm)			Ni (ppm)			As (ppm)		
	A	B	C	A	B	C	A	B	C
Bulk Sample	-	284	1744	-	500	1600	-	8	4
2.0-6.0 mm	3320	400	1780	1050	880	1600	160	5	2
0.25-2.0 mm	3220	294	1852	970	556	1500	157	13	2
0.044-0.25 mm	2520	200	1980	745	267	970	162	4	3
0.004-0.044 mm	1856	236	1424	910	403	1020	245	16	5
0.001-0.004 mm	3560	274	1148	1200	743	2300	553	10	11
<0.001 mm	-	256	1468	-	913	4100	770	13	12

85 SK 22265 Oxidized, sandy, granite-rich till, near Tangier Lake, Nova Scotia

Size fraction/element	W (ppm)	Cu (ppm)	As (ppm)
Bulk Sample	500	106	8
2.0-6.0 mm	60	31	2
0.25-2.0 mm	360	53	3
0.044-0.25 mm	500	90	6
0.004-0.044 mm	550	167	13
0.001-0.004 mm	1800	500	45
<0.001 mm	>2000	609	80

Explanation for Table 1

Bulk Sample	total sample finer than 6 mm
2.0-6.0 mm	fraction almost wholly composed of rock fragments
0.25-2.0 mm	fraction composed of mixture of rock fragments and mineral grains
0.044-0.25 mm	sand and coarse silt; fraction composed almost wholly of mineral grains, dominated by quartz and feldspar (usually >90%)
0.004-0.044 mm	Silt; mineral grains dominated by quartz and feldspar
0.001-0.004 mm	Clay; mineral grains dominated by phyllosilicates, and other soft minerals
<0.001	Clay and colloidal particles.

Analysis by Atomic Absorption techniques after HF-$HClO_4$ – HNO_3 – HCl leach for Cr, Mn, Fe, Co, Ni, Cu, Pb, Zn, Mo, Cd. Sn by x-ray fluorescence. U by fluorometric technique. As by colourimetric technique after HNO_3 – $HClO_4$ leach. Au by neutron activation. W by colourimetric on carbonate sinter. All analyses by Bondar-Clegg & Co. Ltd.

Table 1 (cont'd)

90 KAL-001-Oxidized, slate-rich basal till overlying gold-bearing quartz vein in gabbro, near St-Magloire, Quebec Appalachians

Size fraction/element	Au (ppb)	As (ppm)	Sb (ppm)
<0.064 mm	624	207	0.6
0.064-2.0 mm	399	120	0.5
0.002-0.064 mm	838	215	0.7
<0.002 mm	83	341	1.6

80AR-0772 – Sandy, clay-poor pebbly till, Grenville of E. Ontario

Size fraction/Element	As (ppm)	Zn (ppm)	Cu (ppm)
Bulk Sample	42	56	15
2.0-6.0 mm	2	40	7
0.25-2.0 mm	21	38	8
0.044-0.25 mm	12	42	8
0.004-0.044 mm	189	65	16
0.001-0.004 mm	630	385	165
<0.001 mm	-	830	440

85 TR-041, Till, composed mostly of weathered, tin-bearing granite, near Rocky Brook, New Brunswick

Size fraction/element	Sn (ppm)	U (ppm)	Mn (ppm)	Fe (%)	As (ppm)
Bulk Sample	20	5.2	175	1.0	<2
2.0-6.0 mm	21	1.9	83	0.3	<2
0.25-2.0 mm	20	3.5	169	1.0	<2
0.044-0.25 mm	41	4.3	400	1.4	2
0.004-0.044 mm	-	13.3	893	2.8	10
0.001-0.004mm	82	11.8	1255	3.4	25
<0.001 mm	-	11.3	1528	3.2	30

Table 1 (cont'd)

85 NJ-002, Oxidized flow till in ice-contact gravel complex, Franklin Furnace, New Jersey

Size fraction/element	Zn (ppm)	Cd (ppm)
Bulk Sample	1850	0.6
2.0-6.0 mm	1600	0.7
0.25-2.0 mm	1900	0.4
0.044-0.25 mm	1750	0.7
0.004-0.044 mm	925	0.3
0.001-0.004 mm	2778	3.6
<0.001 mm	6000	3.8

80 AR-0283 Gray, blocky basal till, Grenville of E. Ontario

Size fraction/element	U (ppm)	Zn (ppm)
Bulk Sample	11.9	135
2.0-6.0 mm	2.8	93
0.25-2.0 mm	1.9	93
0.044-0.25 mm	3.7	70
0.004-0.044 mm	11.2	138
0.001-0.004 mm	55.0	470
<0.001 mm	104.0	790

80 - LAAMK 007, Red clayey basal till, rich in Dubawnt Group erratics, District of Keewatin

Size fraction/element	Cu (ppm)	Pb (ppm)	Cr (ppm)
Bulk Sample	600	1850	132
2.0-6.0 mm	1920	3050	240
0.25-2.0 mm	760	1700	180
0.044-0.25 mm	208	620	66
0.004-0.044 mm	300	540	69
0.001-0.004 mm	2040	3150	198
<0.001 mm	7200	7100	410

Table 1 (cont'd)

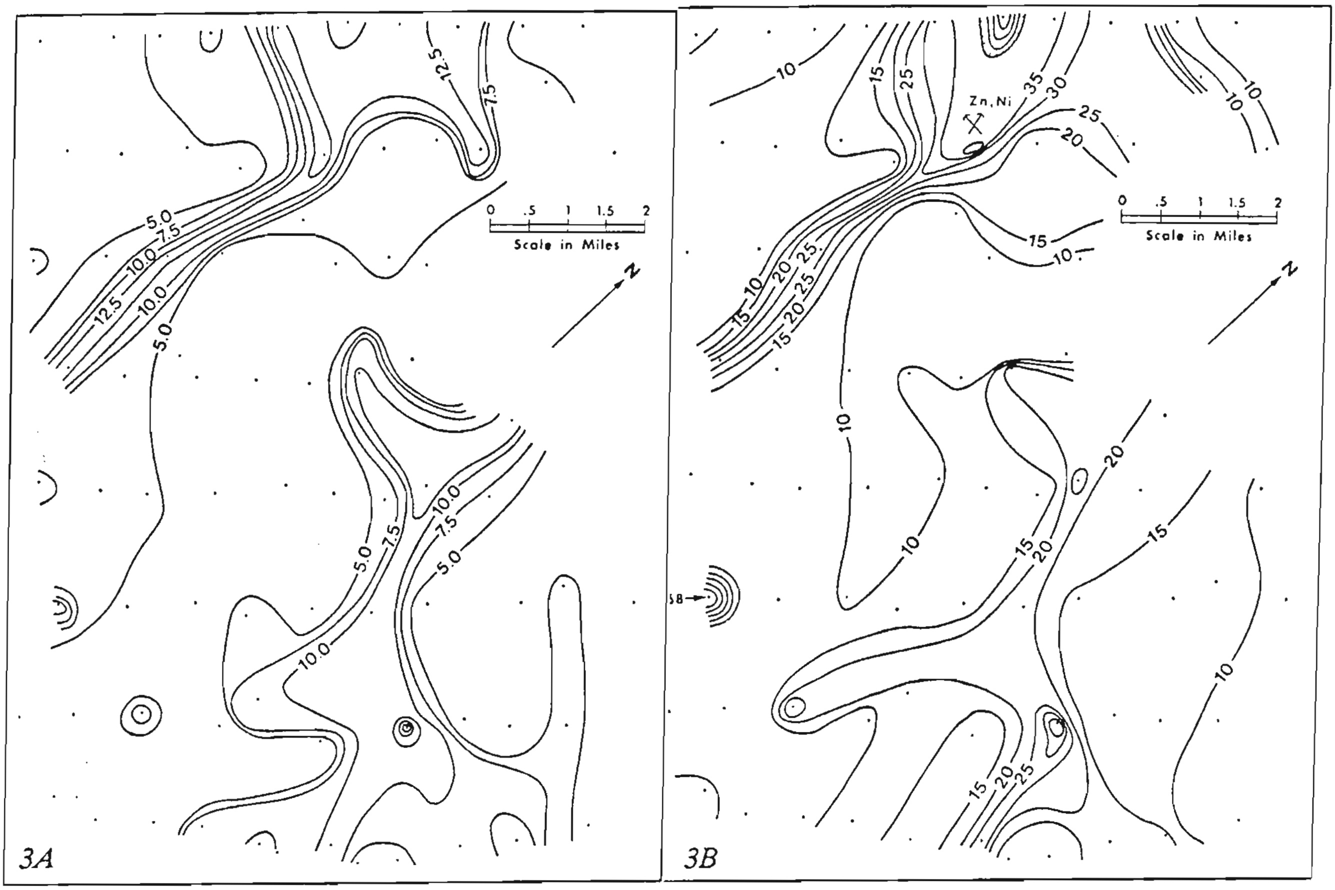
80 SMA - 192 Near-surface basal till, Central District of Keewatin

Size fraction/element	Pb/ppm	U (ppm)	Mo (ppm)	As (ppm)
Bulk Sample	136	1.7	8	23
2.0-6.0 mm	168	0.9	8	5
0.25-2.0 mm	74	1.1	4	7
0.044-0.25 mm	44	1.2	6	8
0.004-0.044 mm	102	5.5	6	25
0.001-0.004 mm	570	8.0	15	76
<0.001 mm	1300	2.6	26	112

80 AR-0109 Oxidized, ice-contact, gravel, poorly sorted, Grenville of Eastern Ontario

Size fraction/Element	Cu (ppm)	Ni ppm	Cr ppm
Bulk Sample	56	326	935
2.0-6.0 mm	36	387	1116
0.25-2.0 mm	27	213	690
0.044-0.25 mm	27	221	1093
0.004-0.044	152	661	1284
0.001-0.004 mm	267	982	1212
<0.001 mm	484	1228	1111

Without adequate attention to the effects of partitioning, a drift geochemical map can become essentially a map of till texture, as graphically illustrated by Figures 3 and 4, compiled from till sampling around volcanigenic base metal mineralization at Spi Lake, in south central district of Keewatin. The true picture of glacial dispersal around this potential ore body was provided by direct analyses of the clay fraction of drift, as discussed by Ridler and Shilts (1974)



% Clay of Silt & Clay
Kaminak Lake Area, NWT

Zinc in Silt & Clay
(ppm)
Kaminak Lake Area, NWT

Figure 3. *3A: Map showing contoured distribution of weight percent clay (<2 μm) in silt-clay (<250 mesh), sieved separates from till, Spi Lake area, District of Keewatin. 3B: Contoured map of zinc concentrations in silt-plus-clay separates from till samples in Figure 3A. Similarity of contour patterns caused by enrichment of zinc in clay (<2 μm) fractions (from Shilts, 1971).*

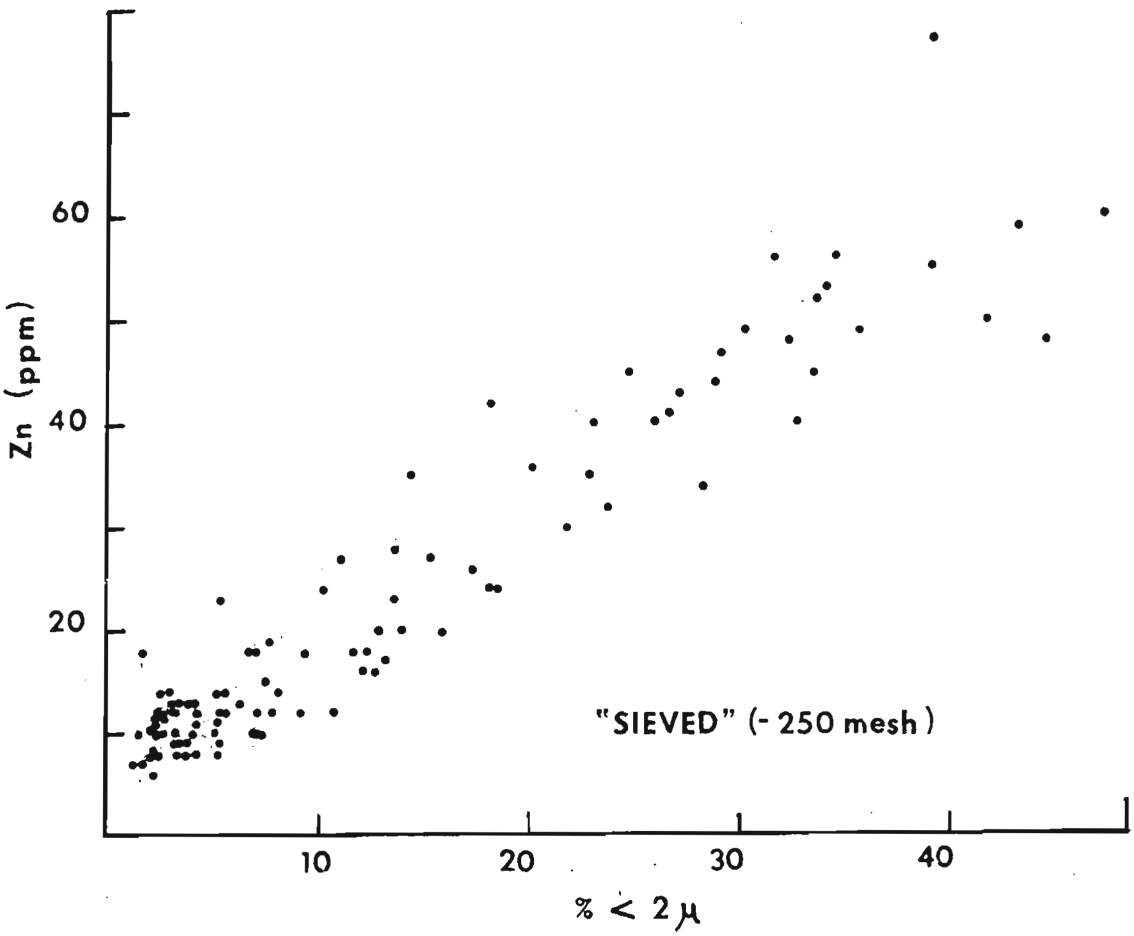


Figure 4. *Plot of zinc in silt plus clay (-250 mesh) fractions against weight percent clay, for samples from vicinity of Figure 3. Note strong textural control of zinc concentrations.*

A question that remains unresolved in many areas of volcanogenic or sediment-hosted massive sulphide bodies is why outcropping massive sulphide and other types of mineralization are indicated by geochemical patterns derived from a size fraction that is dominated by silicate minerals and appears to contain few or no sulphides. In addition, the inference that metal detected in the clay fraction is largely structural and not adsorbed and the fact that most dispersal trains from sulphide bodies are far larger than the outcropping ore body could reasonably be expected to produce, pose important questions about the geochemical pathways from ore to host rock to glacial sediments. In the case of syngenetic ores, perhaps the answers to these questions lie in modern geochemical studies of the relationship between actively forming sulphide deposits and the clays of their surrounding sediments near submarine hydrothermal vents in modern oceans (Barrett, et al., 1988). It is possible that metal in solution near these vents is interstratified with or taken into the lattices of nearby authigenic clays and is retained in the phyllosilicates derived from them during subsequent diagenesis or metamorphic alteration. Thus, ore bodies formed syngenetically in a sedimentary/volcanic sequence may be surrounded ultimately by a 'halo' of host rocks with metal enriched phyllosilicates.

Once glacial sediments are deposited, post-depositional, low-temperature geochemical processes (mostly weathering) will alter and distort the chemistry of their mineral phases, which were originally sorted on the basis of their resistance to abrasion, but in general, the pattern of partitioning will persist. The comparison of a sample of highly altered till, collected near an ultramafic source of platinum-group, precious, and trace metals, to a sample of "normal" till 170 m down-ice demonstrates well the persistence of the partitioning pattern (Table 2). In this example, the absolute concentrations of metals in the altered sample range from 2 to 10 times higher than those in the unaltered sample, but the trends through the various grain sizes persist. Pd, Ni, Cu, and to a lesser extent Co show the typical distinctive trend of significant enrichment in the <2 μm fraction of both samples, as documented in Table 1. In this example, Ni actually may be enriched in the <2 μm fraction because of its presence in serpentine, a very soft mineral which readily abrades to very fine sizes.

The general decrease in gold concentrations in finer sizes is probably related to the way this malleable metal abrades during glacial transport; contacts of gold grains with other clasts cause folding or displacement of gold on the grain in a fashion analogous to a knife being drawn across butter, but material is not appreciably flaked off the grain to be redistributed into finer sizes. Furthermore, large flakes of gold, a common morphology in bedrock, are folded and crumpled during glacial transport until they are reduced to smaller, compact balls, again without losing much mass, much in the way that a large piece of paper can be crumpled into a ball. For chromium, the trend of decreasing metal in finer grain sizes probably reflects the occurrence of Cr predominantly in mineral phases such as magnetite or chromite as opposed to phases such as fuchsite. Because the spinels are hard and non-cleavable, they do not easily reduce to silt and clay sizes by abrasion, whereas easily cleavable, Cr-bearing phyllosilicates, such as fuchsite would tend to be reduced to clay size.

Table 2 – Partitioning in till over ultramafic bedrock, northern Ungava, Quebec*

Raglan 3**	Pd (ppb)	Pt (ppb)	Ni (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Au (ppb)
Bulk Sample (<6.0 mm)	1100	330	2966	91	1305	4460	120
<63 μm (silt + clay)	980	210	3466	84	669	5400	160
2.0- 6.0 mm	2100	500	2579	91	2360	4230	620
0.25-2.0 mm	1400	490	3249	117	1760	4430	230
63-250 μm	1100	220	2306	79	904	3380	130
45-63 μm	900	180	2164	62	913	3300	160
2-45 μm	720	300	2418	72	629	3620	210
<2 μm	2300	110	6355	118	882	>10 000	60
Raglan 5***							
Bulk Sample (<6.0 mm)	130	60	679	53	845	477	20
<63 μm (silt + clay)	100	96	592	41	407	433	44
2.0-6.0 mm	130	85	727	60	1440	411	4
0.25-2.0 mm	140	75	674	64	1010	436	6
63-250 μm	110	50	446	40	538	346	8
45-63 μm	68	100	406	34	469	291	34
2-45 μm	78	70	490	37	445	344	26
<2 μm	390	70	1601	104	1045	1405	10

* Samples collected by and donated by Michel Bouchard, Université de Montréal

** Sample of highly altered till collected from a mudboil 8 m down ice from PGE/Sulphide mineralization

*** Sample of apparently unaltered till collected from till plain 170 m down ice and downslope from gossan near 'Raglan 3'.

WEATHERING OF TILL

Postglacial weathering takes place in the zone of oxidation above the groundwater or permafrost table and can alter drift geochemistry to considerable depths below the surface (Rencz and Shilts, 1980; Shilts, 1976, 1984; Peuraniemi, 1984; Shilts and Kettles, 1990). Furthermore, the effects of weathering on the geochemistry of relatively impermeable silt and clay-rich till are quite different than those on some of its more permeable silt and clay-poor derivatives, such as esker or other ice-contact gravels (Shilts, 1973a). In an oxidizing environment, labile minerals such as sulphides and carbonates are generally destroyed above the water or permafrost tables, their chemical constituents being carried away in solution or precipitated or scavenged locally by clay-sized phyllosilicates and by secondary oxides/hydroxides, depending on the element and the local geochemical environment. In poorly-drained sites, where the water table is at or close to the surface and/or the surface is covered with an organic mat, a reducing environment promotes little or no destruction of primary labile minerals (Peuraniemi, 1984).

In porous and permeable glacial sediments, particularly well-sorted sands and gravels, destruction of labile components also takes place, but additional weathering of primary silicate mineral phases that are unstable in the near-surface environment produces a fine debris of secondary mixed-layer clays, hydroxides, oxides, etc. which can be physically translocated by percolating groundwater from the surface downward through the deposit (Shilts, 1973a). This is especially important for eskers or other coarse-grained deposits that have little or no primary fine fraction because of the high-energy fluvial environment in which they were deposited. Furthermore, many such deposits stand as ridges or hummocks, largely above the ground-water table. The enhanced scavenging ability of these secondary materials gives the fine fractions of glaciofluvial and similar deposits elevated background concentrations of trace elements relative to the same size fractions of nearby till, the fine fractions of which were produced largely by physical crushing of well crystallized primary minerals with much lower exchange capacity (Figure 5).

For reasons cited above, weathering restricts the use of heavy mineral or other coarse-grained fractions of near-surface till and derived, coarse-grained, sorted sediments, except in the case of resistate ore minerals (cassiterite, gold, chromite, etc.). The contrast between the mineralogy and chemistry of fine fractions of till and sorted sediments derived from till makes accurate sample characterization according to sediment facies absolutely essential to interpreting exploration geochemistry results in glaciated terrain. Mixing oxidized samples of till with those of derived sediments, can lead to the classic pattern of non-provenance related geochemical enrichment depicted by Figure 5.

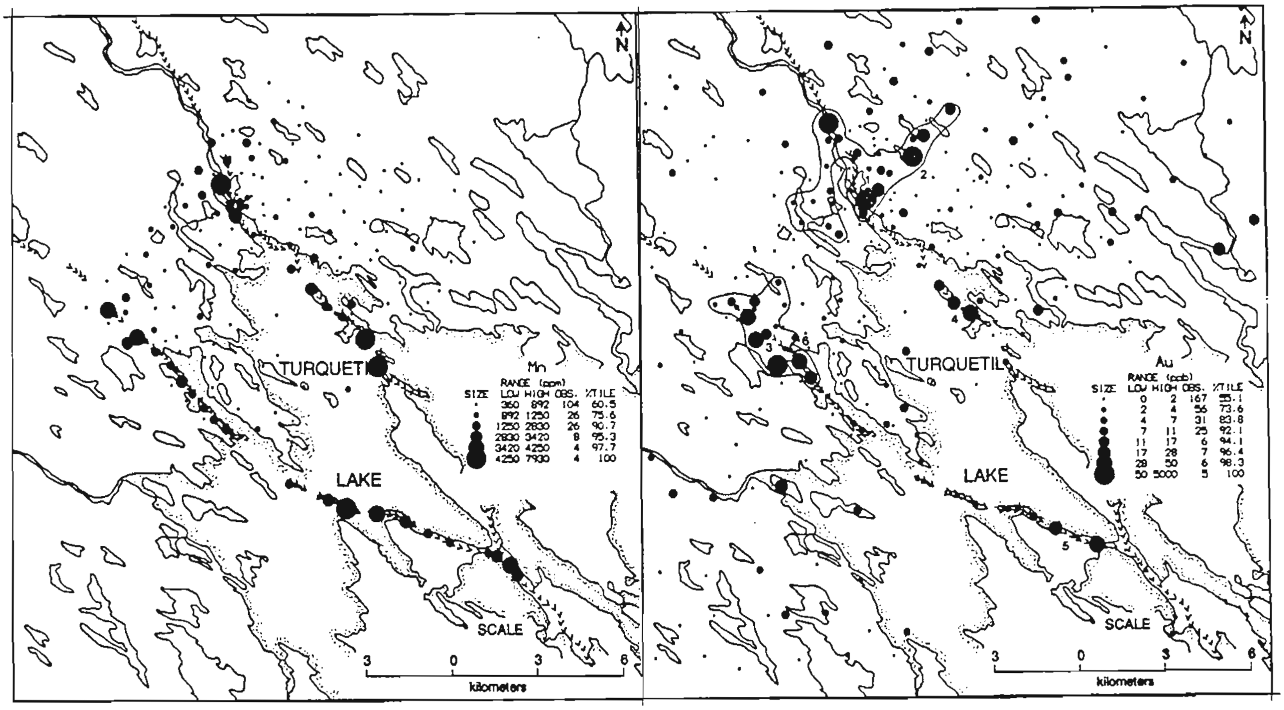


Figure 5. *Concentrations of Mn in clay (<2 µm) and Au in -250-mesh (silt-clay) fractions of till and esker ("Vee" pattern) samples, District of Keewatin. Mn reflects high concentrations of secondary weathering products, Au almost exclusively reflects provenance (from Shilts and Wyatt, 1989).*

Because till and associated sediments in the Appalachian region of Quebec are rich in sulphide minerals, deep till sections in this region have been studied to determine the effects of post depositional weathering on mineralogy and chemistry (Shilts, 1975, 1984; Shilts and Kettles, 1990).

Shilts and Kettles (1990) studied weathering processes in several natural stream banks near Thetford Mines, Quebec. At all sites hard, olive-grey till weathers to a brown to tan colour to a depth of about 2 m below the ground surface. The till contains many cobbles but few boulders and, where unoxidized, has a noticeable component of sand to granule-sized pyrite cubes and fragments. The pyrite is derived from the underlying and surrounding bedrock, quartz-albite-sericite schists with abundant recrystallized pyrite cubes. A northeast-striking belt of chlorite-epidote schists comprising metabasalts and rhyolites with known base-metal mineralization lies less than 15 km northwest (up ice) from most of the sections (Harron, 1976). The most important glacial dispersal direction, presumably the one that prevailed during deposition of the till, was southeastward.

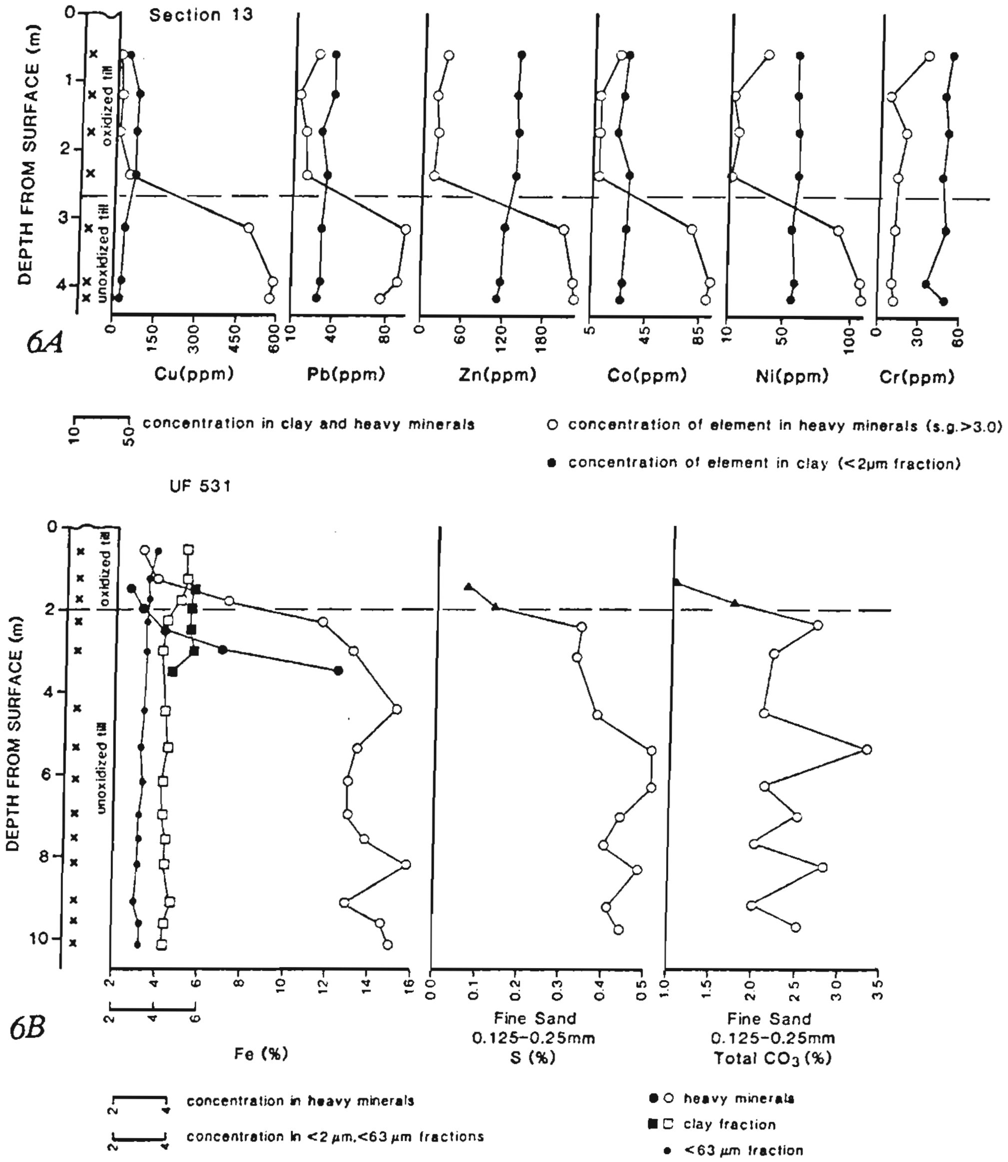


Figure 6. *6A: Vertical profiles of trace element concentrations in clay and heavy mineral separates in till section, Ruisseau Grégoire, Quebec Appalachians. 6B: Fe, S, and carbonate profiles in till section, Ruisseau Nadeau, Québec Appalachians (S and carbonate values derived from total fine sand fractions, including heavy minerals; triangles represent oxidized sand). (from Shilts, and Kettles 1990).*

The effects of weathering on labile minerals are reflected by trace metal concentrations in sand-sized heavy mineral (s.g. >3.3) separates from till samples collected in vertical profile through typical stream-cut sections (Figure 6a). For all the elements studied, except for chromium, there is a sharp decrease in metal concentration in heavy minerals at and above the oxidized zone, through the upper 2 metres of till. Although not apparent in this section, in some nearby sections there is a corresponding increase in concentration of some cations in clay fractions of oxidized samples, which indicates that clay-sized phyllosilicates and/or secondary oxides and hydroxides can scavenge some of the metal released by weathering (Shilts and Kettles, 1990). Although not analyzed at this section, sulphur and iron also decrease markedly in the zone of oxidation at nearby sections (Figure 6b), supporting the conclusion that pyrite and other sulphide phases were the hosts for metal that has been translocated in the zone of oxidation (Shilts and Kettles, 1990).

This and similar studies demonstrate that weathering effects can be important well below the shallow (<1 m thick) postglacial solum. The effects of most importance in mineral exploration are the destruction of primary labile mineral phases, and the redistribution of their cations into secondary or other mineral phases or into groundwater. Thus, it is of paramount importance to have some understanding of this source of vertical geochemical variation when evaluating geochemical patterns obtained from separates containing the silt and coarser fractions of till, particularly if analyses are performed on heavy mineral concentrates. The postglacial weathering problem is, of course, not nearly so important in exploration for resistate minerals such as chromite, tin, gold, etc., but their apparent concentrations can be augmented in oxidized samples if large concentrations of labile minerals present in unaltered samples were removed by weathering processes (Figure 6a).

Assuming that geochemical or other analyses have been carried out in such a way as to avoid non-provenance-related variations, such as those caused by misidentification of sediment facies or stratigraphic position, partitioning, or post depositional weathering, the real variations of geochemical, mineralogical, or lithological parameters may be contoured to provide maps of provenance-related compositional variations. These maps will show, ideally, patterns of glacial dispersal.

DISPERSAL PATTERNS

Glacial dispersal, where reflected adequately by the available sample spacing, can take several forms, depending on where the source outcrops are located with respect to former centres of outflow and with respect to certain dynamic features within the former ice sheets (Boulton, 1984: Bouchard and Salonen, 1990; Shilts and Smith, 1989).

As a glacier transports an indicator[1] component away from a particular source, the concentration of the component is attenuated, both by addition of debris eroded from the dispersal area and by deposition of indicator components along the way. Generally, the decline in concentration of indicator components with distance can be plotted as a negative exponential curve, high frequencies declining rapidly to low frequencies, which are then maintained at levels above background for distances several times greater than the width of the source outcrop. The author has defined the zone of rapid decrease in indicator frequencies as the 'head' of dispersal and the extended zone of lower frequencies as the 'tail' of dispersal. The area of dispersal is called the 'dispersal train' (Figure 7), and the curve itself the 'dispersal curve' (Shilts, 1976) (Figure 8).

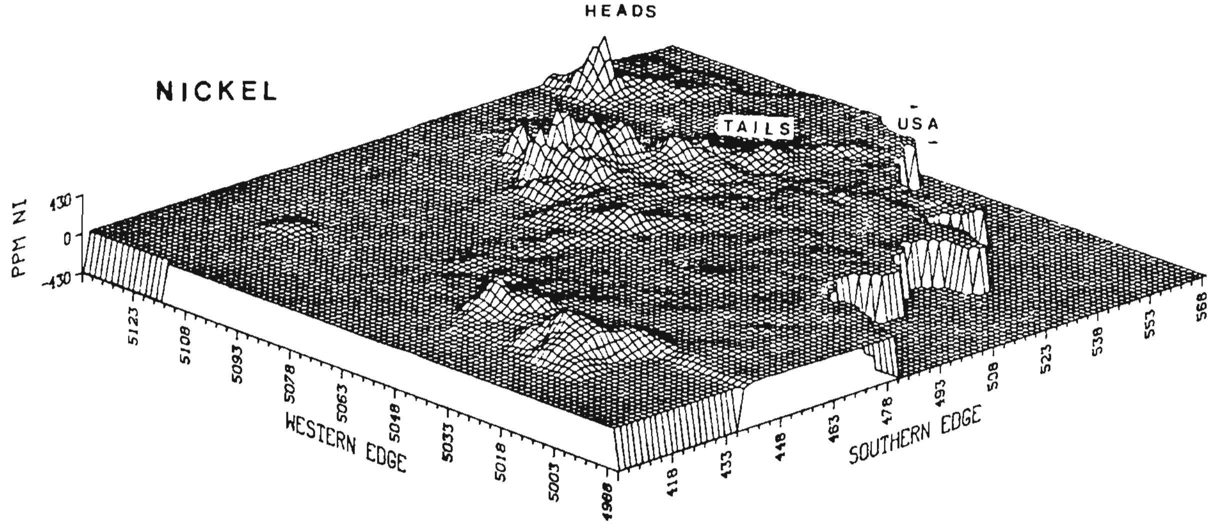


Figure 7. *Three-dimensional representation of heads and tails of nickel dispersal trains from ultramafic outcrops within the Quebec Appalachian ophiolite belt, based on analyses of the <64 um fraction of about 1500 samples of till, view northeast along strike. Southern, southeastern and eastern edges of raised nickel background areas are Vermount, New Hampshire, and Maine portions of U.S.A. border with Quebec. (from Shilts, 1976).*

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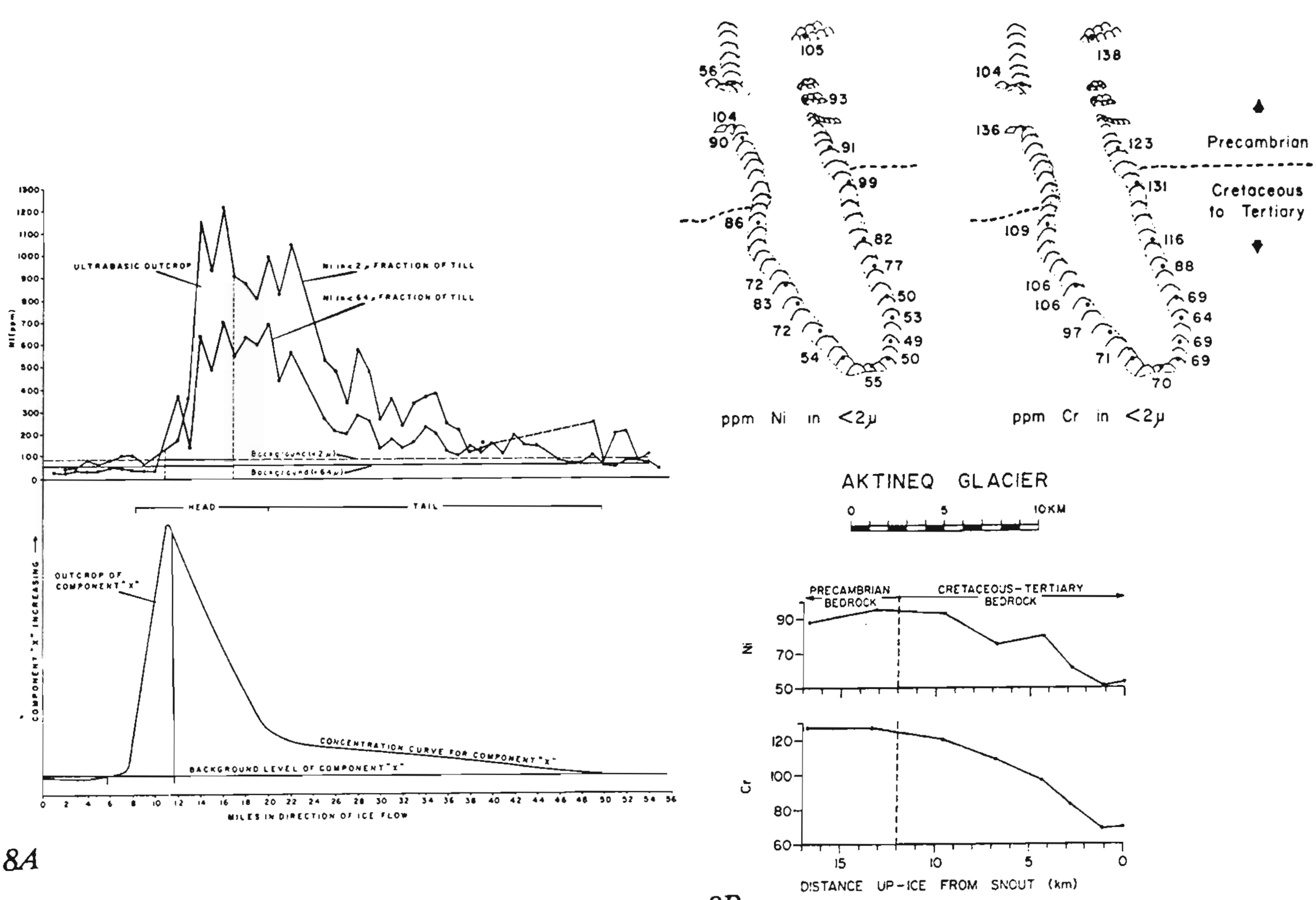
[1] "Indicator" is a glacially transported rock, mineral, or chemical component that is derived from and can be traced to a specific source area.



8A

8B

Figure 8. *8A: True and diagramatic representations of nickel dispersal curves for train depicted on Figure 7. Ice flow from left to right (from Shilts, 1976). 8B: Dispersal curves and maps of Ni and Cr in clay fractions of till samples from lateral moraines of modern glaciers, Bylot Island, Canadian high Arctic (from DiLabio and Shilts, 1979).*

The apparent shape and dimensions of the dispersal curve and dispersal train are influenced in turn by a number of factors:

(1) The lithologic nature and topography of the source area influences how much of a component will be eroded and available for transport. If the source area is a topographically positive feature and is composed of 'soft' rock (limestone, serpentinized peridotite, etc.) or rock that is highly fractured as a result of structural (jointing) or periglacial (frost heaving) disruption, it is likely to provide a source of debris through repeated glacial events. Hard, massive outcrops, such as rhyolites or basalts, provide

comparatively less debris, even if they stand as positive features. If the source outcrops are in narrow depressions aligned with the general direction of glacial flow, the increased velocity of ice flowing through the constriction may generate much more debris than flow on adjacent, flatter terrain. In such cases dispersal trains may be particularly well developed (Shilts and Smith, 1989, p. 51).

(2) The topography of the dispersal area has an important effect on the shape and continuity of both the dispersal curve and dispersal train. In the ideal case, the dispersal area has relatively little relief; the shapes of the curve and the train are controlled principally by the rate of dilution by debris eroded from the dispersal area and mixed with the indicator component and by the rate of deposition of indicator components in the dispersal area. In a topographically irregular dispersal area, ridges, escarpments, valleys, and other features may block or divert debris carried in the ice, destroying, displacing, or truncating dispersal curves or trains. Blocking or diversion is particularly common in geologically (and topographically) complex areas such as parts of the Canadian and Fennoscandian Shield, the Appalachians, and the Cordillera (Figure 9).

(3) Since there are several sedimentary environments associated with deposition of till, it is important to try to recognize the circumstances under which debris that forms the till is transported in and released from glacial ice. In general, glaciers carry two types of sediment load – a dense concentration of debris near their base and a less dense load of debris scattered throughout or on the rest of the ice mass. Basal debris forms relatively dense, compact till which is lodged beneath a glacier or is melted out of the sole of the glacier during the waning stages of glaciation. Debris carried higher in the ice (englacial debris) or on the ice surface (supraglacial debris) is melted out with or without accompanying deformation, or it slumps off the glacier ice by various mass-wasting processes during retreat of an ice sheet or valley glacier. These two groups of till facies, basal and supraglacial, are important to recognize during dispersal studies, because they can vary radically in composition (Figure 9) (Shilts, 1973b). In general, supraglacial deposits tend to be dominated by the lithologies of the topographically higher (often local) or more distant elements of the dispersal area, while basal deposits tend to be dominated by topographically lower elements of the dispersal area. However, where glaciers were advancing up river valleys cut deep into highlands, they may have

carried their basal load far up the valleys, in which case the resulting basal deposits may contain significant amounts of components of distant origin (Holmes, 1952; Shilts, 1976; Aber, 1980).

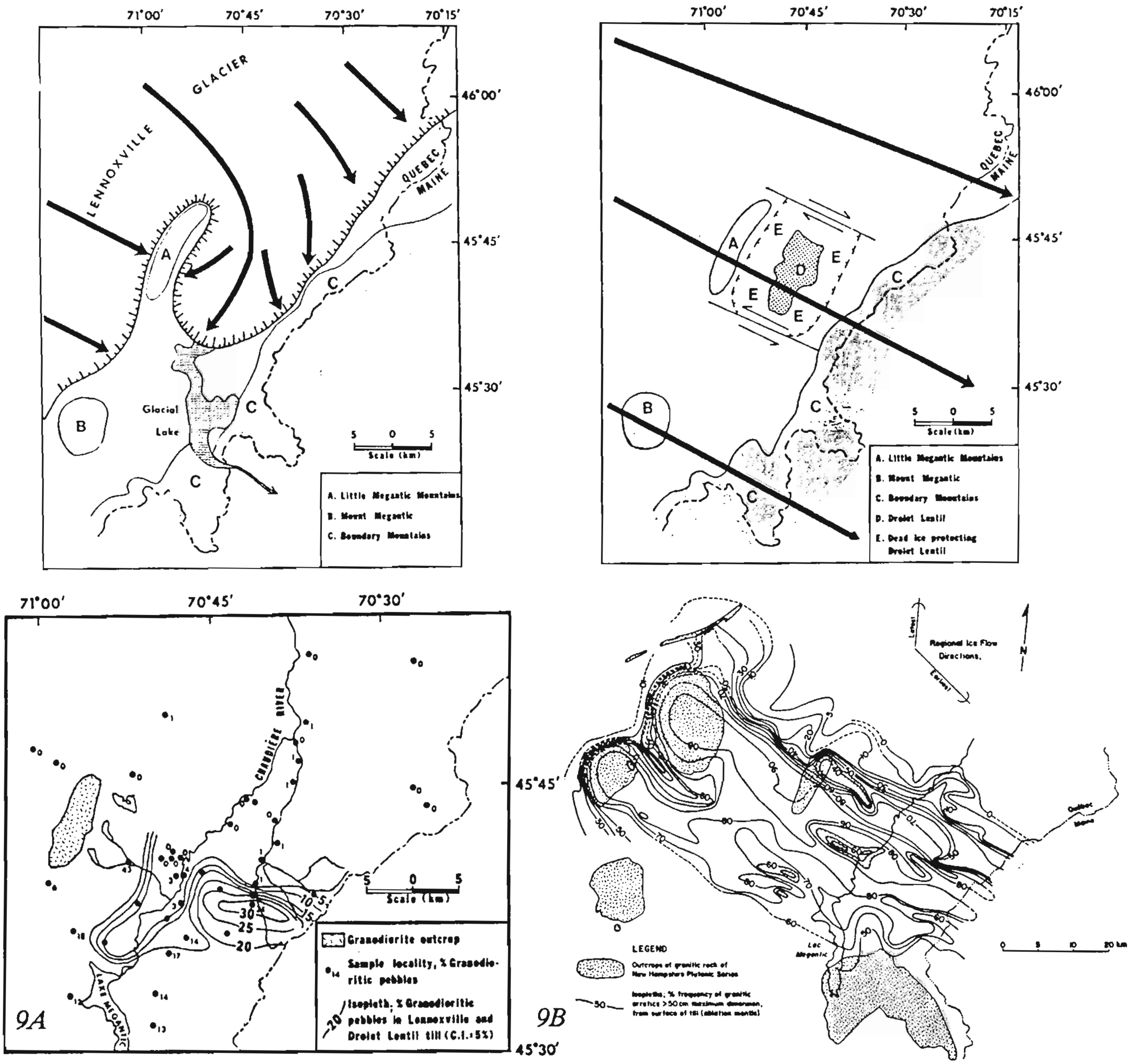


Figure 9. *9A: Granodiorite pebble dispersal in till surrounding basal till deposited by a lobe of granodiorite-poor ice deflected around granodiorite ridge of Little Megantic Mountains, Quebec Appalachians. 9B: Dispersal train of granodiorite surface boulders entrained when expanding ice sheet crossed Little Megantic Mountains. This englacial load was ultimately draped as a sheet of boulders over basal till (ablation mantle). (modified from Shilts, 1973b).*

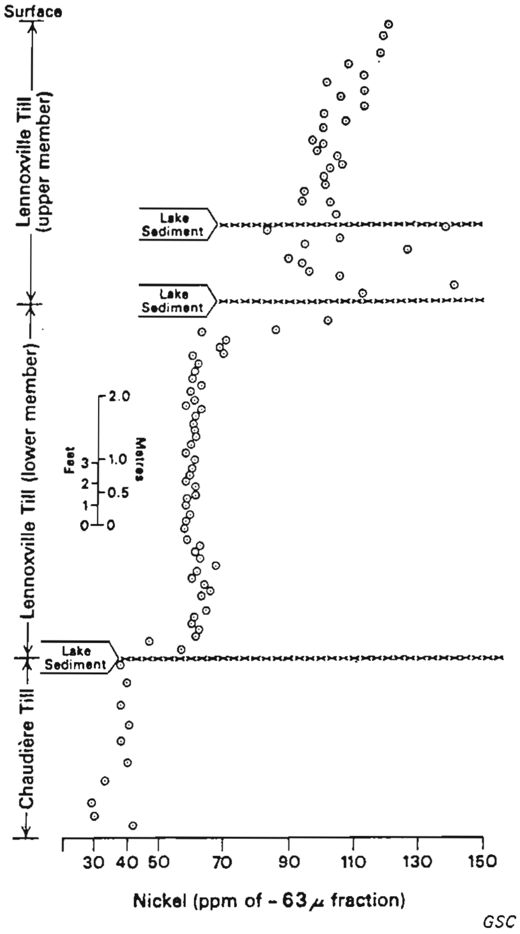


Figure 10. *Vertical profiles of nickel through three till sheets in a section located in dispersal tail of Figure 7. Lowermost till not derived from area of ultramafic outcrops, but lies on older ultramafic-rich drift; Samson River, Quebec.*

(4) In the vicinity of ice divides in Keewatin and Quebec regional dispersal trends do not necessarily agree with other indicators of latest ice movements – striae in particular (Shilts, 1984; Shilts and Smith, 1989). Similarly, in some regions where directions of ice flow are known to have shifted through considerable angles during multiple or single glacial events, individual or multiple tills can show considerable vertical variations, especially in geologically complex areas (Figure 10) (Shilts, 1976, 1978). The reasons for vertical and spatial variations, or lack thereof, during a single glacial event are presently poorly known, but probably are related to the changing dynamics of the base of the glacier in a given region with time. In other words, erosion may be enhanced at some

stage(s) of the glacier's occupation of a particular piece of terrain. The length of time that a glacier was flowing at a particular azimuth also may have affected the distance that debris could be transported, a consideration that is particularly important in the vicinity of ice divides, many of which came into existence or moved to their last position late in a glacial event. It is known that basal ice flow velocities increase exponentially away from centres of outflow, with the result that much of the debris in transit near the centre takes a great deal of time to move any appreciable distance (Boulton, 1984, p. 219).

(5) The magnitude of dispersal and the proportion of "far-travelled" to "local" components in till (and its various varieties and derivatives) are concepts about which it is difficult to generalize, notwithstanding attempts by Clark (1987), Bouchard and Salonen (1990), and others to do so. The complexity of factors governing actual and apparent dispersal in any particular region precludes the development of universal rules. Many studies have drawn conflicting conclusions with respect to these concepts, the conflicts being created largely by the local nature of the studies with attendant influence of local factors on the compositions of the till studied.

Because of the negative exponential character of the ideal dispersal curve, the common observation that most material is dispersed a short distance from its source, and that the bulk of any till sample consists mostly of "local" debris can be considered to be generally true. However, the presence of abundant "local" pebbles and cobbles should not be taken to mean that the finer fractions of the till are of similar local origin, nor should the opposite be taken on faith. For instance, some modern glaciers on Bylot Island (Canada) have been observed to carry almost 100% coarse Precambrian debris at their snouts, which are at least 10 km down ice from the nearest Precambrian outcrop. The local bedrock comprises unconsolidated or poorly consolidated Cretaceous sediments which are so easily disaggregated that they rarely form clasts coarser than granule size. Analysis of the sand and finer sizes of the glacier load reveals that it is made up predominantly of detritus derived from the underlying bedrock (DiLabio and Shilts, 1979), underscoring the caveat against proposing universal rules to quantify dispersal patterns (Figure 11).

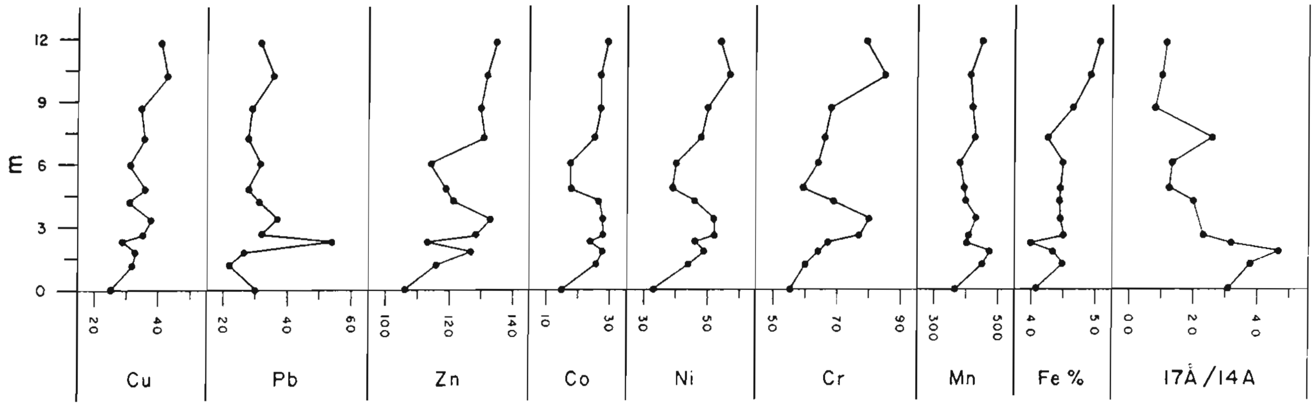


Figure 11. *Vertical profiles of trace elements and clay minerals in debris bands in modern glacier, Bylot Island. Note how mixed layer (17Å) clay derived from local Cretaceous bedrock is concentrated at base; trace elements from distant Precambrian sources increase upward. (from DiLabio and Shilts, 1979).*

(6) Concentration of a component declines gradually in the down ice direction until it merges with and becomes indistinguishable from natural or analytical variations in background. Generally, the more distinctive a component is with respect to the chemistry or lithology of rocks of the dispersal area, the farther it can be traced. Chromium, for instance, is depleted in most crustal rocks; therefore, chromium anomalies generally can be traced for long distances from ophiolitic or other ultramafic complexes that have high chromium concentrations. Likewise, red volcaniclastic pebbles derived from outcrops of late Proterozoic Dubawnt Group bedrock west of Hudson Bay have been traced for long distances, even where present in very small amounts, across terrain underlain by Archean-age gneissic bedrock and by light coloured Paleozoic limestones of northern Hudson Bay (Shilts, 1982).

SCALES OF DISPERSAL

To understand and interpret the significance of the sometimes subtle geochemical tails of dispersal, it is necessary to understand, among factors such as those discussed in previous sections, something about the scales of glacial disperal. In glacial terrain, the composition of a sample is a composite of many overlapping dispersal trains. The trains occur at a variety of scales and emanate from sources up-ice from where the sample was collected. For convenience of discussion, four geologically meaningful scales of dispersal have been defined (Shilts 1984); (1) Continental, (2) Regional, (3) Local, and (4) Small-Scale.

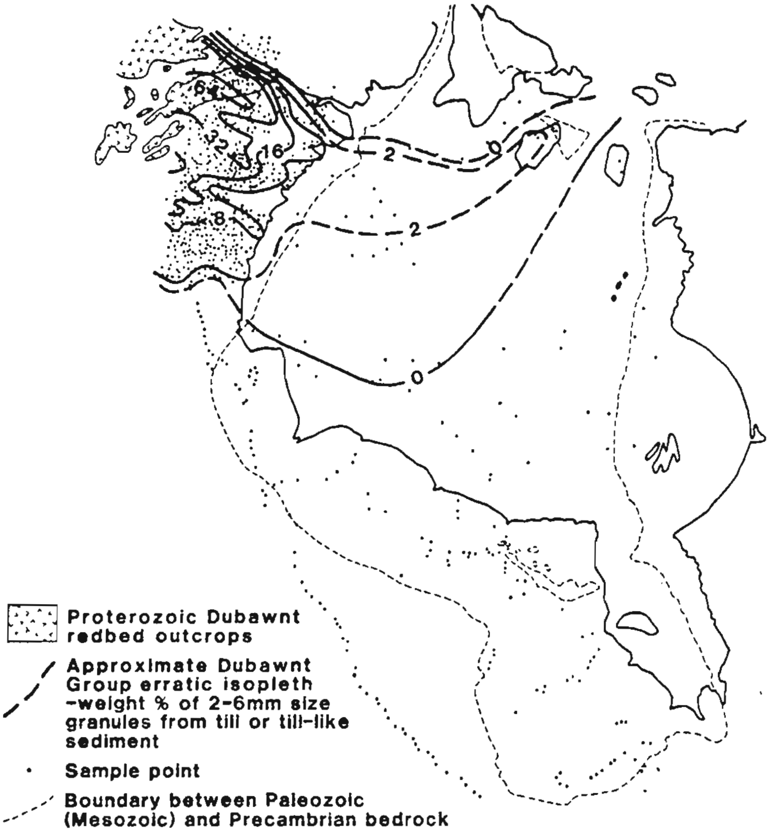


Figure 12. *Continental-scale dispersal of Dubawnt Group erratics in Hudson Bay region (from Shilts, 1982).*

(1) Dispersal on a <u>continental scale</u> can be measured in hundreds to more than a thousand kilometres (Prest and Nielsen, 1987) (Figures 1, 12). Although not usually important in mineral exploration, very far-travelled coarse clasts and fine-grained components, if detected and not properly related to a distant source, may be thought to come from local sources, creating severe exploration problems. The occurrence of diamonds in drift of the American midwest (Stewart, et al., 1988) is perhaps the best example of this problem. Although very rare, diamonds are easily identifiable and may come from as far away as northern Ontario (Brummer, 1978) and the Hudson Bay region, from which an immense train of Paleozoic debris has been dispersed southward and westward during repeated glaciations (Figure 1).

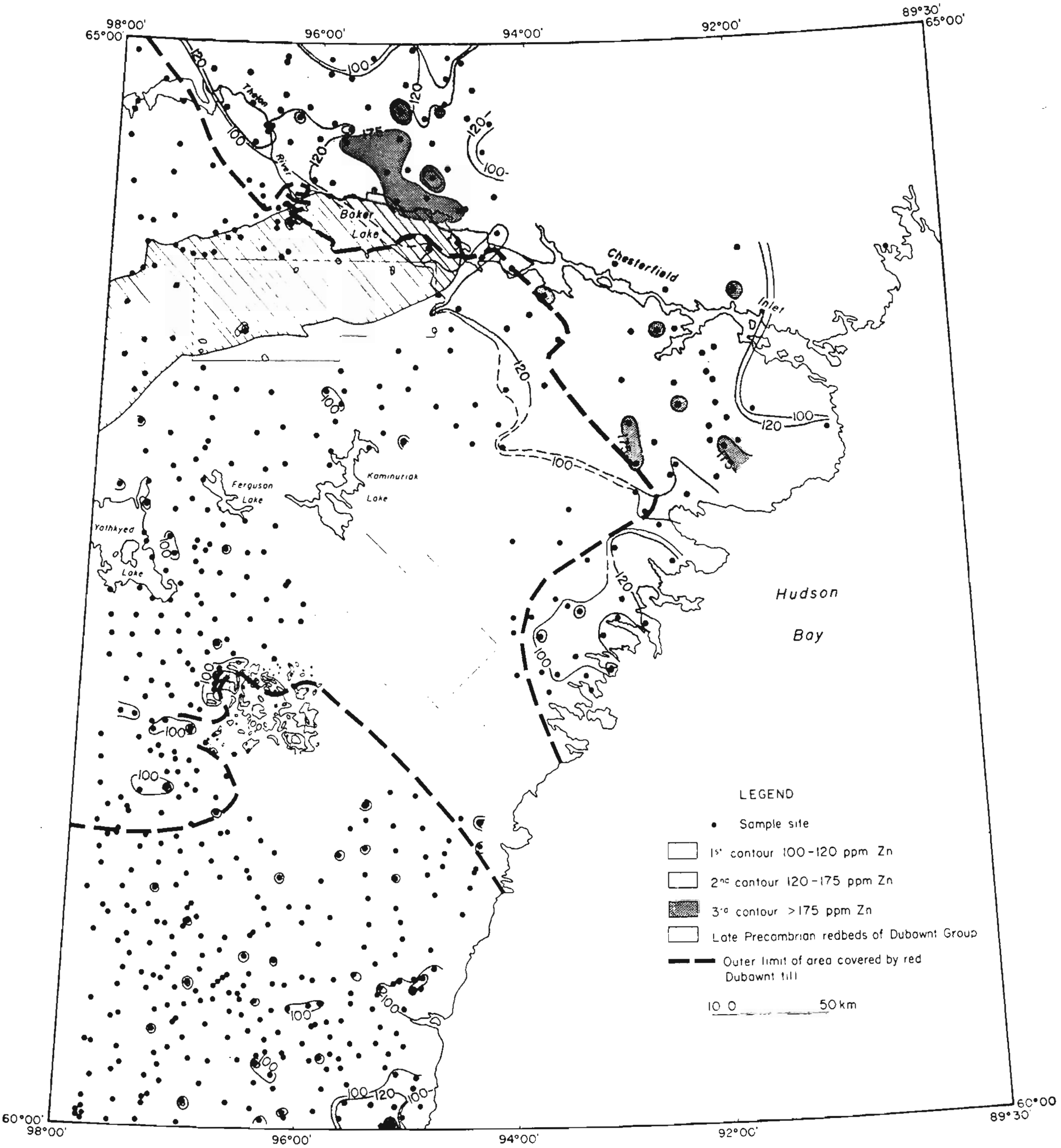


Figure 13. *Regional scale dispersal of zinc in clay fractions of till, District of Keewatin. Outlined polygons are areas in which several thousand samples were collected to test local dispersal. Sediment rich in Dubawnt Group erratics is metal-poor and can depress metal concentrations. (from Shilts, 1984).*

(2) Geochemical dispersal on a regional scale can be measured in tens or hundreds of kilometres. We have mapped this scale of dispersal in the District of Keewatin for till that overlies Archean and younger Precambrian bedrock (Figure 13). The reasons for the consistently elevated metal levels in some parts of this region are not clearly understood. At this low sample density some areas of metal enrichment may have been caused by the areal homogenization, with distance, of several relatively small bodies of geochemically distinctive rocks. For instance, elevated nickel, cobalt, and chromium concentrations could result from dispersal from a cluster of komatiitic or other ultramafic bodies. In other cases, trace element levels in till are known to be suppressed as a result of far-travelled, metal-poor debris being mixed with more metal-rich debris from local rocks (Shilts and Wyatt, 1989). The large dispersal train of clay-sized hematite and kaolin (Figure 12) from the easily eroded Dubawnt group (Donaldson, 1965) has depressed background and anomalous levels of metal from local rocks over a large area, making the higher levels of metal in till outside the train appear anomalous by contrast (Figure 13). Also, within the area of the Dubawnt dispersal train, geochemical expression of mineralized outcrops is depressed because of the diluting effects of Dubawnt detritus.

(3) Local glacial dispersal can be detected by reconnaissance sampling at the scale of one sample per one to four square kilometres. We have sampled over 10 000 km^2 of terrain in southern Keewatin at this scale, and reconnaissance sample spacing in Finland and on the northern Fennoscandian Nordkalott project (Kautsky, et al., 1986) is similar. Geochemical anomalies detected at the local scale are much more easily related to mineralization than are those of the larger scales of dispersal. At this scale of sampling, the tails of dispersal trains from potential ore bodies are likely to be detected, but sample and analytical control (particularly sediment facies, partitioning, and weathering effects) must be precise enough to allow them to be differentiated from background or from the tails of trains of regional or continental scale. Figures 14 and 15 illustrate some examples of local dispersal. In Figure 14, zinc anomalies from known zones of zinc mineralization are superimposed on a regional train of zinc from an unknown source (see Figure 13 for regional context). Figure 15 shows a "negative" dispersal train in which metal-poor kaolin that cements the poorly consolidated Precambrian (Dubawnt Group) sediments that underlie Pitz Lake has been dispersed southeastward, depressing regional

metal levels so much that a distinct train of metal-poor debris has been formed. This is a local expression of the dilution phenomenon illustrated by Figure 13.

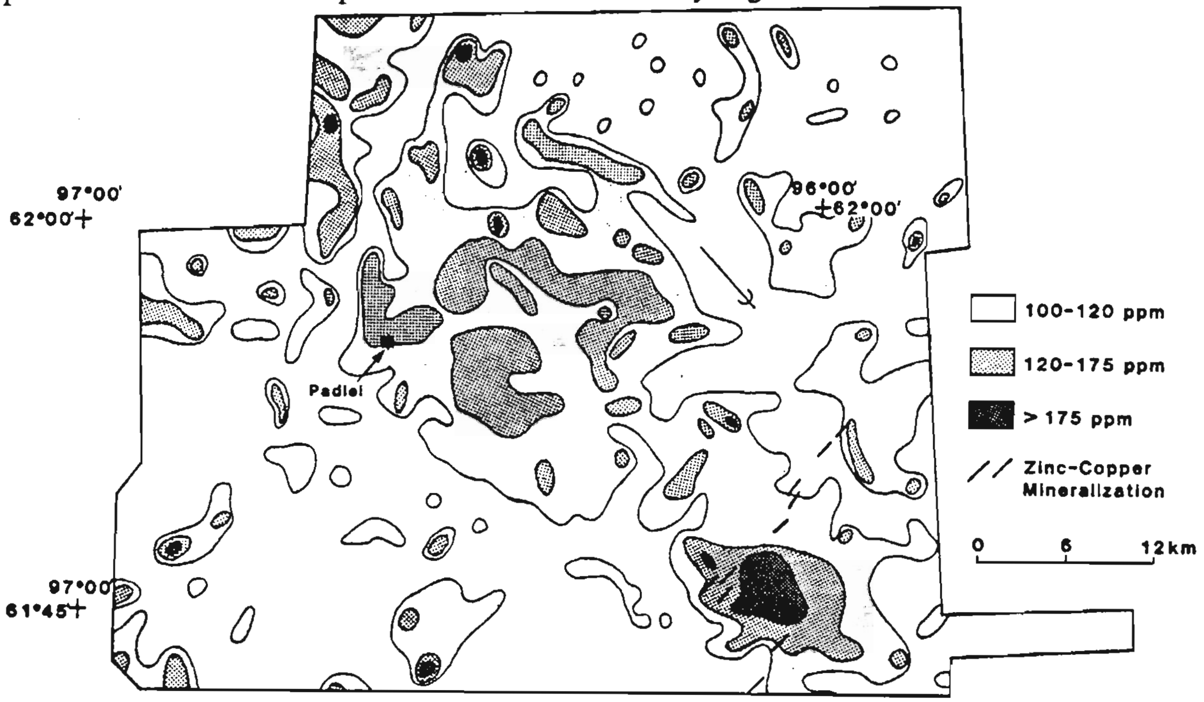


Figure 14. *Local scale of zinc dispersal in south central District of Keewatin, (see figure 13 for regional context). Glacial flow was southeastward (from Shilts, 1984).*

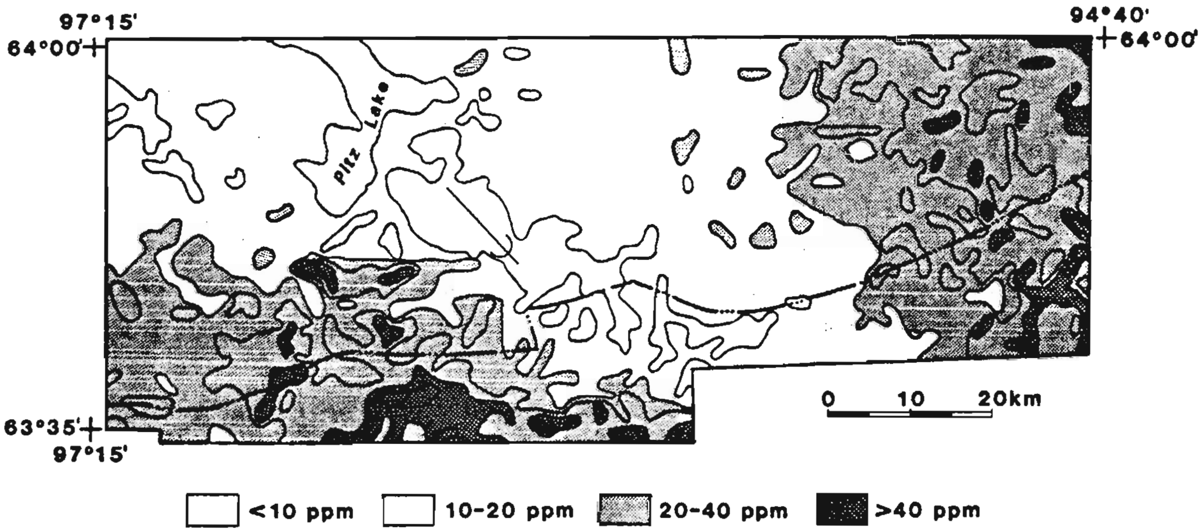


Figure 15. *Negative dispersal train caused by dilution of till matrix by metal poor clay derived from Dubawnt Group, near Baker Lake, District of Keewatin. See figure 13 for location and context of grid (from Shilts, 1984).*

(4) Small-scale dispersal is usually encountered in the last stages of mineral exploration. The boulder train tracing routinely carried out in Finland (Hirvas, 1989) is designed to map this scale of dispersal. While there are many published case histories showing examples of small-scale dispersal, a small nickel dispersal train extending down-ice from outcrops of presently uneconomic nickel-copper mineralization in District of Keewatin (Figure 16) has been chosen because it also illustrates the importance of correct identification of sediment facies and of chosing proper sample processing and analytical techniques. The train of nickel that is so clearly defined by analysis of the <2 μm fraction of till (AAS after hot HNO_3-HCL leach) is very poorly expressed by analyses of sand-sized heavy minerals (s.g. >3.3) and of -250-mesh (<64 μm) fractions, the former because weathering has destroyed the labile, Ni-bearing sulphides, and the latter because the metal-poor, quartz-feldspar-rich silt fraction dilutes the sample in an unpredictable pattern. Note also that the Ni concentrations of the <64 μm fractions of samples from the esker are 4 to 7 times higher than these for similar fractions of nearby till, as predicted in the discussion of weathering.

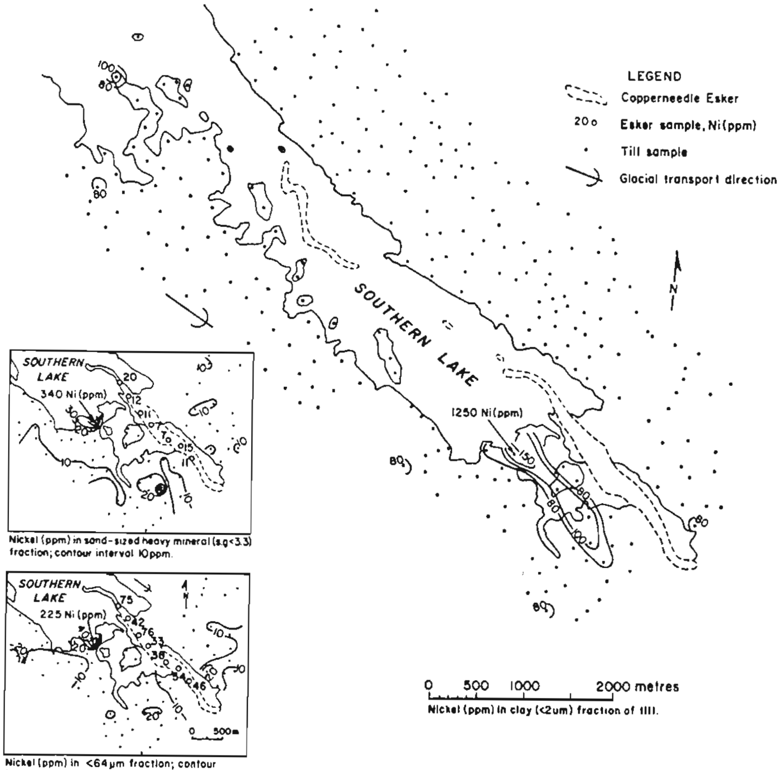


Figure 16. *Detailed scale dispersal train of nickel for clay, heavy mineral, and -250-mesh fractions of till and esker sediments, south-central District of Keewatin. Ni-Cu showing is located near highest Ni values. Esker is outlined by dashed line. (from Shilts, 1984).*

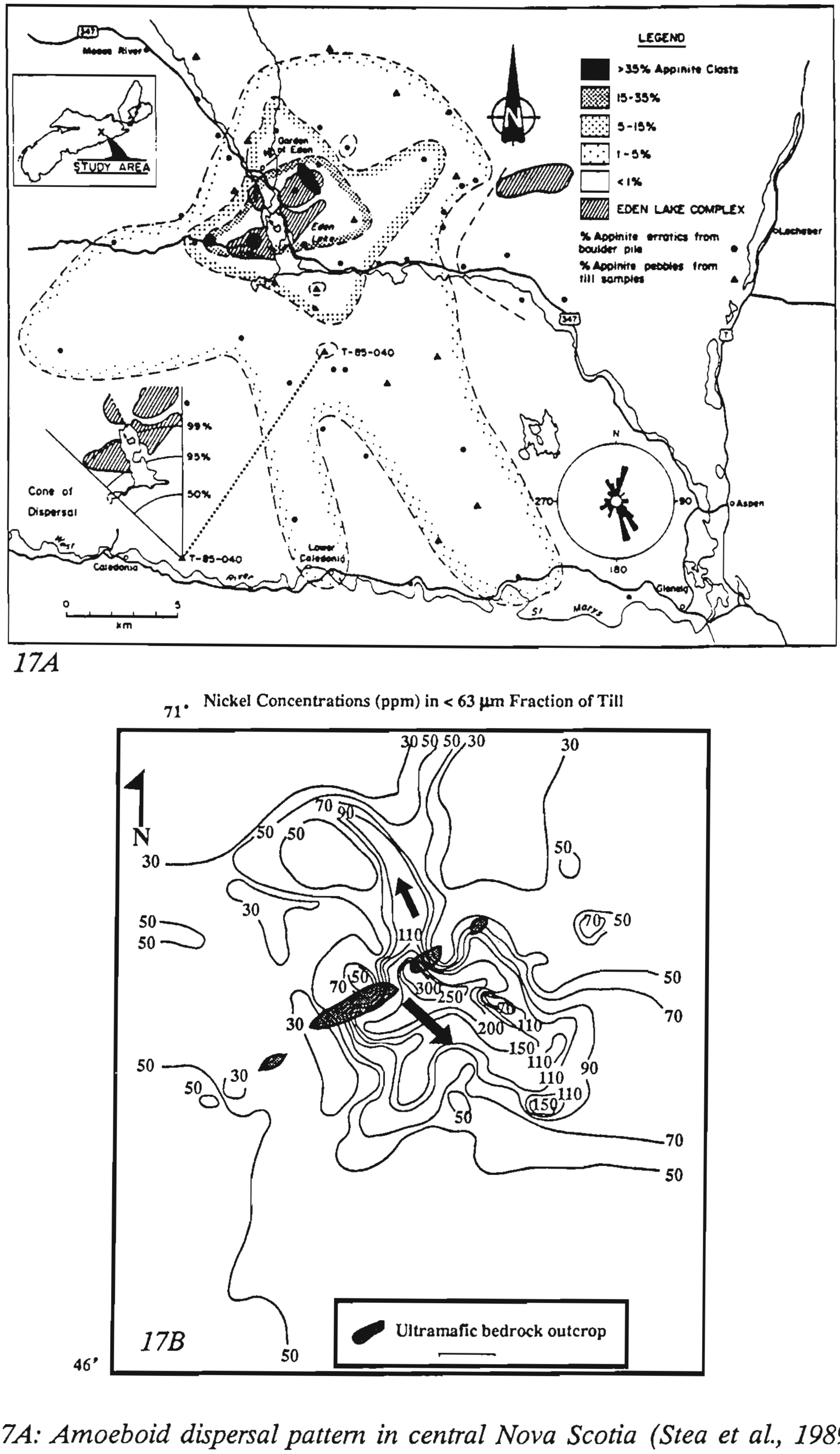
SOME IMPORTANT EXCEPTIONS TO CLASSICAL DISPERSAL PATTERNS

The classic 'head and tail' form of dispersal is a useful model for interpreting or indicating the composition of a glaciated landscape, but recent research has shown that there are other important types of dispersal trains, particularly in regions formerly or presently covered by the great continental ice sheets. It has long been known that shifting ice flow directions throughout a major glaciation may form fan-shaped dispersal patterns, though within a fan, there may be one or more distinctive, ribbon-shaped dispersal trains. The edges of a fan are really the absolute limits of dispersal of a component and reflect the maximum range of ice flow directions across an area during one or more glaciations (Flint, 1971; Salonen, 1987).

One variation of the fan pattern is the amoeboid pattern[**] described by Klassen and Thompson (1989) for dispersal trains near or on the major ice dispersal centre in Labrador – Nouveau Québec. Similar examples have been described by Blais (1989), Lowell et al. (1990), and Stea et al. (1989) in areas of late glacial ice divides in Quebec, Maine, and Nova Scotia, respectively. As these ice divides migrated in a complex way around and across source outcrops or suddenly developed in areas of former unidirectional ice flow as a result of drawdown of parts of the glacier margin into rising marine waters, debris was dispersed first one way, then another. The ultimate results of this constant shifting of positions of ice flow centres were irregular or 'amoeboid' areal patterns of dispersal (Figure 17).

Even far from centres of ice flow, where lobes of ice from different centres coalesced, the zone of coalescence probably shifted with time, depending on the relative health of competing ice sheets (Veillette, 1989). Irregular or amoeboid dispersal can result from such shifting where the "suture" marking the point of coalescence swept back and forth across source outcrops. Kaszycki (pers. comm; Kaszycki et al., 1988) has shown the potential for this in northern Manitoba, where the Keewatin and Labradorean ice sheets merged. The suture marking the zone of confluence shifted continually according to the climatic ascendency of one or the other ice sheet, producing, in the case of the Wheatcroft Lake arsenic dispersal train, westward striae formed by Labradorean ice in an area where southward dispersal was effected by Keewatin ice.

[**] author's terminology



Nickel Concentrations (ppm) in < 63 µm Fraction of Till

Figure 17. *17A: Amoeboid dispersal pattern in central Nova Scotia (Stea et al., 1989). 17B: Amoeboid pattern of Ni dispersal from ultramafic rocks, Rivière des Plante, Québec Appalachians (modified from Blais, 1989). Bar is 5 km long.*

Recently, a third major type of dispersal train, formed by rapidly flowing streams of ice within the decaying North American continental ice sheet, has been recognized (Dyke and Dredge, 1989, p. 198-199; Hicock, 1988; Hicock et al., 1989; Thorleifson and Kristjansson, in preparation; Aylsworth and Shilts, 1989). The areal compositional pattern of this type of dispersal train is similar to that of the classical dispersal ribbon, and it is commonly expressed geomorphologically by trains of drumlins and dense development of eskers. The compositional profile, however, is radically different from that of the ideal dispersal curve, and the width of the train often bears little relationship to the width of the source outcrops.

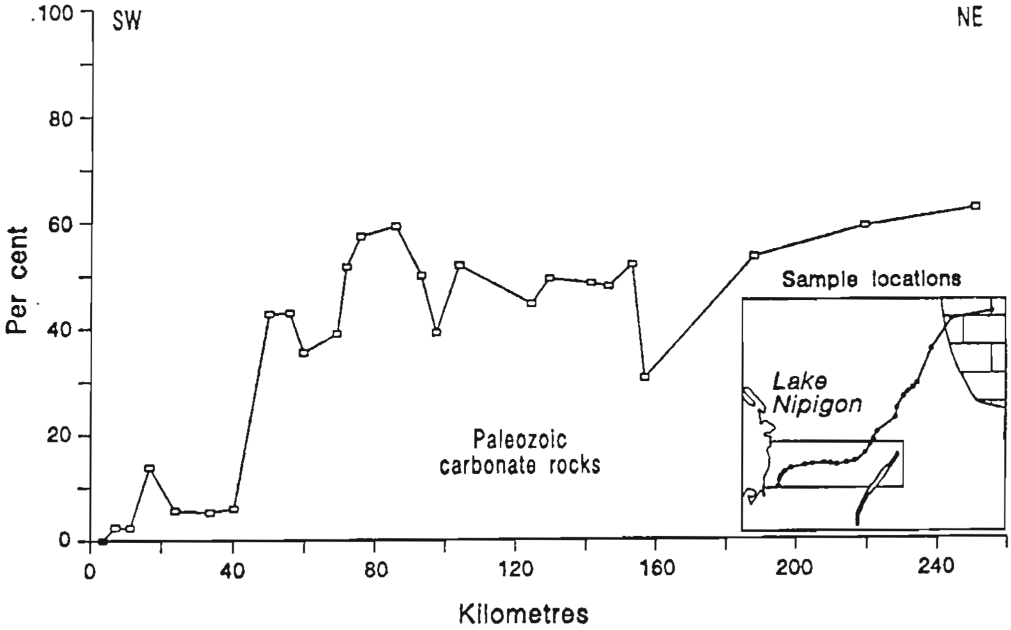


Figure 18. *Characteristic, flat dispersal curve for carbonate erratics in ice-stream till, southwest of Hudson Bay (modified from Thorleifson and Kristjansson in preparation).*

In profile, the composition of a train formed by "streaming" is flat, maintaining high concentrations of the dispersed component from the source outcrops to the end of the train (Figure 18). Little bedrock in the area of dispersal is incorporated into the train. The end of this type of train is marked by a sharp drop to background of the source component and probably marks the position of the ice front of the retreating glacier at the time the ice stream was activated. The width of the dispersal train usually reflects the width of the ice stream and not that of the source outcrops. Compositions change abruptly at the sides of the trains also. For instance, on Boothia Peninsula in northern District of Keewatin, [Canada] a sharp sided train of carbonate detritus several tens of kilometres wide, emerges from a small area within a large Paleozoic carbonate basin (Dyke and Dredge, 1989). Likewise, several narrow trains of Paleozoic carbonate debris extend southwestward across the Canadian Shield like fingers from the large Paleozoic platform that underlies Hudson Bay and the Hudson Bay Lowlands. The till in these trains, even 100 km from the source outcrops, is almost totally composed of clasts eroded from Paleozoic and Proterozoic outcrops within and adjacent to Hudson Bay (Hicock, 1988; Hicock, et al., 1989).

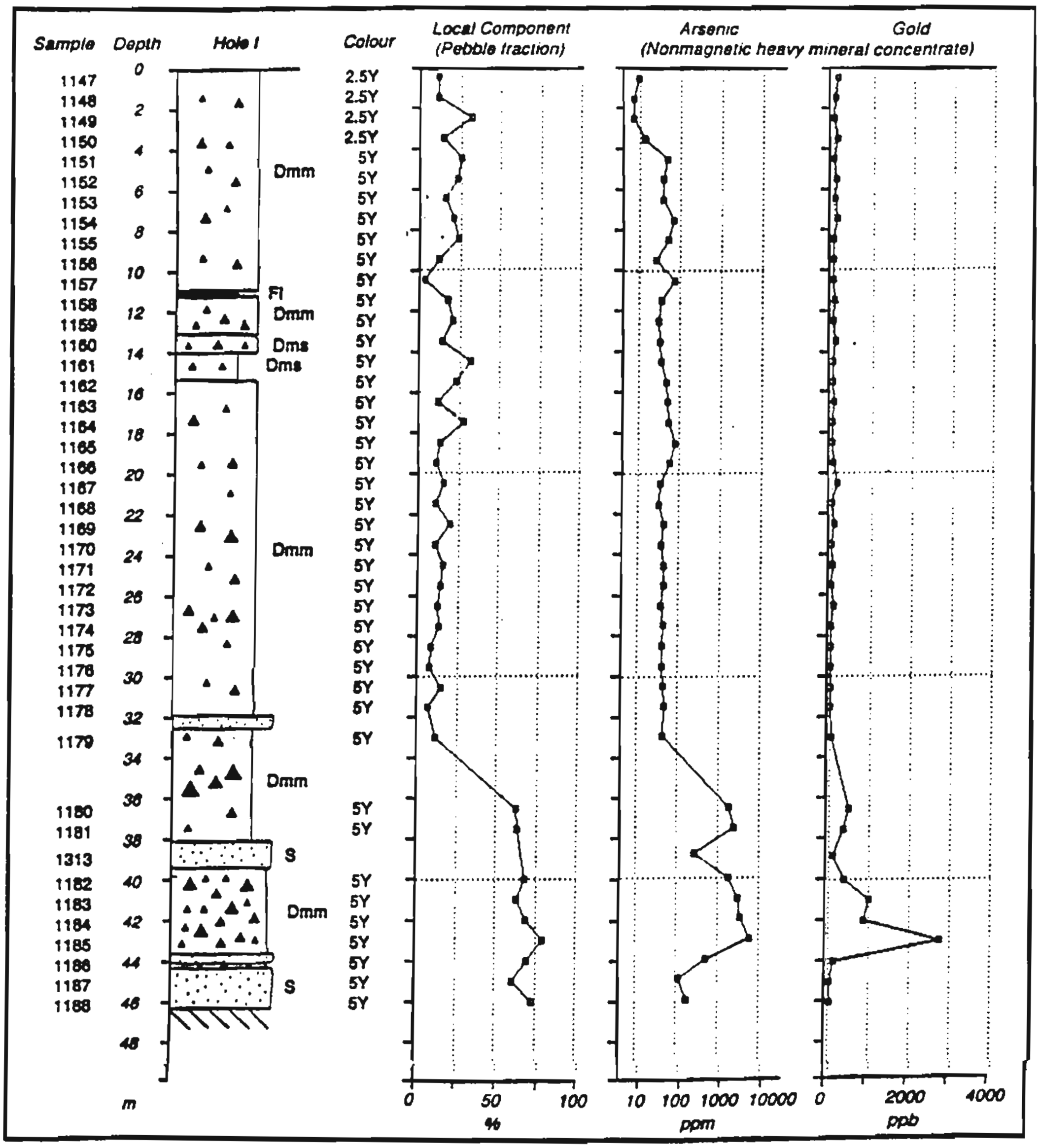


Figure 19. *Vertical profile through carbonate-rich ice stream till covering "local" till, Beardmore-Geraldton area, Ontario. Note the geochemical masking effect of the 30+ metres of ice-stream till (from Thorleifson and Kristjansson, in prep.).*

The Ontario ice stream dispersal trains have important implications for the application of drift compositional studies to mineral exploration. The fact that exotic ice stream drift is relatively undiluted by local bedrock makes it a mask that conceals the compositional signal of bedrock beneath areas that it covers. In many places, the exotic till overlies till composed of more local components, presumably with dispersal characteristics reflecting the normal head-and-tail type of dispersal train (Figure 19). The local till is assumed to have been deposited earlier in the same glaciation for which the retreat phase was marked by ice sheet instability resulting in ice streaming. Till with significant admixtures of local components also forms surface deposits adjacent to former ice streams, but may be encountered only in boreholes in areas covered by exotic, ice stream drift.

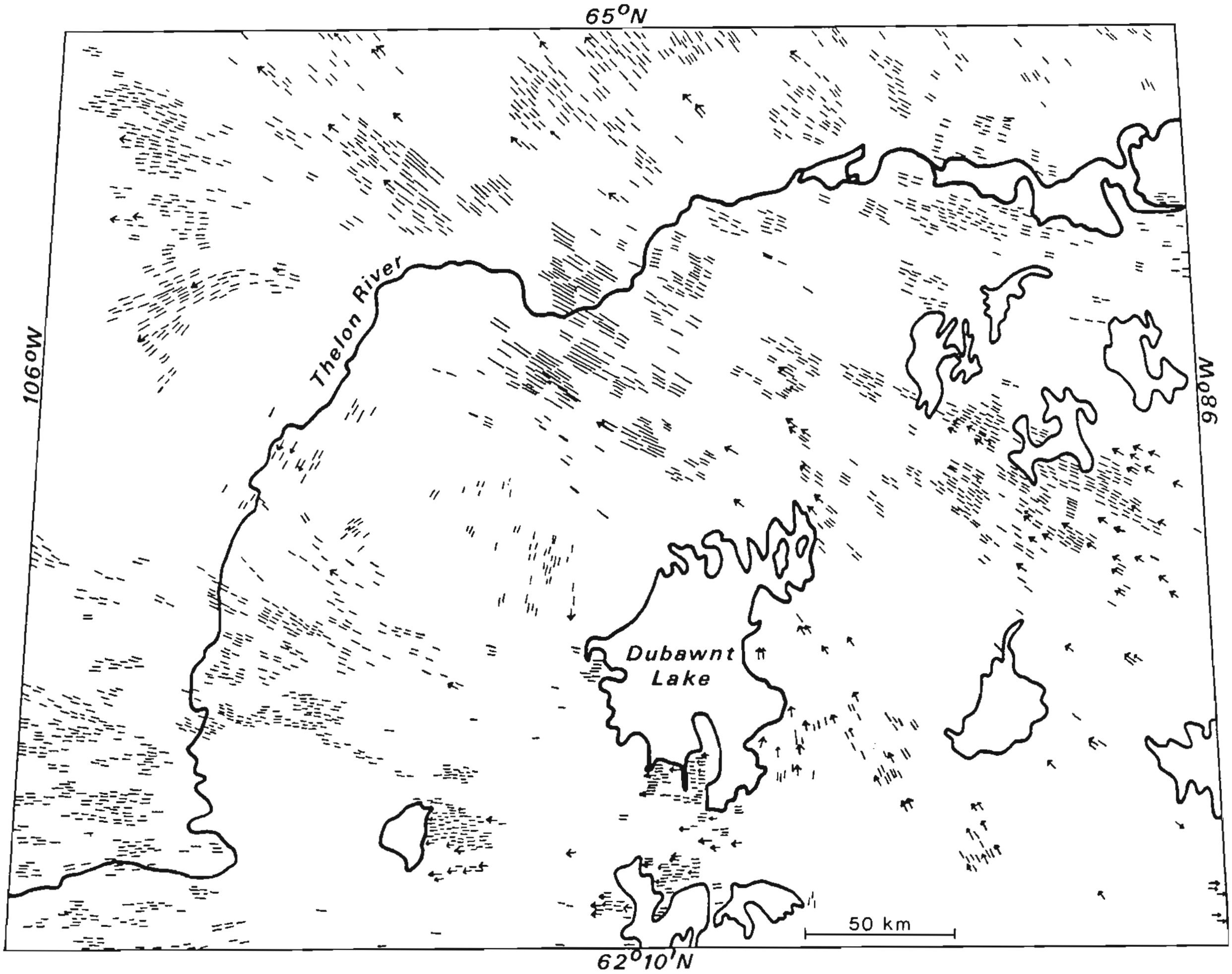


Figure 20. *Expression of two ice streams by WNW-trending trains of drumlins, north and south of Dubawnt Lake, Districts of Keewatin and Mackenzie. Short lines are individual or groups of drumlins or flutings (modified from Aylsworth and Shilts, 1989).*

The late glacial ice sheet failures which resulted in narrow, rapidly flowing ice streams, probably represent instabilities created by excessive water trapped over strata of low permeability at the base of the decaying ice sheet (Hicock et al., 1989), and may be much more common in continental glaciers than formerly recognized. They are presently recognized only where drift compositions are strongly anomalous or where they are marked by distinct trains of drumlins (Figure 20) and esker fields (Aylsworth and Shilts, 1989).

Finally, one more peculiarity of glacial dispersal with presently unevaluated implications for mineral exploration and drift composition should be mentioned – the "conveyor belt effect". Taken as a whole, a glacier works in a way somewhat analogous to a conveyor belt, continuously entraining material from many source outcrops and transporting it to the end of the glacier. During transport, much of the debris from one type of outcrop is deposited or is diluted by incorporation of debris from other outcrops. This results in the head and tail type of dispersal curve, with the tail eventually being obscured within background compositions. However, there is the potential for debris from every outcrop along the path a glacier follows, from its source or centre to its end, to reach the glacier's margin or snout, albeit in small amounts. If the glacier front stands in one place for some time, either at its terminal position or during halts during the active phase of its retreat, there is the opportunity for small amounts of debris from distant sources to be dumped and concentrated at its terminus (Stewart and Broster, 1990). With time, small amounts of material will increase in concentration in water and ice-lain sediments associated with either terminal or end moraines, particularly if the debris has high specific gravity or is too large to be transported far in the proglacial fluvial system. High concentrations of gold in outwash and in alluvium derived from outwash at the Wisconsinan terminal moraine in the midwestern United States as well as diamond occurrences in moraines around the driftless area in Wisconsin may be products of this type of conveyor-belt concentration.

Because of the lack of lateral mixing of debris transported in ice, sampling of terminal moraines in modern or ancient valley glaciers – in the Cordillera for instance – can provide an efficient way to find clues to mineralization in their catchment basins (DiLabio and Shilts, 1979; Evenson and Clinch, 1987). The concentrations of far-travelled components in water-sorted sediments of the terminal moraines are likely to be much higher than those in the drift deposited over most of the glacier's bed. If carried out properly, a single sampling traverse along an end moraine should yield detailed information about mineralization and composition of bedrock in the glacier's catchment – whether the glacier is of continental scale, in which case the interpretation would be complex, or of the local scale typical of Alpine terrain, in which case relatively precise geochemical information about its catchment may be gleaned from limited, judicious sampling.

CONCLUSION

This brief overview of the relationship of drift geochemistry to the principles of dispersal draws heavily on Canadian examples, and particularly on work carried out at the Geological Survey of Canada. Similar glacial sedimentological/geochemical work, which has led to similar conclusions, has been carried out in many glaciated regions, that of geoscientists in Finland being probably the most varied and most prolifically published. Developments in the field of drift prospecting, the geochemical aspects of which have only blossomed since the late 1960s (Kauranne, 1975; Coker and DiLabio, 1989), are summarized in many Fennoscandian publications and in dedicated publications such as the semi-annual Prospecting in Areas of Glaciated Terrain (PAGT) series, sponsored by the Institution of Mining and Metallurgy in London. Recent books dedicated to mineral prospecting in drift covered areas have been published or sponsored by the Geological Surveys of Canada (Dilabio and Coker, 1989) Ontario (Garland, 1989), and Finland (Kujansuu and Saarnisto, 1990) or in special issues of journals (Bjorklund, 1984).

Finally, it should be recognized that in this era of environmental concerns, the very geochemical data that can lead to discovery of mineralization in a glaciated area, may serve as an invaluable source of baseline data for planning "environmentally friendly" mining and for evaluating and mitigating the ultimate effects of mining activities. Drift geochemical surveys in general can and should be used to provide a chemical baseline from which to evaluate the plethora of environmental geochemical problems that will continue to beset industrialized areas in the decade and century to come.

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PAPER #3

OVERBURDEN GEOCHEMISTRY IN MINERAL EXPLORATION

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Abstract

Mineral exploration in regions that were glaciated during the Quaternary is hampered by the scarity of outcrops and by the variable thicknesses of allochthonous glacial drift that mantle the bedrock. Geochemical strategies that have been successful in exploration usually involve an understanding of the history of the glaciated landscape.

The past decade has seen a substantial increase in our knowledge of glacial stratigraphy and associated ice flow directions. In many areas of thick drift, the glacial succession has been found to contain multiple tills having different provenances related to distinct ice flow directions. The use of drilling and trenching has been instrumental in providing data on the glacial succession. Of particular value has been the ability of sonic drills to recover intact core of the entire glacial sediment sequence. Light portable drills have been used similarly in areas of thin drift. The increased use of till geochemistry in mineral exploration and regional surveys has resulted in the discovery of several ore deposits and the documentation of many dispersal trains derived from mineralization and from distinctive bedrock units.

Stratigraphic drilling programs and major reconnaissance surveys of till geochemistry have provided baseline data for other geochemical data sets, mineral exploration, bedrock mapping and environmental studies. Data on surficial geology, glacial stratigraphy and ice flow directions have been collected to aid interpretation of the till geochemistry. Research on the residence sites of metals in till has indicated that specific grain size ranges and mineralogical forms hold the bulk of the metals, depending on the species of primary metal-bearing mineral and the history of glacial comminution and weathering.

Résumé

L'exploration minérale dans les régions soumises à l'action des glaciers pendant le Quaternaire est difficile en raison de la rareté des affleurements et de l'épaisseur variable des dépôts glaciaires allochtones recouvrant le socle rocheux. Les stratégies d'exploration géochimique efficaces exigent généralement une compréhension de l'évolution du paysage glaciaire.

Au cours de la dernière décennie, les données recueillies ont permis d'élargir considérablement le niveau de connaissances de la stratigraphie glaciaire et des directions d'écoulement glaciaire associées. Dans de nombreuses régions où l'épaisseur des dépôts est importante, la succession de dépôts glaciaires renferme des tills de provenance différente correspondant à des directions d'écoulement glaciaire distinctes. Les forages et les tranchées ont joué un rôle déterminant dans l'acquisition de données sur la succession des dépôts glaciaires. La foreuse à vibrations est particulièrement utile parce qu'elle permet de prélever des carottes intactes représentant toute la succession de sédiments glaciaires. Des foreuses légères et portatives ont également été utilisées dans des régions où l'épaisseur des dépôts est peu importante. Le recours accru à la géochimie des tills dans le cadre de l'exploration minérale et des levés régionaux a mené à la découverte de nombreuses traînées de débris provenant de zones minéralisées et d'unités lithologiques particulières.

Des programmes de forages stratigraphiques et d'importants levés de reconnaissance de la géochimie des tills ont fourni des données de base pouvant servir à l'interprétation d'autres types de données géochimiques, à l'exploration minérale, à la cartographie géologique et aux études environnementales. De nombreuses données sur la géologie des dépôts meubles, la stratigraphie glaciaire et les directions d'écoulement glaciaire ont été recueillies dans le but de faciliter l'interprétation de la géochimie des tills. Plusieurs études sur la localisation des métaux dans les tills ont démontré que certaines granulométries de même que certaines phases minéralogiques particulières renferment la majeure partie des métaux et que ceci est fonction des propriétés du minéral primaire, de l'histoire de la microdésintégration glaciaire et de l'altération.

INTRODUCTION

In regions that were glaciated in the Quaternary, mineral exploration can be hampered by the complexity of the surficial sediments, which are largely allochthonous in relation to the bedrock they overlie. In the context of almost totally glaciated landscapes, which includes most of North American north of 40°N, Greenland and Iceland, most of Europe north of 50°N, extensive parts of Asia north of 60°N, parts of South America, and Antarctica, the glacial sediments have particular characteristics that influence the selection of sample media, sampling design and interpretation of data. Foremost among these sediments is till or recycled derivatives of till. Till has distinctive provenance features, is first-cycle sediment, is widespread, and is the parent material for most of the other surficial sediments.

Over the last several years a large number of papers have been published on till geochemistry, boulder tracing, glacial dispersal trains, the history of ice flow patterns and glacial sediment stratigraphy as related to mineral exploration and regional till geochemical/Quaternary mapping programs. The bulk of this work has been carried out in Canada and Finland. The salient features and trends from these works (1977-1987) are summarized in the paper by Coker and DiLabio (1989) which follows on, to a degree, from the review paper of Bolviken and Gleeson (1979) at Exploration '77. The main sources of information have been the proceedings volumes from the biennial symposia on Prospecting in Areas of Glaciated Terrain (Institution of Mining and Metallurgy, 1979, 1984, 1986; Davenport, 1982), articles in scientific journals, in particular the Journal of Geochemical Exploration, and publications by government agencies.

GLACIAL STRATIGRAPHY AND ICE MOVEMENT DIRECTIONS

Mineral exploration, using techniques appropriate for glaciated terrain, is still often conducted, particularly so in Canada, without attempting to understand the regional glacial history. If exploration is to succeed it is essential to know the glacial sediment succession and which sedimentary package (i.e., which till) is related to which ice movement direction.

Till that is derived directly by erosion of bedrock is a first-cycle sediment (first derivative of bedrock of Shilts, 1976) and is the optimum glacial sediment type for mineral exploration. Sediments resulting from the reworking of till or other unconsolidated sediments (i.e.,stratified drift) are second-cycle sediments; they have been subjected to sorting and have undergone an episode of transport in water along a different path from the original sediment. In this way, glaciofluvial gravel and sand represent the coarse fractions and glaciolacustrine silt and clay represent the fine fractions of the till(s) from which they were derived. Because these sediments have travelled along transport paths consisting of two vectors, and have been transported first by ice then by water, it is very difficult if not impossible, in thick sediment sequences, to interpret their provenance. It is far easier to trace till to its bedrock source. Till is clearly the optimum glacial sediment type to use in mineral exploration since it has the least complicated source-transport-deposition history.

Data on ice movement directions may be obtained from a variety of glacial features including: striations, crescentic marks and ice flow land forms; dispersal trains; and, fabrics. Recently, there has been a movement towards 1:50,000 or 1:100,000 scale mapping of surficial geology in areas of active mineral exploration; ice-flow and provenance data at such scales can be applicable to exploration at the property scale.

The past decade has seen an increase in our knowledge of glacial sedimentation, dispersal, stratigraphy and associated ice flow directions. Several examples can be cited.

The Nordkalott Project, which included a regional surficial geochemistry and mapping component, was carried out by the Geological Surveys of Finland, Norway and Sweden, in those countries, north of latitude 66° N (Geological Surveys of Finland, Norway and Sweden, 1986a, b, c, d, e, f and 1987). Ice movement directions were ascertained which revealed areas of simple ice flow in coastal areas and of multiple ice flows inland. Trenching and drilling, using techniques developed in major regional sampling projects by the Geological Survey of Finland in the late 1960's and 1970's, provided data on the Quaternary stratigraphy.

In Labrador, Klassen and Thompson (1987) identified ice flow patterns that are simple near the coast and that become quite complex inland, reflecting the complicated ice-flow history of the central ice divide area. As a direct result, dispersal trains are ribbon-shaped near the coast and become fan-shaped and even ovoid, inland in the area of complex ice flow around the Labrador-New Quebec ice divide (Figure 1, Klassen and Thompson, 1989).

In Nova Scotia, Stea et al. (1989) also found, as in Labrador, that complex dispersal is recorded in areas of multiple ice flow events. Stea was able to classify different areas of Nova Scotia as to their expected sequence of ice flow events (Figure 2).

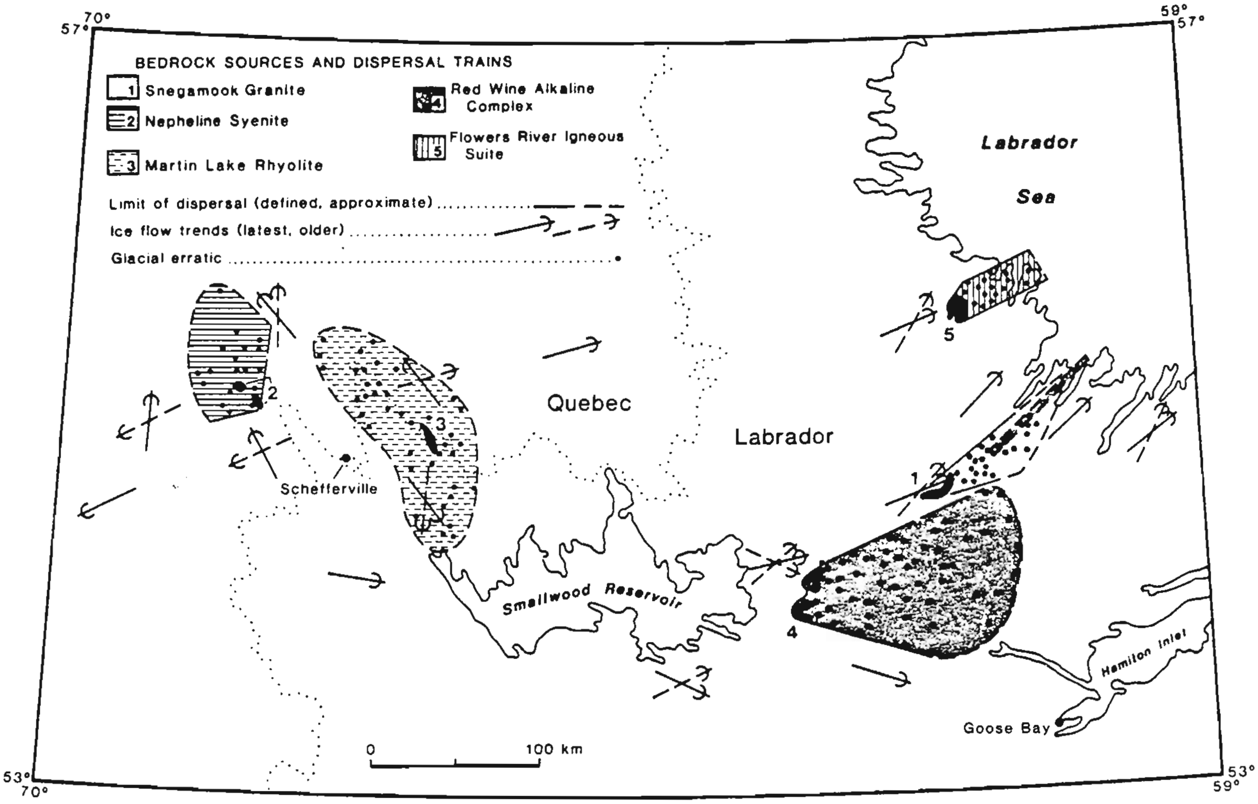

Figure 1. *Dispersal trains in Labrador (Klassen and Thompson, 1989). Broad fan shapes reflect transport in two or more phases of ice flow.*

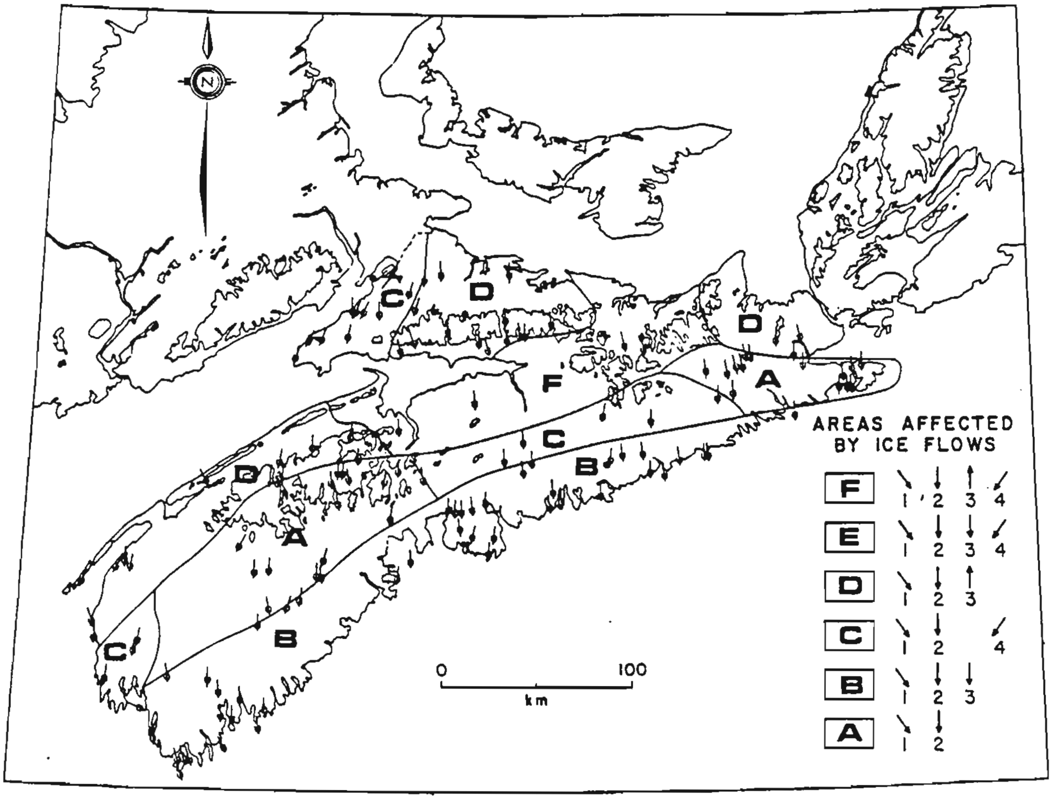

Figure 2. *Sequences of ice flow directions recorded in Nova Scotia (Stea et al., 1989)*

Veillette (1986, 1989) identified three ice flow events in western Quebec (Figure 3), and showed that the middle one was responsible for the bulk of the drift transport. In an area of active exploration by drift prospecting, this interpretation was immediately useful in exploration. In parallel with the work of Veillette in the Abitibi - Timiskaming area is that of Baker et al. (1984a, b, 1985, 1986), Baker and Steele (1987) and Steele et al. (1986a, b) in the Matheson area of Ontario, and that of Bird and Coker (1987) in the Timmins area of Ontario. On the basis of these studies Steele et al. (1989) propose a preliminary stratigraphic sequence with related ice flow directions for these areas of Ontario and Quebec (Figure 4). This western part of the Abitibi greenstone belt is also explored by drift prospecting, relying on overburden drilling to sample the tills in this sequence; hence correct ice flow directions are crucial for data interpretation.

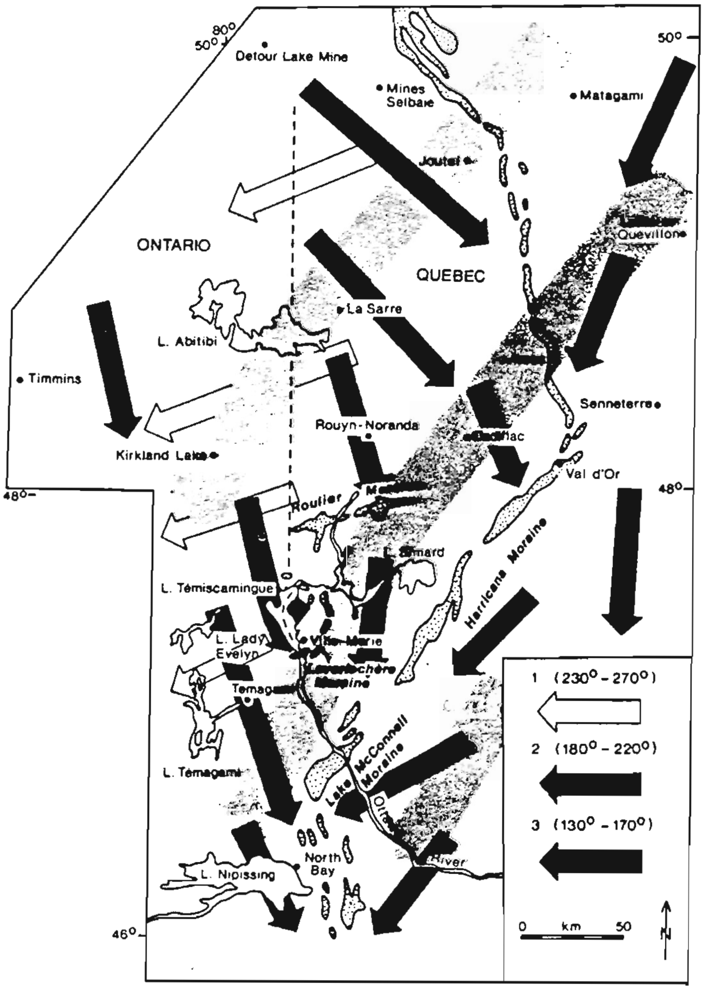

Figure 3. *The three ice flow directions recorded in the Abitibi-Timiskaming area of Quebec and Ontario (Veillette, 1989).*

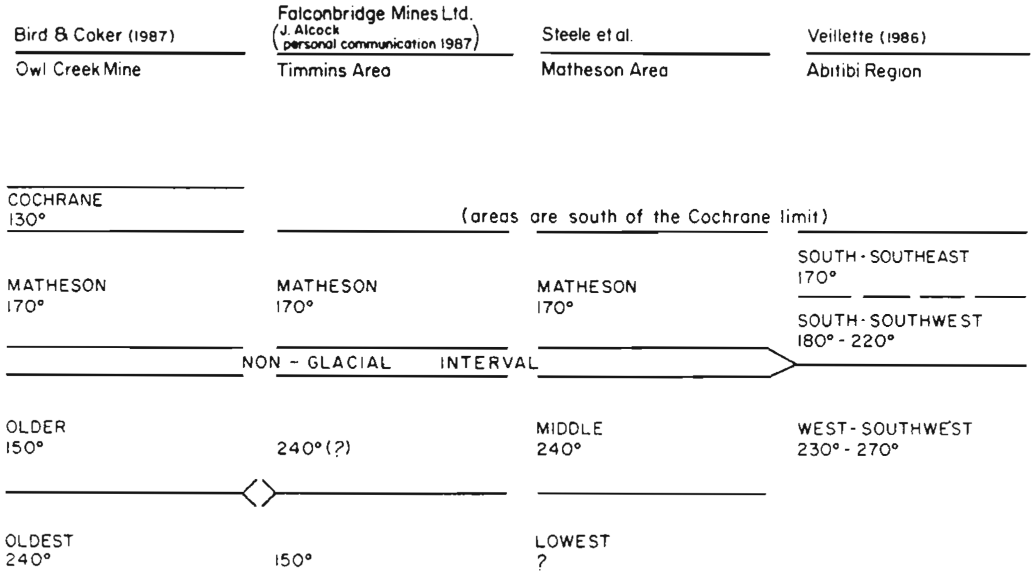

Figure 4. *A preliminary stratigraphic sequence and related ice flow directions for the Matheson-Timmins area of Ontario (Steele et al., 1989).*

SAMPLING AND ANALYTICAL METHODS

The most important aspect of data collection, and the resultant sample treatment and geochemical analyses of glacial overburden, starts in the field or on the drill where it is essential to make the best possible identification of the type of glacial sediment being sampled. Appropriately educated and trained people, Quaternary geologists, or at least geologists who have had some training in Quaternary geology and/or sedimentology as well as applied geochemistry, are essential to ensure that the glacial sediments are adequately identified and logged. In Fennoscandia the use of Quaternary geologists/applied geochemists on overburden geochemical programs is accepted and routine. In Canada this is not the case, most overburden drilling and sampling is undertaken by personnel trained in neither Quaternary geology nor applied geochemistry.

Correct identification of the genetic class of glacial sediments is the key to tracing geochemically anomalous overburden back to a bedrock source. It is also essential that the stratigraphic position of till be properly determined. In particular, it is important to determine to which sedimentary package and which ice movement direction till belongs. It is only when identification of till and its stratigraphic position and associated ice movement direction are understood that one can confidently start tracing a pattern of geochemically anomalous till samples back to a bedrock source. Without these controls, even the most sophistocated preparation, analyses and interpretation of the data for overburden samples may be inadequate or, at best, inefficient for locating mineralization. The glacial history of an area must in many instances be determined as part of the overburden drilling and sampling programs.

Samples used in regional geochemical/Quaternary mapping programs are usually collected at or near the surface to cover a specific area, for example, an NTS map sheet or favourable geological environment or structure. These samples are usually obtained from hand dug pits (<2 metres) or by using small portable hand held auger or flow-through bit type drills, or back hoes (<5 metres) (see Table 1). Sample collection in areas of deep overburden usually involves drilling. A number of techniques have been used for overburden drilling including augers, percussion drills, reverse circulation rotary drills (RCD) and rotasonic drills (Table 1). The widest experience and greatest success has been with reverse circulation drilling, although in recent years rotasonic drills have started to play a more significant role, particularly in stratigraphic drilling programs. To date, however, no cost-effective drilling system for recovering large till samples at depths around 10 metres has been devised.

In reverse circulation drilling, water, sometimes used in conjunction with compressed air, is pumped down the outer tube of the dual tube rods. The water mixes with the cuttings at the tricone bit (tungsten carbide buttons) and the slurry is forced to the surface through the inner tube. The sample slurry discharges into a cyclone, to reduce the velocity of the discharge material, and empties through a 2 mm (10 mesh) sieve into a series of sample buckets. Logging is carried out by the Quaternary geologist on the drill. The geologist sees a washed and disturbed sample which makes logging difficult for qualified personnel, and just about impossible for unqualified personnel. There is only one chance to log the sample material as it goes by. In addition, the fine fraction of the material, such as the fine ore minerals including some forms of gold, is generally lost (Shelp and Nichol, 1987), and cross-contaminated by the recirculated water.

The rotasonic drill uses high frequency (averaging 5000 cpm) resonant vibration and rotation to obtain continuous solid cores. Sediments are cored with tungsten carbide fronted bits. The cores are extruded, in 5 foot lengths, into plastic sleeves and placed into core boxes. Logging and sampling of the cores can be carried out on-site or at a later time. Rotasonic drills

Table 1. *Features of various overburden drilling systems (averages based on 1985 data).*

	Reverse Circulation Drills (Longyear or Acker) (Nodwell Mounted)	Rotasonic Drills (Nodwell or Truck Mounted)	Small Percussion and Vibrasonic Drills (Various)	Auger Drills (Various)
1. Production cost estimate per: - day (10 hrs) - metre	$1,800 – $2,000 $25 – $40	$3,000 – $4,000 $50 – $80	$500 – $1,000 $20 – $40	$800 – $1,500 $25 – $50
2. Penetration depth	Unlimited (125 m?)	Unlimited (125 m?)	10 – 20 metres (greater?)	15 to 30 metres (boulder free)
3. Environmental damage	5 metre wide trails (may have to be cut in areas of larger trees)	5 metres wide cut trails	nil	2 – 3 metre wide cut trails (Nodwell, muskeg, all terrain vehicle mounted quite manoeuverable)
4. Size of sample	5 kg (wet)	Continuous core	300 g (dry), or continuous core	3 – 6 kg (dry or wet)
5. Sample of bedrock	Yes (chips)	Yes (core)	Yes (chips) if reached	Unlikely, if hollow auger, split spock sampler can be used for chips
6. Sample recovery a) till b) stratified drift	Good Moderate	Excellent Excellent	Good Good	Good Poor to moderate
7. Holes per day (10 hrs)	4 @ 15 – 20 metres 1 @ 60 – 80 metres	4 @ 15 – 20 metres 1 @ 60 – 80 metres	5 @ 6 to 10 metres	1 to 3 @ 15 to 20 metres
8. Metres per day (10 hrs)	60 – 80 metres	60 – 80 metres	30 to 50 metres	20 to 60 metres
9. Time to pull rods	10 min @ 15 metres	10 min @ 15 metres	30 to 60 min @ 15 metres	20 to 40 minutes @ 15 metres
10. Time to move	10 – 20 minutes	15 – 30 minutes	30 minutes	15 to 60 minutes
11. Negotiability	Good	Moderate	Good (poor if manually carried on wet terrain)	Good to reasonable
12. Trails required	Yes, may have to be cut in areas of larger forest	Yes, must be cut	No	Yes and no
13. Ease in collecting sample	Good	Excellent, continuous core	Sometimes difficult to extract from sampler	Good (contamination?)
14. Type of bit	Milltooth or tungsten carbide tricone	Tungsten carbide ring bits	Flow through sampler, continuous coring	Auger with tungsten carbide teeth
15. Type of power	Hydraulic-rotary	Hydraulic-rotasonic	Hydraulic percussion (gas engine percussion, vibrasonic)	Hydraulic-rotary
16. Method of pulling rods	Hydraulic	Hydraulic	Hydraulic jack, hand jack or winch	Winch or hydraulics
17. Ability to penetrate boulders	Excellent	Excellent, cores bedrock	Poor	Poor to moderate
18. Texture of sample	Slurry (disturbed sample)	Original texture (core can be shortened, lengthened and/or contorted)	Original texture	Original texture (dry) to slurry (wet)
19. Contamination of sample	Nil, fines lost (tungsten)	Nil (tungsten)	Nil (tungsten)	Nil to high (tungsten)

may produce cores that are equal in length to, longer than, or shorter than the interval sampled. These variations appear to be due mainly to the manner in which different sediment types react to the drilling stresses. In addition, surface and internal secondary deformation due to the drilling have also been observed in rotasonic drill core (Smith and Rainbird, 1987).

When considering whether to use heavy mineral concentrates or a fine fraction of the till one must consider the nature and type of mineralization being sought. In the case of gold mineralization associated with iron formation the usefulness of the removal of the magnetic fraction should be carefully considered.

In the case of the rotasonic core or surface till samples the fine fraction (e.g., clay sized material (<2 μm) or -250 mesh (<63 μm)) can be separated and analyzed. In some instances, when a till has sufficient fine material to come up the reverse circulation drill in balls or lumps, it is possible to collect, in the sieve above the collection bucket, a relatively uncontaminated sample from which to obtain the fine fraction.

Heavy mineral concentrates (HMCs) and the other size fractions of tills are commonly analyzed for a wide but varied suite of elements, determined by the type of mineralization and nature of deposit being sought (see Tables 2, 3, and 4). All analytical work should be quality controlled using control reference and duplicate sample analysis. Analytical techniques generally include various combinations of fire assay- dissolution-atomic absorption/DCP or ICP methods. This series of analytical techniques usually involves splitting, which in the case of analysis for gold, particularly in HMC's, is problematic at best due to the nugget effect. These techniques all result in the destruction of the sample. Instrumental neutron activation analysis (INAA) allows non-destructive analysis of the whole sample, however, one must be aware of the type of irradiation used because in some cases the samples, depending on their matrices and/or chemistry, will be permanently rendered too radioactive to handle. Getting the whole HMC sample back following INAA facilitates later mineralogical work on anomalous samples to identify the nature of the mineralization, in some instances its geologic environment and in certain cases some idea of distance of transport. Contamination for elements such as W and Co, due to fragments from tungsten carbide bits, can be detected during examination of HMC's. Caution must be exercised in utilizing the shape of gold grains, or any other mineral grain for that matter, as an indication of distance of transport, because of variability in the original shape and form of the grains and in the style of glacial transport, either over short distances in the active basal zone or over long distances in the passive englacial zone of the ice.

Exploration reliability, and success, can be increased by using properly trained personnel to log, sample and interpret till geochemical data based on a framework of overburden stratigraphy and ice movement directions. The drilling method and analytical techniques employed should be considered carefully in terms of costs and the quality of data needed. The use of fine fraction and heavy mineral concentrate fraction geochemistry to complement each other will increase exploration reliability.

OCCURRENCE OF TRACE ELEMENTS IN TILL AND SOIL AND THE EFFECTS OF WEATHERING

In recent years, more attention has been placed on trying to understand the comminution behaviour of ore minerals, the residence sites of metals in tills and the effects of weathering on trace metal levels vs. grain size (Shilts, 1975). However, the amount of published information on the partitioning of metals and minerals in till is still quite small. Studies have shown that the mineralogy, petrography and major element chemistry of tills are clearly dependent on till-forming processes as well as on bedrock variations (Haldorsen, 1977, 1983; Taipale et al., 1986).

Lithophile trace elements (Figure 5), tend to be enriched in the coarser grain size ranges including rock fragments (DiLabio, 1989). In the case of till derived from the Strange Lake REE-Nb-Zr-Y-Li-Be deposit, Labrador the lithophile elements are also enriched, to a lesser degree, in fine size ranges, reflecting the fine grain size of the glacially liberated resistate and silicate minerals in which they occur in bedrock.

Chalcophile trace elements from unstable minerals such as sulphides, tend to be enriched in the finer grain size ranges as shown for Cu, U and As (Figure 6) (DiLabio, 1979; Shilts, 1984a). The geochemically more active fraction of weathered till lies in its finer grain sizes because of the tendency of phyllosilicate minerals and secondary minerals to be enriched in the fine sizes (see DiLabio, 1979; Peuraniemi, 1982, 1984; Nikkarinen et al., 1984; Shilts, 1984a).

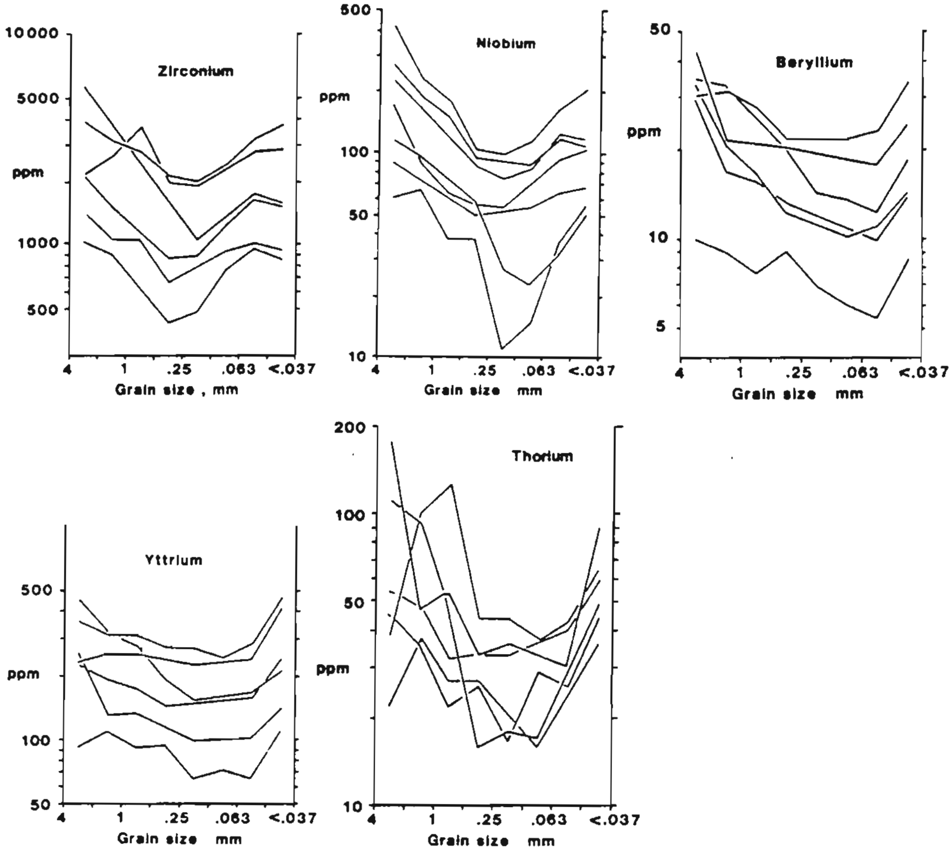

Figure 5. *Abundance of lithophile elements vs. grain size of analyzed fraction of till from the Strange Lake dispersal train at Lac Brisson, Quebec and Newfoundland. Samples represent anomalous to background sites (DiLabio, 1989).*

These phases have a high total surface area and exchange capacity, so they act as scavengers, adsorbing trace metals released during weathering of primary, particularly sulphide, minerals. Unweathered till also shows preferential enrichment of trace metals in specific grain size ranges, and this probably reflects the grain size of primary metal-rich minerals that have been glacially comminuted (Shilts, 1984a). As shown in Figure 6, the <2 µm fraction is the best fraction of weathered till to analyze, being the most enriched in metals and generally having the best geochemical contrast. Often, however, the <63 µm (-250 mesh) fraction is analyzed because of insufficient <2 µm material and because it is cheaper to recover.

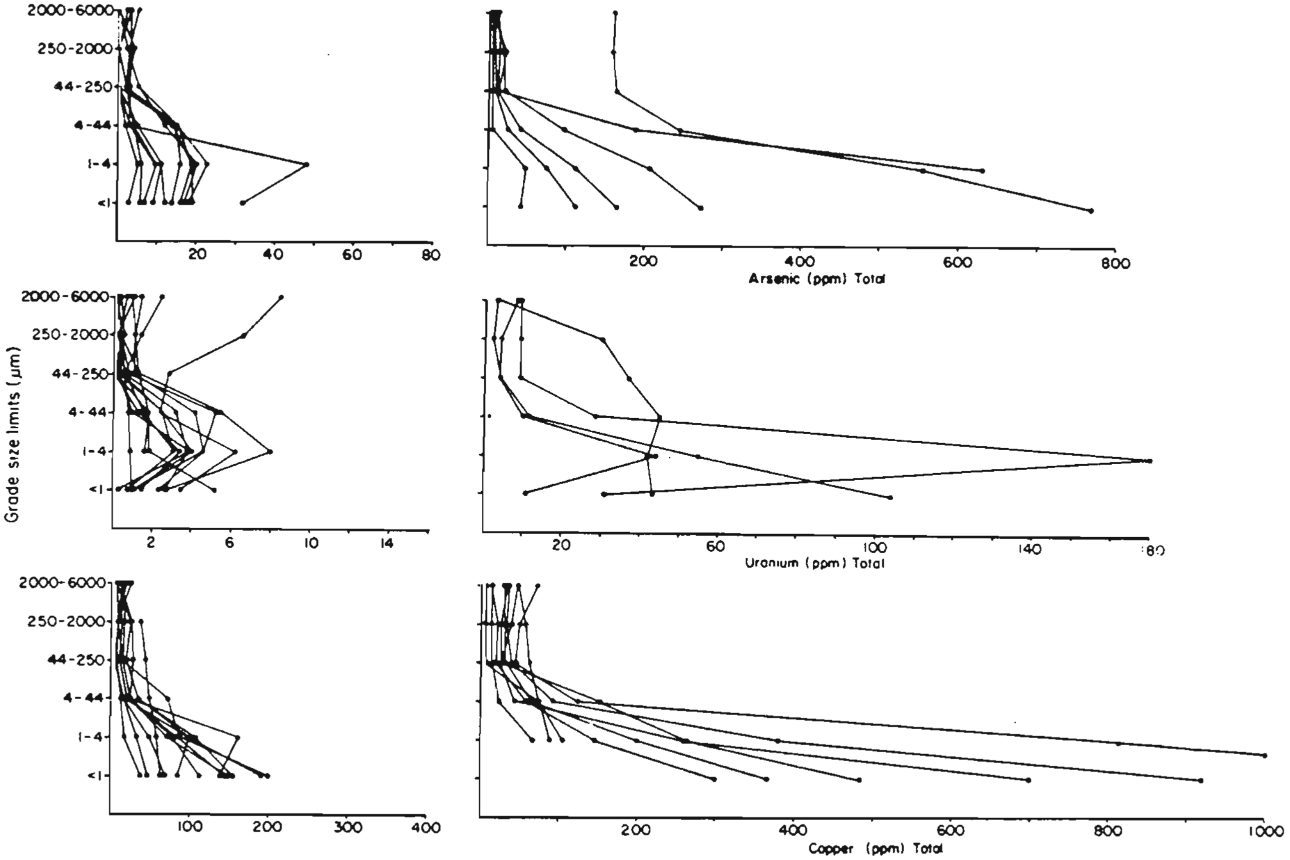

Figure 6. *Abundance of Cu, U, and As in different grain size ranges in a variety of till samples from the Canadian Shield (after Shilts, 1984a). Samples in right-hand figures considered to be anomalous; those on left background. Each line represents one sample. Concentrations are from perchloric acid leach and represent "total" metal.*

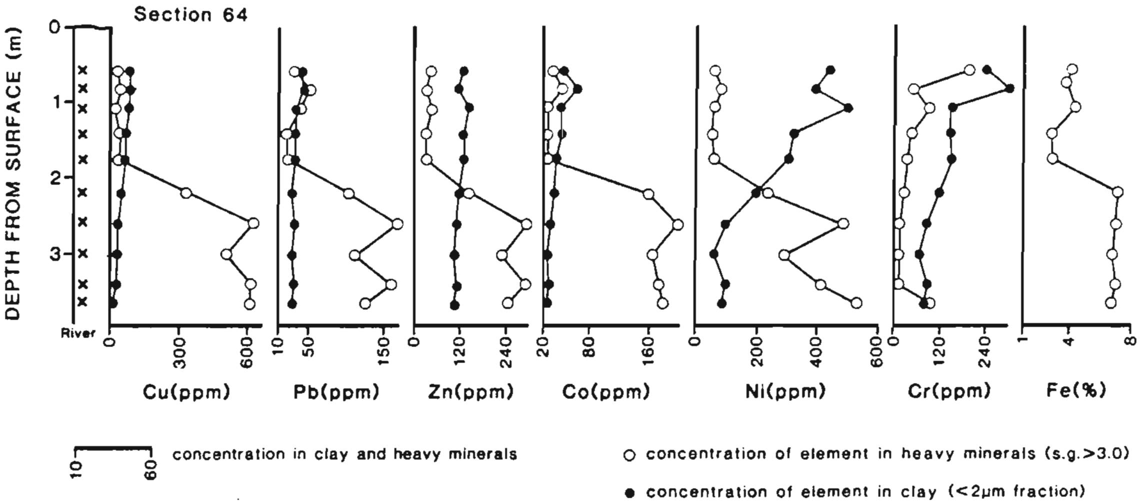

Figure 7. *Chemistry of till fractions in a section of oxidized and unoxidized til southeastern Quebec (Shilts, G.S.C., Pers. Comm., 1988).*

A typical response of till to postglacial weathering is clearly illustrated by the example in Figure 7. In the section of till shown, the upper part is relatively more highly oxidized and weathered than the lower part (Shilts, pers. comm.). In the upper weathered part of the till, the HMCs contain very low concentrations of the chalcophile elements Cu, Pb, Zn, Co and Ni because the detrital sulphides containing these elements have been destroyed. The loss of iron-bearing sulphide grains in the weathered part of the till is also reflected in the low Fe contents of the HMCs. On the other hand the distribution of Cr, which occurs in the resistate mineral chromite, is unaffected by weathering and shows similar patterns in both the HMCs and <2 µm fractions. The original distribution of Ni, which occurs in sulphides, silicates (i.e., serpentine) and chromite, is more correctly shown by the <2 µm fraction and not by the HMCs which have been weathered out in the upper part of the till.

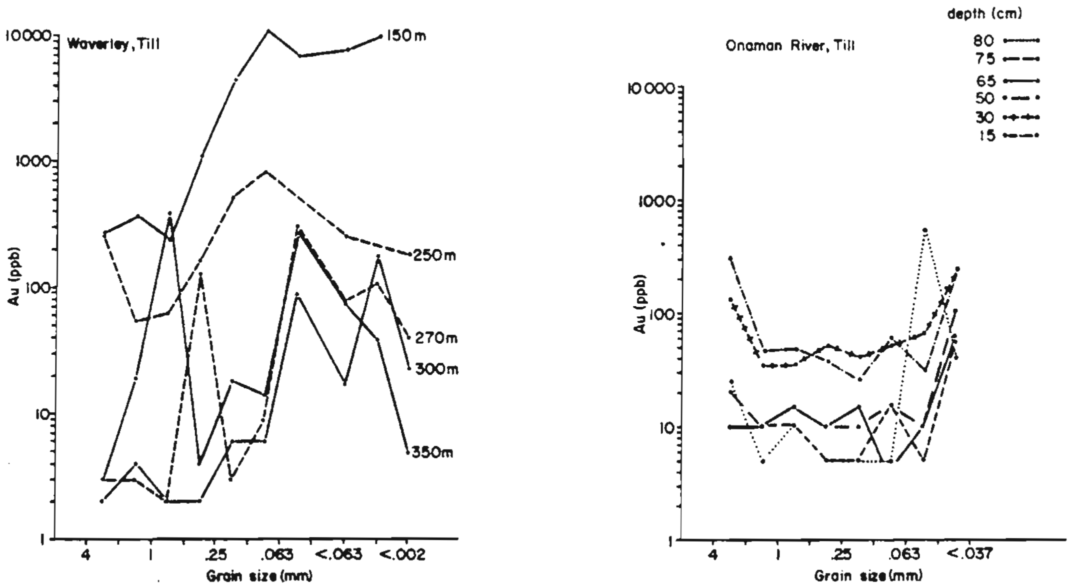

Figure 8. *Abundance of gold vs. grain size of analyzed fraction of till at different distances down-ice from a gold deposit at Waverley, Nova Scotia (after DiLabio, 1982a) and at varying depths below surface in a dispersal train at Onaman River (after Dilabio, 1985).*

Fractionation experiments on gold-bearing till (DiLabio, 1982a, 1985; Guindon and Nichol, 1983; Nichol, 1986; and Shelp and Nichol, 1987) indicate gold distributions in till are rather complex, being the result of the combined effects of the grain size of glacially comminuted detrital particulate gold, the grain size of the gold released from weathered sulphides, the grain size of precipitated or adsorbed gold and the original size of the gold at its source. In general, till is richest in gold in its finer size ranges, although coarse sizes are often auriferous (Figure 8).

At the base of the thick (>30 metre) Quaternary sequence at the Owl Creek gold deposit near Timmins, a green till and its oxidized equivalent are preserved. The unoxidized green till contains its maximum Au levels and abundant fresh pyrite in the fine sand sizes (Figure 9) (DiLabio, 1985). These have been altered to earthy limonite-goethite grains in the oxidized layer. The oxidized till is much more auriferous in all size fractions than the unoxidized till. It appears that gold has been added to the limonite-goethite grains in the oxidized till, perhaps from ground water.

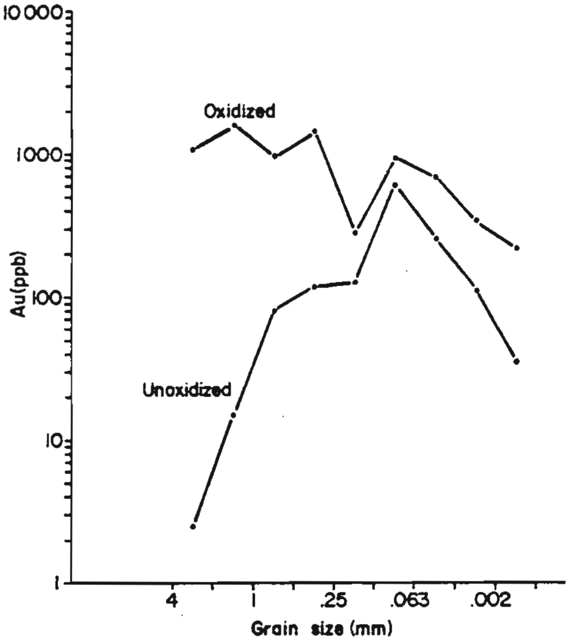

Figure 9. *Abundance of gold vs. grain size of analyzed fraction of unoxidized till and its oxidized equivalent in the Owl Creek Gold Mine, Timmins, Ontario (Dilabio, 1985).*

Work by Shelp and Nichol (1987) at the Owl Creek gold mine shows that both the gold content of the HMCs and of the <63 μm (clay and silt) material clearly depict the anomalous glacial dispersal train (Figure 10). The lengths of the anomalous dispersal trains are similar in both cases although the contrast and absolute levels of gold in the <63 μm fraction are lower. On the other hand, for Hemlo type mineralization (Figure 10), they found that anomalous heavy mineral concentrates are restricted to right over the deposit and show little dispersal down-ice. The <63 µm fraction shows significant down-ice dispersal. Thus, fine fraction and heavy mineral concentrate analyses can provide different, often complementary, information.

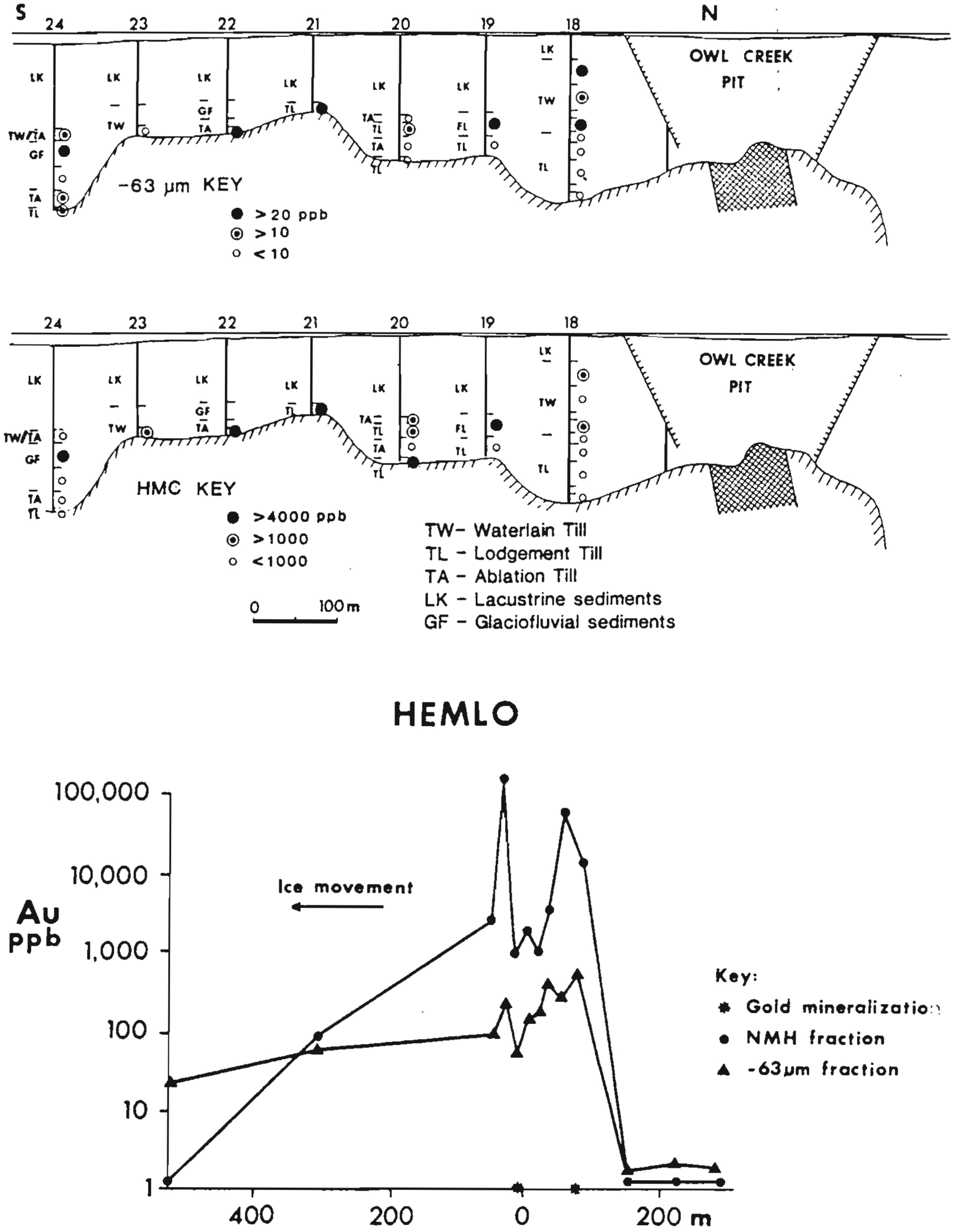

Figure 10. *Comparison of the Au distribution in the heavy mineral concentrate and the <63 µm fractions of till at the Owl Creek Gold Mine, Timmins, Ontario; and, associated with Au mineralization at Helmo, Ontario (from Shelp and Nichol, 1987).*

It should be apparent that the routine use of -80 mesh material for till geochemical surveys should be carefully examined. Orientation surveys should be conducted to determine the optimum size fraction to use for analysis. Fine grained materials appear to be the best media in many instances. The nature of the weathering history of the material also determines the appropriateness of the grain size to be used for analysis. The use of fine fraction and heavy mineral concentrate fraction geochemistry to complement each other may well increase exploration effectiveness and reliability.

DRIFT PROSPECTING

Drift prospecting is the use of data on the geochemistry and lithology of glacial sediments (mainly till) to identify economically significant components in the sediments and to trace them up-ice to their bedrock source (DiLabio, 1989). The concept of predictable patterns within dispersal trains (described by Shilts in this workshop volume), when considered during the design of a geochemical exploration program, will influence the choice of sample types, the sampling plan, the analytical scheme, and the interpretation of the data. Compared to other types of geochemical anomalies, once a dispersal train has been detected, it can be traced up-ice to its source because simple clastic dispersal is the main mechanism involved in the formation of a train.

Over the last several years many studies of dispersal trains have been documented within Fennoscandia and Canada. Details of these studies/case histories are summarized in Tables 2, 3, and 4 and their locations are shown on Figures 11 and 12. It is impossible to go into much depth of discussion for all of these examples so only a small selection are discussed more fully in the following text. The studies reviewed emphasize points such as: understanding ice movement directions; glacial stratigraphy and bedrock topography as they control the nature of glacial dispersal; and the resultant dispersal trains.

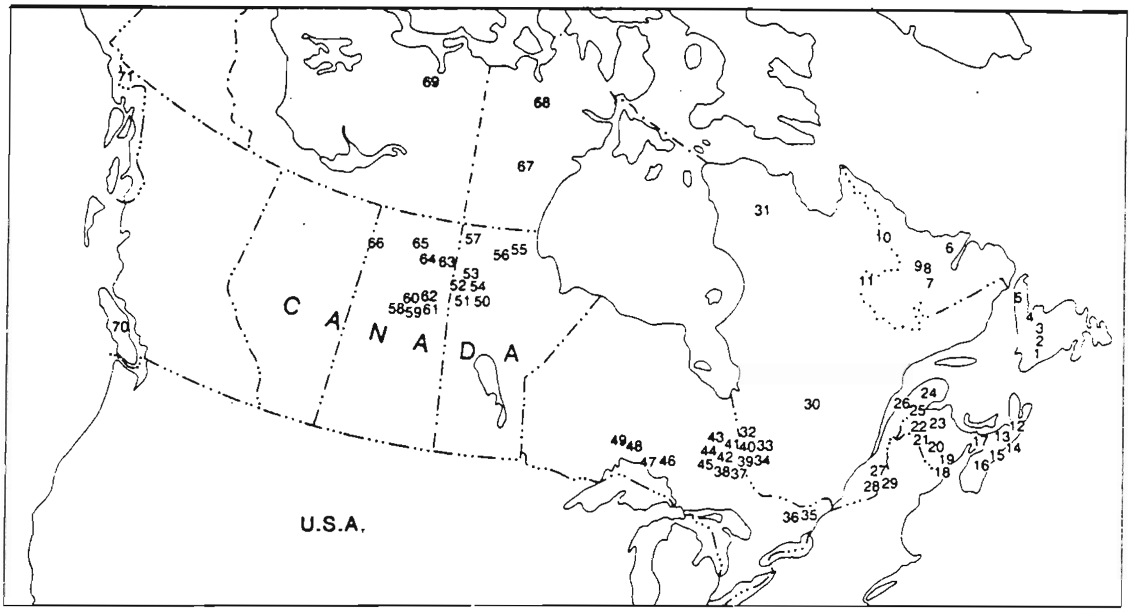

Figure 11. *Drift prospecting and related overburden studies in Canada (numbers on map refer to Table 2).*

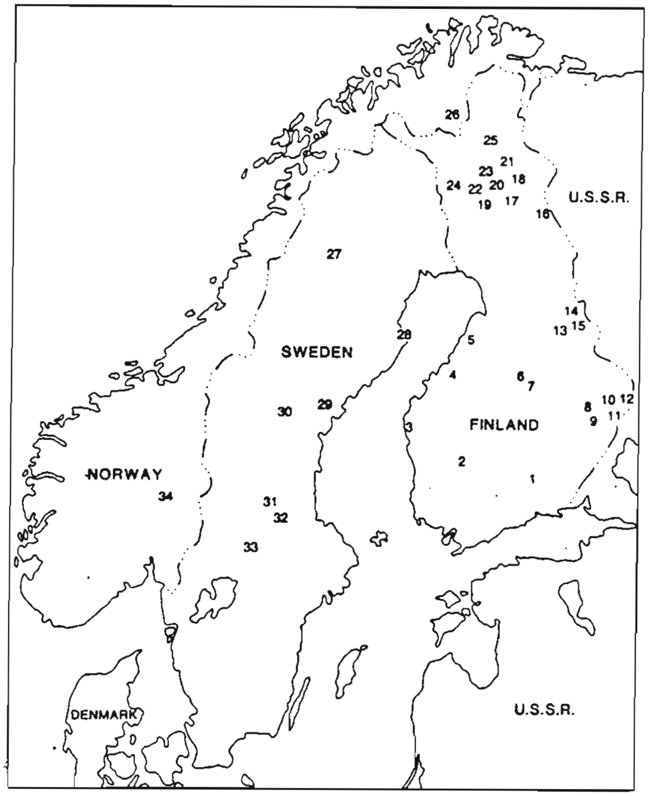

Figure 12. *Drift prospecting and related overburden studies in Fennoscandia (numbers on map refer to Table 2).*

Table 2. *Summary of drift prospecting and related overburden studies in Canada (1977-1987) (Study type: A - Regional - 1 - Reconnaissance, 2 - Detailed; B - Research - 1 - Orientation, 2 - Follow-up; C - Exploration case history. HMC - Heavy mineral concentrate, RCD - Reverse circulation drilling.)*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
1. Peter Snout and King George IV Lake, S.W. Nfld.	Au	A-1	C-horizon till and pebble counts; <63 µm; Cu, Pb, Zn, Co, Ni, Ag, Mn, Fe, Mo, U, W and Au.	N/A	Results to be published.	Sparkes and Neuland (1986)
2. Victoria and Tally Pond Areas, Nfld.	Cu, Pb, Zn	B-1	Profile sampling of B, B-C and C-horizons, pebble/boulder counts.	N/A	Study still in progress.	Mihychuk (1985)
3. Buchans Area, Nfld.	Zn, Pb, Cu, Ag and Au (Buchans orebodies)	A-2	B-horizon soil and till; -80 mesh for both and HMC of till; Cu and Zn.	Ribbon, 8 km x 2 – 4 km.	Broad zone of soils with anomalous Zn. HMC gave better anomaly contrast than -80 mesh for tills.	James and Perkins (1981)
4. Sops Arm Area, Nfld.	Au and Cu, Pb, Zn	A-1	Till and pebble.	Dispersal in terms of 100's of metres.	Study still in progress.	Vanderveer and Taylor (1987)
5. Bellburns Map and Trapper Cove Areas, Nfld.	Zn (Trapper Prospect)	A-2	C-horizon matrix and clasts.	N/A	Study still in progress.	Mihychuk (1986)
6. East Part of Central Mineral Belt, Labrador	U, Be, REE, Cu, Pb and Zn	A-1	Pebble counts/ boulder tracing.	Ribbon near source (20 to 30 km) fanning further away.	Study still in progress.	Batterson *et al.* (1987)
7. East-central Labrador	U and Cu	A-1	Till; <2 µm, <63 µm and 2 – 4 mm; Cu, Pb, Zn, Ni, Fe, Mn, U, Ce, Sr, Th, Nb, Y, and Zr.	Broad ribbon to flame, from 30 to 100 km from bedrock sources.	Till geochemistry reflects broad variations in bedrock geology.	Klassen (1983, 1984); Klassen and Bolduc (1984, 1986); Thompson and Klassen (1986)
8. Moran Heights, U Labrador	U	B-1	Till and pebble counts.	Ribbon, 1 km x 300 m.	U in till defines dispersal train.	Vanderveer (1986)
9. Letitia Lake, Labrador	REE, Be and Nb	A-2	C-horizon and pebbles counted.	Flame to ribbon, 600 m x 200 m.	Scintillometer survey and mineralized boulders define dispersal train.	Batterson and LeGrow (1986)
10. Strange Lake, N. Labrador	Zr, Nb, Y, Be and REE (Strange Lake deposit)	A-2	Till from mudboils; <63 µm; Cu, Pb, Zn, Co, Cd, Ni, Mn, Fe, Be, F, Li, and U.	Ribbon, up to 30 km x 5 km	Results show that Be and Pb are good indicators of the peralkaline complex.	McConnell *et al.* (1984); Batterson *et al.* (1985); McConnell and Batterson (1987); Vanderveer *et al.* (1987)
11. Labrador Trough, Labrador	Fe, Cu, Pb, Zn, and Au	A-1	Till.	Fan to flame, 60 to 70 km long.	Study still in progress. Tied into #7.	Klassen and Thompson (1987)
12. Forest Hill, Guysborough County, N.S.	Au (Forest Hill Gold District)	B-1	Till profiled, pebbles counted, fabrics and striations measured; <63 µm and HMC; Ag, Cu, Ni, Cr, Mn, Fe, Hg, As, Pb, Zn, W and Au, also examined HMC for gold grains.	100 to 300 m long.	Gold and As in <63 µm best for exploration. Panning for visible Au also recommended.	MacEachern *et al.* (1984); MacEachern and Stea (1985)

Continued

Table 2. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
13. Eastern Shore, Central N.S.	Au, Cu, Pb, Zn, and W	A-1	Till; <2 µm; Cu, Pb, Zn, Ni, Co, Fe, Mn, Mg, Ca, Hg, As, Mo, Ag, Cd and U.	N/A	Established regional till geochemical characteristics as a framework for mineral exploration in N.S.	Stea and Fowler (1979); Henderson and Wyllie (1986)
14. Eastern Shore, Central N.S.	Au	A-1	Till and lake sediments; <2 µm – Cu, Pb, Zn, Ni, Co, Fe, Mn, Ca, Mg, Mo, Cd, Ag, As, and U; HMC – Sn and W.	N/A	Compared geochemical relationships between tills and lake sediments. As and Pb in lake sediments and Cu and in tills were pathfinders for gold.	Rogers *et al.* (1984)
15. Oldham, N.S.	Au	B-2	Till, C-horizon soils; <63 µm; Au and As.	Ribbon, 2400 m x 600 m.	Both Au and As showed dispersal from known Au mineralization.	DiLabio (1982b)
16. Nova Scotia	Au, Cu, Pb, Zn, W, Sn, and U	A-1	Tills; <63 µm – Cd, Ag, Cu, Pb, Zn, Co, Ni, Fe, Mn, Ca, Mg, Mo, As, and U. HMC – Sn and W.	Various, local tills 1 km to 4 km with exotic till clasts from 20 to 70 km.	Baseline data on distribution and chemistry of tills in N.S. Documented dispersal from chemically distinct lithologies and mineralization of various types.	Stea and Fowler (1981); Stea and Grant (1982); Stea and O'Reilly (1982); Stea (1982a, b; 1983)
17. North Central, N.S.	Pb-Zn, Cu and U	A-1	Bedrock and till; <2 µm; Cu, Pb, Zn, Co, Ni, Fe, Mn, Ca, Mg, Mo, U and As.	N/A	Emphasized need to recognize different till sheets. Dispersal is a multistage process.	Stea *et al.* (1986a, b); Stea and Finck (1986)
18. Mascarene Peninsula and West Isles, N.B.		A-2	Humus, B and C-horizon; ? and HMC.	N/A	Study still in progress.	Chiswell (1986)
19. St. George Batholith, Southern N.B.	W, Cu, Mo and Au	A-1	B and C-horizon (till); B-horizon – Cu, Pb, Zn, Ag, Co, Mo, U and Sb, HMC (till) – W, Sn and Au.	Flame, 1 to 5 km long.	New possible exploration targets identified and most known mineral occurrences located.	Rampton *et al.* (1986); Thomas *et al.* (1987)
20. Sisson Brook, N.B.	W-Cu-Mo	B-1	Till; -10 + 80, -80 + 200, -200, -10 (ground to -200) mesh and HMC; Cu, Pb, Zn, Ni, Ag, Mo, Fe, As, F, W, Sn and Bi.	Ribbon to flame, 300 to 400 m x 700 m.	Short dispersal on property due to bedrock ridge. Anomalous till carried over ridge and deposited 8 km down-ice with no connecting dispersal train.	Snow and Coker (1987)
21. West Central N.B.	Cu, Pb, Zn, Sn, W and Mo (Miramichi Zone)	A-1	Till; <2 µm; Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Cd, Pb, W, As, U, Sn and F.	Several km in the direction of ice flow.	Till down-ice from known mineralization shows dispersal. New unexplained anomalies exist. Study still in progress.	Lamothe (1986)

Continued

Table 2. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
22. Trousers Lake Area, N.B.	Zn, Pb, Cu and Ag	A-2	B and C-horizon (till); -80 mesh; Cu, Pb, Zn, Mn, Fe, Ag, Co, Ni, Mo, U and Au.	Local, 1 to 2 km long.	Anomalous patterns related to known mineralization or distinct bedrock lithologies.	Fyffe and Pronk (1985)
23. Tetagouche L. and Upsalquitch Forks Map Areas, N.B.	Cu, Pb, Zn and Au	A-2	B and C-horizon (till); -80 and -250 mesh; Cu, Pb, Zn, Ag, Mn, Fe, Ni, Co, Cd, Mo, As, Sb and Au.	N/A	Outlined presence of known Au mineralization and targets for further exploration	Pronk (1985, 1986a, b, 1987)
24. Central Gaspé Peninsula, Quebec	Cu, Mo, Pb and Zn	A-2	Back-hoe pits profile sampled (till); <2 µm and HMC.	Two trains of granitic erratics – one is 110 km x 20 to 50 km and the other is 40 km x 20 km.	Recognized dispersal from two distinct glacial events.	David and Bedard (1986); Chauvin and David (1987)
25. Southwest Gaspé Peninsula, Quebec	Au, Cu, Pb and Zn	A-1	C-horizon (till); -60 (ground to -200) mesh; Au, trace and major elements, -60 + 230 mesh HMC; Au + 25 elements and examined for mineralogy and Au grains.	N/A	Au analysis of HMC's provided a good estimate of Au variation across area and outlined a number of anomalies.	Bernier *et al.* (1987)
26. Northwest Gaspé Peninsula, Quebec	Au, Cu, Pb and Zn	A-1	Till – pebble counts.	N/A	Pebble counts indicate a complex ice flow history for the area. Study still in progress.	Prichonnet and Desmarais (1985)
27. Lac Magantic Area, Quebec	Au, Mo, Cu, Pb, Zn, W	A-1	Till, pebble and boulder counts, fabrics; <64 µm; Al, Fe, Mg, Ca, Mn, Ba, Co, Sr, Ti, Zr, Cu, Ni, Cr and V. Mineralogy of various fractions studied.	Ribbon to flame, 80 km x 15 km.	Detailed study of the Quaternary history and sediments of the area, including glacial dispersal from Thetford Mines ultrabasic outcrops.	Shilts (1973a, 1976 and 1981)
28. Eastern Townships, Quebec	Au	A-1	Variable - till (and stream sediments or other sediment types); HMC; Au, Fe, Ni, Cu, Zn, Ag, Pb, Cr, Co, Sb, La, Hf, S, As, Ti, Nb, Sn, Y, Ta, Ir, Th, U.	Flame, 20 to 30 km x 15 to 20 km.	Widespread anomaly patterns related to glacial rather than alluvial processes for HMC from streams.	Maurice and Mercier (1985); Maurice (1986a, b)
29. Beauceville, Quebec	Au (placer)	B-1	Till and other sediments; <2 µm; Ni.	N/A	Rotasonic drilling program confirmed presence of three tills and associated sediments from at least three glacial events. Characteristics of Au placer-bearing strata outlined. Study still in progress.	Shilts and Smith (1986a, b); Smith and Shilts (1987)

Continued

Table 2. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
30. Lac Mistassini – Lac Waconichi Area, Quebec	Cu (Icon Mine)	A-2	B-horizon; <80 mesh Cu; Till – pebble counts.	Ribbon to flame, Two trains 1650 m x 75 m and 600 m x 300 m	Thorough documentation of a glacial dispersal train. Mapping abundance of mineralized pebbles most efficient guide to ore zones.	DiLabio (1981)
31. Ungava, Quebec	Ni, Pt, Pd	A-1	Till, <63 µm – $CaCO_3$ and multielement geochemistry, HMC – mineralogy, granule lithology counts.	Several dispersal trains ranging from 6 to 10 km up to 70 km in length.	Documents the glacial history including ice flow patterns of the Ungava Peninsula. Geochemistry of the till is still under study.	Bouchard and Marcotte (1986)
32. Casa-Berardi Area, Quebec	Au (Golden Pond and Golden Pond East)	C	Till, sand and gravel from RCD holes; HMC; Au, As, and S, also carried out gold grain counts.	400 m x 200 m, but truncated against a bedrock ridge by later glacial advance and erosion.	Successful application of RCD/HMC in a new gold camp.	Sauerbrei *et al.* (1987)
33. West Central Quebec	Au, Cu, Pb and Zn	A-1	Till; <80 mesh and HMC; Cu, Zn, Pb, Ni, Co, Mn, Ag, Rb, Zr, Sr, Mo, Nb and Y.	N/A	Provided regional data on till geochemistry.	LaSalle and LaLonde (1982); LaSalle *et al.* (1982a, b)
34. Bousquet Area, Malartic, Quebec	Au (Doyon Mine and Bousquet Mine)	B-1	Humus, Till -100 mesh and HMC; Au, Cu, Pb, Zn and Ag.	Doyon Mine – 200 m long; Bousquet Mine – 15 to 30 m long.	Shows the influence of bedrock topography on size and shape of dispersal train in till. Au content of -100 mesh and HMC fractions of till both define trains. Humus can be ineffective in areas covered by glaciolacustrine clays.	Gleeson and Sheehan (1987)
35. Hopetown, Ontario	Zn	B-1	C-horizon (till); <2 µm; Zn, Cd and hg. Also mapped mineralized boulders and analyzed plants.	Ribbon, 400 m x 70 to 200 m.	Dispersal train best defined by mineralized boulders and Zn and Cd in tills, Plant metal levels reflect those in underlying till.	DiLabio *et al.* (1982); Sinclair (1986)
36. Lanark County, East Ontario	Au	B-1	Humus, B-horizon soil and till (total -250 mesh and HMC); Au. Pebble counts and mineralogy of HMC's determined.	Irregular flame, 100 to 3000 m x variable widths.	Au in all media reflected mineralization. Au in HMC's gave best anomaly definition and contrast. The -250 mesh fraction was most cost effective.	Gleeson *et al.* (1984); Rampton *et al.* (1986)

Continued

Table 2. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
37. Matachewan, N.E. Ontario	Barite	B-1	Till; pebble lithology and roundness examined, barite content of 5 size fractions of till determined. Excavated trench sampled.	20 m x 50 m.	Variation of barite with distance from vein obeys negative exponential function in all fractions except fine sand. Very short dispersal due to bedrock topographic effects.	Stewart (1986a)
38. Matachewan, N.E. Ontario	Au	B-1	Backhoe and auger sampling of tills; <63 µm and HMC; Au and Ag.	Ribbon to irregular flame, 200 m to 800 m x 60 to 150 m.	Outlined at least three dispersal trains.	Stewart and Van Hees (1982)
39. Kirkland Lake Area, Ontario (KLIP)	Au and Cu, Pb and Zn	A-1	RCD and backhoe sampling of tills and related sediments; <63 µm and HMC; Cu, Pb, Zn, Ni, Mo, As, Ag, Au and U. Collected and analyzed bedrock chips.	N/A	Provided baseline data for a regional Quaternary stratigraphic framework. Also provided geochemical and mineralogical data on tills in the area.	Thomson and Guindon (1979); Thomson and Wadge (1980, 1981); Averill and Thomson (1981); Thomson and Lourim (1981); Lourim and Thomson (1981); Routledge *et al.* (1981); Lourim (1982a, b); Fortescue and Lourim (1982); Averill and Fortescue (1983); Fortescue *et al.* (1984)
40. Kirkland Lake Area, Ontario	Au	B-2	Tills (-250 mesh) and humus (-50 mesh); Au. Mapped bedrock and surficial geology, collected and analyzed rocks for Au.	N/A	Used available surficial sample media to cost effectively follow-up RCD data and outline viable gold targets for future exploration.	Gleeson and Rampton (1987)
41. Matheson - Lake Abitibi Area, NE Ontario (BRIM)	Au, Cu, Pb and Zn	A-1	Rotasonic drill and backhoe used to obtain tills and other sediments; HMC, -250 and -10 mesh fractions; variously analyzed for a suite of some 45 trace and major elements.	N/A	Provided baseline data on the regional Quaternary stratigraphic sequence and on the geochemical character of tills and other sediments in the area.	Baker *et al.* (1984a, b; 1985; 1986); Jensen *et al.* (1985); Steele *et al.* (1986a, b); Averill *et al.* (1986); Jensen and Baker (1986); Ontario Geological Survey (1986a, b, c; 1987); Baker and Steele (1987); Bloom (1987)
42. Macklem Township, NE Ontario (Nighthawk L)	Au (Aquarius Deposit)	C	RCD continuous sampling of glacial sediments (till); -10 mesh HMC; Au and Au grain counts.	Ribbon to narrow fan, >1 km in length.	One of the first case histories documenting the successful use of RCD data in the discovery of a Au deposit.	Gray (1983)

Continued

Table 2. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
43. Currie – Bowman Towhships, NE Ontario	Cu (Currie – Bowman Deposit)	C	RCD sampling of tills; -10 mesh HMC; Cu, Pb, Zn, Ag and Au.	Ribbon to narrow fan 1000 + m x 500 m.	One of the first published works on the successful use of RCD in mineral exploration in an area of thick overburden. Resulted in the discovery of the Currie – Bowman Cu deposit.	Thompson (1979)
44. Hoyle Township, 18 km. NE of Timmins, Ontario	Au	C	RCD sampling of glacial sediments; -10 mesh HMC; Au, Cu, Zn and As.	Ribbon, 1.5 to 2.0 km x 500 m.	Defined anomalous area, but dispersal limited due to a bedrock ridge.	Harron *et al.* (1987)
45. Hoyle Township, 18 km NE of Timmins, Ontario	Au (Owl Creek Gold Mine)	B-1	RCD and sonic sampling of glacial sediments; -10 mesh HMC; Au. Pebble lithologies determined.	Two dispersal trains at different stratigraphic levels. Ribbon, 450 m x 200 m and 650 m x 200 m	Dispersal controlled by bedrock topography. Established Quaternary stratigraphy and ice movement directions.	Bird and Coker (1987)
46. Hemlo Area, North Central Ontario	Au	A-2	Surficial mapping to outline the Quaternary stratigraphy and terrain types.	N/A	Stresses importance of understanding the Quaternary stratigraphy in terms of composition and thickness for selection of sample media for Au exploraiton.	Geddes and Kristjansson (1986)
47. Hemlo Area, Bomby Township, North Central Ontario	Au (Williams Property)	B-1	Percussion drill and flow through sampler; Humus, B-horizon soil and till; humus, various fractions of soil and till (including HMC) analyzed for Au, Cu, Pb, Zn, Ag, Fe, Mn, Mo, Sb, Ba, As and W.	Irregular ovoid, 200 m x 250 to 500 m (limited down-ice dispersal due to bedrock topography).	Varied, but similar response in all sample media, controlled by bedrock topography, overburden thickness and the presence/absence of calcareous till.	Gleeson and Sheehan (1987)
48. Beardmore – Geraldton Area, NW Ontario	Au (Northern Empire, Knox Lake and Archie Lake areas)	B-1	B-horizon soil (-80 mesh) and till (-250 mesh and HMC); Ag, As, Cu, Cr, Zn, Pb, Sn, B and Au.	N/A	Orientation study that Au, in all fractions, was the best indicator of the Au mineralization.	Closs and Sado (1978)
49. Onaman River, 80 km N of Beardmore, Ontario	Au (Tashota Nipigon Gold Mine)	B-1	Till (C-horizon soils); <2 µm for Cu, Zn, Ag, Bi, Ni, Co, Mn, Fe and As, <63 µm for Au and carbonate content. SEM examination of selected HMCs.	Flame, 600 m x 100 to 200 m.	Au gave restricted anomalies whereas the mineralized boulders and Cu, Ag and Zn defined the dispersal train.	DiLabio (1982b)

Continued

Table 2. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
50. Ruttan Mine Area, Leaf Rapids, Manitoba	Cu-Zn (Ruttan Mine), Au	B-1	Till; <2 µm for As and HMCs for As and Au. Gold grains counted.	Irregular ovoid to fan, up to 1 km long.	As in <2 µm and Au in HMCs define dispersal from fault zone.	Nielsen (1986a)
51. NW Manitoba (1:250 K map sheets 64C and F)	Various	A-1	Till (2 – 3 per 100 km^2); <2 µm; Cu, Pb, Zn, Ni, Cr, Mo, Fe, Mn and As	Irregular ovoid to fan, up to 25 km long.	Trace element contents of till reflect large scale chemical variations in bedrock and mineralization. Carbonate content of the tills related to provenance.	Kaszycki and DiLabio (1986a, b)
52. Lynn Lake, Manitoba	Au (Agassiz Deposit)	A-1/2	Till; <2 µm and HMCs; Cu, Pb, Zn, Co, Ni, Cr, Mn, Fe, Mo, U, Hg, Ag, Au, As, W and Sb	Flame to fan, 150 m to 400 m long.	Dispersal defined by Cu, Pb, Zn, Ni, As and Au in <2 µm and by Au in HMCs.	Nielsen (1982, 1983); Fedikow (1983, 1984); Fedikow *et al.* (1984)
53. Farley Lake, Manitoba, 40 km E of Lynn Lake	Au (Agassiz Metallotect)	A-2	Till; <2 µm and HMC; Cu, Pb, Ni, Zn, Co, Cr, Fe, Mn, As, and Au.	Very local dispersal.	Till in area mainly derived from bedrock to the north of the greenstone belt. HMCs indicate gold mineralization; <2 µm fraction does not.	Nielsen and Graham (1984, 1985)
54. Minton Lake – Nickel Lake Area, E of Lynn Lake, Manitoba	Au (Agassiz Metallotect)	B-1	Till; <2 µm and HMC; Cu, Pb, Zn, Ni, Co, Cr, Fe, Mn, As and Au. Gold grain counts.	Dot Lake – 1.5 km long; Agassiz Deposit – 150 m long.	Mineralization shown by As in <2 µm fraction and Au in HMCs. Length of dispersal related to local topographic controls.	Nielsen (1985, 1986b); Nielsen *et al.* (1985); Nielsen and Fedikow (1986)
55. Seal River Area, E of Great Island, Manitoba	Au	B-2	Till; <2 µm, <63 µm and HMC; various of Cu, Pb, Zn, Ni, Co, Cr, Fe, Mn, As, Sb and Au. Textural analyses and pebble lithologies.	Ribbon to fan, 1.3 km x 0.5 km.	As in <2 µm and Au in <63 µm gave highest values and contrast. Au and As in <63 µm gave short and narrow dispersal.	Dredge and Nielsen (1986); Nielsen (1986b, 1987)
56. Northern Manitoba	Various	A-1	Till; <2 µm; Cu, Pb, Zn, Co, Ni, Cr, Mo, Mn, Fe, As and U.	0 to 5 km in the west, greater in the east.	Anomalies in sandy till indicate local bedrock source; those in silty till are unrelated to underlying bedrock.	Dredge (1983a, b)
57. Northwestern Manitoba	Various	B-1	Till and esker sediments; <2 µm; Cu, Pb, Zn, Co, Ni and Ag.	0 to 5 km from source.	Till geochemistry reflects bedrock underlying or directly up-ice from till sample.	Dredge (1981)

Continued

Table 2. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
58. Duddridge Lake, 60 km NW of LaRonge, Saskatchewan	U (Duddridge Lake Prospect)	B-1	Used percussion drill with flow through bit to collect till; -230 mesh and HMC (-80 + 230 mesh); Cu, Zn, Co, Pb, Ag, Mo, As, Fe, Mn and U.	Ribbon to narrow fan, 3 km x 60 to 400 m.	Both the -230 mesh material and HMCs depicted anomalous dispersal patterns in U, As and Cu.	Sopuck and Lehto (1979)
59. Waddy Lake, 160 km NE of LaRonge, Saskatchewan	Au (EP Zone at Waddy Lake)	C	Sonic drill used to obtain tills; HMC; Au, Pb, Ag, and Zn. Gold grain counts done.	Classic ribbon to narrow fan, 600 m x 50 to 100 m.	Successful use of HMC and grain counts to discover a new gold deposit.	Averill and Zimmerman (1986)
60. Waddy Lake NE of LaRonge, Saskatchewan	Au (Star Lake Deposit and Tower Lake Prospect)	B-1	Till; <2 µm, -80 mesh and HMC; Au. Gold grain counts. Size fractionation and analysis of the fractions for selected tills.	Ribbon to ovoid, Star Lake – 300 m x 75 to 100 m. Tower Lake – 600 m x 150 m.	Gold grain counts and Au in till define large distinct dispersal patterns. Au in the <2 µm and -80 mesh give only restricted patterns near mineralization. Fractionation data indicate most gold is in the silt-sized fraction.	Sopuck *et al.* (1986)
61. Waddy Lake Area, NE of LaRonge, Saskatchewan	Au (several Au deposits in the area)	A-2	Till; <0.1 mm and HMC; Au, Cu and As. Gold grain counts, pebble counts and textural analysis performed on the samples.	N/A	Bulk till from C-horizon is an effective sample medium. HMCs and <0.1 mm fractions contained anomalous Au. The Au is mainly fine grained.	Campbell (1986)
62. Sulphide – Hebden Lake Area, 50 km NW of LaRonge, Saskatchewan	Au (a number of sulphide-hosted Au deposits occur in the area)	A-2	Till; <0.1 mm and HMC; Au, Pb, Ni, Co, Cu, Zn and Ag. Gold grain counts and textural analysis performed on the tills.	N/A	Au was the best indicator of mineralization. Both HMCs and fine fraction should be analyzed for Au in exploration.	Campbell (1987)
63. Vixen Lake, Athabasca Basin, N Saskatchewan	U – Ni (Collins Bay "B" Zone)	C	RCD used to sample tills; HMC; U, Cu, Pb, Ni and As.	Isolated ovoid block of anomalous till.	A block of anomalous till was transported ~13 km and deposited isolated from its source.	Geddes (1982)
64. Mahon Lake, Athabasca Basin, N Saskatchewan	U (Midwest U Deposit)	B-1	Percussion drill with flow through bit used to collect till; -80 + 250, -250, <2 µm and HMC (-80 + 250); Cu, Ni, Co, Zn, Ag, Mg, V, Fe, Mo, As, Se and U.	Ribbon, 3 km x 500 m.	The mineralization was best depicted by U in the <2 µm material.	Simpson and Sopuck (1983)

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Table 2. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
65. Athabasca Basin, N Saskatchewan	U (several U deposits occur in the area)	A-1	Boulder tracing program.	Ribbon to fan, from 3 km to 35 km long.	Used the distribution of glacial erratics to locate fracture zones and mineralization.	Ramaekers *et al.* (1982)
66. Cluff Lake Carswell Structure, N Saskatchewan	U (Claude Orebody)	C	Percussion drilling used to sample tills; -80 mesh; Ag, As, Au, B, Cu, Mo, Ni, Pb, Se, Th, U, V and Zn.	Ribbon 1.5 to 2.0 km x 250 m.	Successful use of till geochemistry in locating U mineralization.	Wilson (1985)
67. S of Baker Lake, District of Keewatin, N.W.T.	U-Cu, Ni-Cu and Cu-Zn (Kazan Falls, Ferguson Lake, and Heninga Lake)	B-1	Till from mudboils, plants; <2 µm and, from selected samples <63 µm and sand-size fractions; Cu, Pb, Zn, Co, Ni, U, Ag, Mo, Cd, Cr, Mn and Fe.	Flame to fan, ~1100 m x 150 m (three dispersal trains).	The zones of mineralization are best outlined by trace elements in the <2 µm fraction of the tills. Plant metal levels reflect those in till	DiLabio (1979); DiLabio and Rencz (1980)
68. Bathurst Norsemines, 90 km SSW of Bathurst Inlet, N.W.T.	Zn, Pb and Cu (Bathurst Norsemines)	B-1	Soil profile (organic layer and at 0 – 35 cm and 35 – 64 cm); -80 mesh; Ag, Ca, Cd, Cu, Fe, Mg, Mn, Pb and Zn.	Ribbon to flame, >400 m x 100 to 400 m.	In zone of weathering all sulphides destroyed. Ag, Fe and Pb show well developed dispersal patterns Cu and Zn have undergone hydromorphic dispersion.	Miller (1979); Miller (1984)
69. Aberdeen Lake, 125 km W of Baker Lake, District of Keewatin, N.W.T.	U	B-1	Soil (till?) from mudboils; U, Mo Cu, Pb, Zn, Ni, Co and Ag.	Ribbon to flame 1 to 2 km x 100 to 400 m.	Successful use of multivariate statistics to interpret a large till geochemistry database.	Riese *et al.* (1986)
70. Buttle Valley, Vancouver Island, B.C.	Cu, Zn, Pb, Au and Ag (Lynx, H-W, Myra and Price Mines)	A-2	Till; <2 µm; Cu, Zn and Pb. Clast lithology counts, textural analysis of selected tills and HMC mineralogy.	Confined to alpine valleys, <20 km long.	The <2 µm fraction was anomalous in Cu, Zn and Pb over a distance of 20 km. Dispersal controlled by and confined to valleys.	Hicock (1986)
71. St. Elias Mountas, Northwestern B.C.	Co, Cu, Zn, Pb, Ag (Windy-Craggy)	B-1	Glacial erratics (mineralized clasts); pulverized; Co, Cu, Zn, Pb, Ni, Cd, Mo, Ag, Mn and P.	N/A	Compared chemistry of mineralized erratics to ore from Windy-Craggy. Statistical analyses showed that mineralized erratics were not from Windy-Craggy and likely came from another source.	Day *et al.* (1987)

Table 3. *Summary of drift prospecting and related overburden studies in Fennoscandia (1977-1987) (Study type: A - Regional - 1 - Reconnaissance, 2 - Detailed; B - Research - 1 - Orientation, 2 - Follow-up; C - Exploration case history. HMC - Heavy mineral concentrate, RCD - Reverse circulation drilling.)*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
1. Ahvenisto, S.E. Finland	Sn	A-2	Till - preconcentrated in the field and HMC, <63 µm; Humus; variously analyzed for wide range of elements. Mineralogy of HMC studied.	Flame, 8 km x 3 km.	HMCs anomalous in Sn, are effective for reconnaissance exploration. The <63 µm fraction gave anomalies in Sn and Cu, was more effective for detailed work. Program discovered Sn mineralization. Mineralogical work classified different types of cassiterite related to different deposit types.	Mattila and Peuraniemi (1980); Peuraniemi *et al.* (1984); Peuraniemi and Heinanen (1985); Peuraniemi (1987)
2. Ylojarvi, S.W. Finland	Cu and W	B-1	Till; 250 - 50 µm fraction counted for mineralogy: 225 - 50 µm analyzed for Cu.	Flame, >2 km x 800 m.	Defined down-ice maxima for dispersal of different ore and gangue minerals and related their positions to their mechanical stabilities.	Kinnunen (1979)
3. Korsnas, S.W. Finland	Pb	B-1	Till, profile sampled to bedrock; <60 µm; Multielement analysis.	<150 m long.	Searching for more ore in an area containing abundant ore boulders. Dispersal is short and from several small sources.	Bjorklund (1977)
4. Kaustinen, W. Finland	W	B-1	Till; 250 - 62 µm HMC counted for scheelite: <62 µm analyzed for W.	Ribbon to flame, 2 km x 250 m.	Developed scheelite - tracing method which led to the discovery of mineralization.	Nikkarinen and Bjorklund (1976)
5. Susineva, W. Finland	Mo, Cu and Au	B-1	Till; <60 µm; Cu and Mo. Also collected and analyzed bedrock and stream sediments.	N/A	Mo and Cu in the till anomalous over metalliferous parts of the granitic batholith and reflected underlying bedrock because dispersal was short. Lithogeochemistry recommended if samples can be obtained cheaply.	Nurmi and Isohanni (1984)

Table 3. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
6. Pielavesi, South Central Finland	Zn, Cu and Ni	A-1	Percussion drill with flow through bit used to collect till; whole till and >4000 μm, 4000 – 2000 μm, 2000 – 500 μm, 500 – 62 μm and <62 μm; Cu, Zn, Ni, Co and Cr.	Numerous boulder trains up to 10 km long by 2 km wide. Till gave much more localized dispersal patterns in terms of 100s of m.	Successful use of till geochemistry in the evaluation of geophysical anomalies.	Ekdahl (1982)
7. Tervo, South Central Finland	Ni, Cu	B-1	Till; <50 μm, and 50 – 500 μm; Ni, Cu, Co and Zn.	Ribbon broken into several segments, 700 m x 90 m.	Extremely detailed three dimensional dissection of a dispersal train.	Nurmi (1976)
8. North Karelia, S.E. Finland	Cu, Pb, Zn and Ni (Outokumpu Area)	A-2	Till; <64 μm and 64 – 500 μm; Co, Cu, Mn, Ni, Pb and Zn. Stone counts carried out on several size fractions.	Clasts dispersed from 100s of m to km down-ice, whereas short distances of transport seen in trace element data on till.	Several curves of down-ice abundance of indicator clasts and trace element data give the range of expected dispersal distances for the area.	Nikkarinen and Salminen (1982); Salminen and Hartikainen (1985)
9. Kivisalmi, North Karelia, S.E. Finland	Cu, Pb, Zn and Ni (Outokumpu Area)	A-1	Till; HMC; number of uvarovite grains counted. Boulders (>200 mm) also counted.	Ribbon, but edges not clearly defined, 20 km x 4 km.	In an area of two ice flows, dispersal of boulders and uvarovite, an indicator mineral of the Outokumpu association, were from the same source.	Aumo and Salonen (1986)
10. North Karelia, S.E. Finland	U	A-2	Till and stratified drift; <63 μm; U.	N/A	U leached out of the top 1 m of till in well drained sites. Anomalies in stratified drift classified as hydromorphic. Resulted in discovery of U mineralization.	Bjorklund (1976)
11. Kiihtelysvaara North Karelia	Cu	A-1	Till, stream sediments and lake sediments; <63 μm; Cu, Pb, Zn, Co, Ni and Mn. Clast lithologies in the tills determined. Bedrock samples collected and analyzed.	Transport distance was on the order of 500 to 600 m.	Data on Cu content of tills divided into subpopulations on the basis of underlying bedrock type. Compares data from several sample media.	Salminen (1980)

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Table 3. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
12. Ilomantsi, S.E. Finland	Au, Mo and W	A-2	Till; <63 µm; Co, Cu, Mn, Ni, Pb and Zn and later analyzed for As, Mo, W and Au.	Ribbon, 12 km x 3 km (defined by Mo data).	Au, Mo and W patterns in till differed; each related to a different source. Stepwise increase in sampling density in follow-up of reconnaissance data. Discovered mineralization.	Salminen and Hartikainen (1985, 1986)
13. Kuhmo-Suomussalmi, E. Central Findland	N/A	A-1	Till; <63 µm; Major elements by XRF and Cu, Ni and Zn.	N/A	Normative composition of the fine fraction of till reflects broad provenance areas; useful in identifying different tills.	Taipale *et al.* (1986)
14. Kuhmo-Suomussalmi, E. Central Finland	Ni, Cu, Zn and Pb	A-1	Till; <63 µm; Co, Cr, Cu, Mn, Ni, Pb, Zn and Fe.	N/A	Evaluated hydromorphism on the geochemistry of till. Detected original clastic geochemistry despite hydromorphism. Factor analysis classified till samples into geologically reasonable groups.	Piispanen (1982)
15. Kuhmo-Suomussalmi, E. Central Finland	Ni, Cu, Zn and Pb	A-1	Till; <63 µm – Co, Cr, Cu, Mn, Ni, pb, Zn and Fe; 2 to 6 mm – clast lithologies.	N/A	Measured metal contents of the fine fraction of the till lower than expected based on amount of pebbles of mafic affinity, although their influence is strong.	Saarnisto and Taipale (1985)
16. Hautajarvi, Lapland, N.E. Finland	N/A	B-1	Bedrock and till (6 fractions) were measured for magnetic susceptibility. Anisotropy of tills was compared to conventional grain fabrics.	Dispersal on the order of 2 km long.	Established magnetic susceptibility (magnetite content) as a measure of clastic dispersal.	Puranen (1977)
17. Lapland, N. Finland	N/A	A-1	Regional study of Quaternary stratigraphy. Fabric analyses, stone counts and samples for later lab studies.	Dispersal from 2 to 40 km down-ice.	Key paper defining the 6 tills in Lapland and the ice flow patterns related to them.	Hirvas (1977)

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Table 3. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
18. Visasaari and Vuonelonoja, Lapland, N. Finland	Magnetite	B-1	Till; <63 μm – Fe, Mg, Ca, Na, K, Ti, V, Cr, Mn, Co, Ni, Cu and Zn; <63 μm and 0.06 – 0.25 mm for magnetic susceptibility.	Dispersal from 50 to 300 m long.	Clastic dispersal shown best by magnetic susceptibility and Cr and Ni content of the tills. Short transport distances shown in the ice divide area of Lapland.	Pulkkinen *et al.* (1980)
19. Lapland, N. Finland	Cu, Pb, Zn and W	B-2	Till; <63 μm; Cu, Ni, Co, Fe, Mn and W.	Dispersal is restricted to 10's or 100's of metres in the ice divide area.	Showed the importance of close spaced sampling in areas of short transport.	Lehmuspelto (1987)
20. Lapland, N. Finland	N/A	B-1	Till, sorted sediments and fresh and weathered bedrock; <63 μm; a wide range of elements.	N/A	Defined geochemical properties of weathered bedrock and the till overlying it.	Lehmuspelto (1985)
21. Maaselka, Lapland, N. Finland	Cu and Co	A-2	Till and weathered bedrock; <63 μm; analysis of up to 17 elements. Organic stream sediments were also collected, ashed and analyzed.	Dispersal short in the order of 100's of metres.	Stepwise increase in the sampling density. Till and organic stream sediment geochemistry both reflect anomalous weathered bedrock and mineralization. Resulted in the discovery of Co-Cu mineralization.	Pulkkinen and Rossi (1984)
22. Sattasvaara, Lapland, N. Finland	Au	A-2	Till; <63 μm; Fe, Mg, Ca, Na, K, Ti, V, Cr, Mn, Ni, Cu, Zn and Pb.	Flame, up to 12 km x 15 km.	Regional to follow-up till sampling found several Au-bearing zones. These were identified by anomalous values of Ni, Cu and Co in till followed up by high Cu/Ni ratios with elevated Au in till.	Pulkkinen *et al.* (1986)
23. Sodankyla, Lapland, N. Finland	N/A	B-1	Till; <63 μm, 63 to 250 μm and <2 mm (ground); analyzed for 24 elements.	N/A	Orientation survey determined the <63 μm fraction was best to use for exploration. No favoured sampling depth but suggested testing in areas of mineralization.	Ayras (1977)

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Table 3. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
24. Soretiapulju, Lapland, N. Finland	W (Au, Mo and Co)	B-1	Till; <63 µm, 63 to 500 µm – analyzed for Co, Cu, Mn, Ni, Pb, Zn, Au and W; Panned HMCs were counted for scheelite grains under a UV light.	N/A	Follow-up of Nordkalott Project which resulted in the discovery of W mineralization by counting the scheelite grains in panned HMCs.	Johansson *et al.* (1986)
25. N. Lapland, N. Finland	Au	B-1	Till; <63 µm and HMC; Au and other trace elements. Also examined glaciofluvial sediments and weathered bedrock. Microprobe analyses of selected Au grains.	N/A	Most of the Au is in glaciofluvial deposits. Microprobe analyses of the Au grains showed sulphide inclusions indicating a bedrock source was likely.	Saarnisto and Tamminen (1987)
FINLAND	Various	A-1	Fine fraction of till, pebbles and boulders; analyzed for a wide range of elements and other parameters.	Fan, flame and ribbon, 100's of metres to 100's of kilometres.	Comprehensive descriptionof the sizes and shapes of several dispersal trains, including those related to multiple ice flows, and how they can be used in prospecting.	Hyvarinen *et al.* (1973)
FINLAND	N/A	A-1	N/A	N/A	Showed the close link between till and bedrock geochemistry and the control on the geochemistry of lake and stream sediments by that of till. Recommended analysis of the fine fraction of till.	Kauranne *et al.* (1977)
FINLAND	Various	A-1	N/A	N/A	Describes the national program of boulder tracing and the data bank compiling all ore boulder finds.	Saltikoff (1984)
FINLAND	N/A	A-1	Indicator boulders.	Length of boulder fans vary from 0.2 to 600 km with a median length of 3.0 km.	Produced a map of Finland showing expected transport distance and variability in different parts of the country. Classified landforms as to expected transport distances.	Salonen (1986a, b; 1987)

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Table 3. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
FINLAND	N/A	A-1	N/A	N/A	Key paper on the ice-flow sequence and stratigraphy to be expected in the different physiographic regions of Finland.	Hirvas and Nenonen (1987)
FINLAND, NORWAY AND SWEDEN N. OF 66 – NORDKALOTT PROJECT	Various	A-1	Till – <63 µm and HMC; stream sediments – <180 µm and HMC; stream organic matter and moss – <100 µm; analyzed for up to 26 elements using a variety of techniques.	N/A	Major multi-media regional survey which outlined regional geochemical patterns for integration and interpretation with bedrock and geophysical compilations.	Geological Surveys of Finland, Norway and Finland (1986e, f)
26. Karasjok, N. Norway	Au	A-2	Till; <63 µm and HMC; Au. Also did Au grain counts on HMCs, fabrics, stone counts and roundness.	N/A	Identified a provenance area for an occurrence of placer gold, in till and sorted sediments, for follow-up exploration.	Often and Olsen (1986)
27. Norbotten, N. Sweden	Cu, U, Mo and Cr	B-1	Till; <100 µm and various other selected fractions; Cu, U, Mo and Cr. Mapping of mineralized and indicator boulders.	Ribbon; >300 m x 70 m, >600 m x 50 m, 400 m x 50 m, >600 m x 50 m, 600m x 100 m, 550 m x 30 m and 3500 m x 400 m.	Interpretation of the glaciological processes involved in the formation of 7 dispersal trains. Textbook examples of dispersal mapped by geochemistry and boulder distributions.	Minell (1978)
28. Mjovattnet, N.E. Sweden	Ni	A-1	Tracing mineralized boulders. Use of dogs for sniffing out boulders described.	Ribbon, 1400 m x 100 m.	Interdisciplinary exploration program using boulder tracing, geochemistry and geophysics to discover mineralization.	Nilsson (1973)
29. Vastana – Jarkvissle, E. Central Sweden	Sn and Li	A-2	Till; HMC; Sn and Li. Mapped mineralized boulders.	N/A	Progressed from wide to close spaced sampling to discover Sn and Li-bearing pegmatites.	Toverud (1987)
30. Raggen, Central Sweden	Sn	A-2	Till; HMC; Sn.	Ribbon, 3.3 km x 500 m	Designing a methodology for exploring for Sn. Recommended 1 sample per 2 km^2 increasing to 9 per km^2 from regional to follow-up.	Toverud (1982)

Continued

Table 3. *Continued.*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
31. Dalecarlia, Central Sweden	Cu, Pb and Zn	A-1	Till; HMC; Magnetite separated and analyzed for Ti, V, Co, Ni, Mn, Zn and Cu.	From 1 km to 5 km long.	Compared chemistry of magnetites from tills and different bedrock sources to arrive at a signature for magnetite derived from base metal mineralization.	Granath (1983)
32. Falun Area, Central Sweden	Cu, Pb, Zn and Ag	A-1	Till; <63 μm; Cu, Pb and Zn. Till fabrics measured and boulders mapped.	Ribbon, 2.2 km x 100 m.	Commented on the influence of old preserved tills, exotic debris and sampling depth on till geochemistry and boulder tracing.	Eriksson (1983)
33. Hogfors, Central Sweden	W	B-1	Till; <500 - 100 μm, <100 μm and HMC; W. Counted HMC for scheelite grains. Analyzed humus for W.	Ribbon, 1.6 km x 300 m	Recommended sampling of till and analysis of the HMC for W at both regional and follow-up stages as most cost effective exploration procedure.	Toverud (1984)
34. Astadalen, S.E. Norway	N/A	B-1	Till; up to 11 grain size fractions; wide range of major and trace elements. Grain size analysis. Compared to chemistry and grain size of source rocks.	N/A	Showed that the texture, facies and mineralogy of till should be considered when choosing a grain size range for geochemical analyses.	Haldorsen (1977, 1983)

Table 4. *Summary of drift prospecting and related overburden studies in Ireland and the U.S.A. (1977-1987) (Study type: A - Regional - 1 - Reconnaissance, 2 - Detailed; B - Research - 1 - Orientation, 2 - Follow-up; C - Exploration case history. HMC - Heavy mineral concentrate, RCD - Reverse circulation drilling.)*

Location	Mineralization	Study Type	Sample Media, Fractions and Elements	Shape and Size (L x W) of Dispersal Train	Comments	Reference(s)
1. Lough Derg, County Galway, Central Ireland	Pb	B-1	percussion drill with flow through bit used to sample till; < 177 µm; Cu, Pb, Zn and Ba.	Ribbon, 600 to 1000 m long and 1 to 3 m thick.	Three dimensional study of a dispersal train. Several sections parallel to ice flow show the internal structure of the train.	Miller (1984)
2. Eastern County Offaly, E. Central Ireland	Pb and Zn	B-1	Soil developed on till; Fe, Mn, Cu, Pb, Zn, Ni, Cd, Li, Ca, Mg, Ba and Organic C.	> 200 m x 75 m.	Showed that a preglacial regolith could produce a dispersal train; the regolith survived glaciation.	Maurice and Meyer (1975)
3. Avoca, Ireland	Pb and Zn	B-1	B-horizon soil and till sampled with a percussion drill; < 190 µm; As, Sb, Bi and Se.	N/A	The pathfinder elements As, Sb, Bi and Se were anomalous in soil and till. Till geochemistry was more useful than soil geochemistry.	Moon and Hale (1983)
4. Central Plain, Ireland	Pb and Zn	B-1	Percussion drill and power auger used to sample till; Multi element – including Pb, Zn, Ba, Sr, Mn, Ag, As and Sb.	Wide fan related to two ice flows gives a boulder train 6 km long.	A dispersal train in till anomalous in Pb and Zn underlay peat and other sediments. Drilling was required to map it.	Nawrocki and Romer (1979)
5. Ireland	Various	B-1	Soils and till – review of previous work.	Flame to ribbon, varying from 200 to 1000 m long.	Documented the change from soil to till sampling near surface and at depth from 1971 to 1981.	Cazalet (1982)
6. Trident Glacier, Alaska, U.S.A.	Unknown	B-1	Medial and lateral moraines; fine grained material – HMC; Ag, As, Cr, Cu, Mo, Ni, Pb, Sb, Sn, W and Zn. Boulder, cobble and pebble samples also were collected and counted *etc.*	N/A	Showed how the geochemistry and petrology of morainal debris could be used to evaluate the geology and mineral potential of up-valley catchment areas.	Stephens *et al.* (1983)
7. Duluth Complex, Minnesota, U.S.A.	Pt, Pd and Au	A-2	Esker sediments; < 63 µm and HMC; wide variety of elements.	N/A	Evaluated the geochemistry of esker sediments and found anomalies warranting follow up.	Martin and Eng (1985)

In the Strange Lake area of Labrador (see Table 2-#10), a large glacial dispersal train of debris (McConnell and Batterson, 1987) from a peralkaline complex containing REE, Nb, Zr, Yu, Be and Li is clearly shown by airborne radiometric data (eqTh). The dispersal train from the peralkaline complex was originally located by a U anomaly in a regional reconnaissance lake sediment survey (Geological Survey of Canada, 1979). It is important to note that depending on the nature of a source, for example its radioactivity, and the amount of bedrock exposure and/or thickness of overburden cover, remote techniques (e.g., airborne radiometrics) or other regional reconnaissance methods (e.g., lake sediment geochemistry) can detect glacial dispersal trains. Detailed till sampling carried out on the Strange Lake dispersal train found that Pb as well as Nb, Y, and Zr in the <63 µm fraction of the till best defined the dispersal train and outlined the details within it (Figure 13).

At Sisson Brook, New Brunswick, Snow and Coker (1987) (see Table 2-#20) demonstrated that the W mineralization on the property is detectable by W in all size fractions of the till, as shown for the -200 mesh (<75 µm) and HMCs from Trench 1 located immediately down-ice from the mineralization (Figure 14). The dispersal train from the W mineralization, based on whole till (-10 mesh (<2 mm) ground to -200 mesh (<75 µm)) truncates against a quartzite ridge. It appears that debris, containing components of the W mineralization, has been sheared up into the glacier and carried 8 kilometres down-ice before eventually being deposited. Trenching through the transported lenses of till, anomalous in W, and sampling and analyzing the underlying local granitic till and bedrock revealed no W mineralization. This example clearly illustrates the importance of understanding the nature of glacial transport and deposition, as well as the stratigraphy, of the glacial overburden.

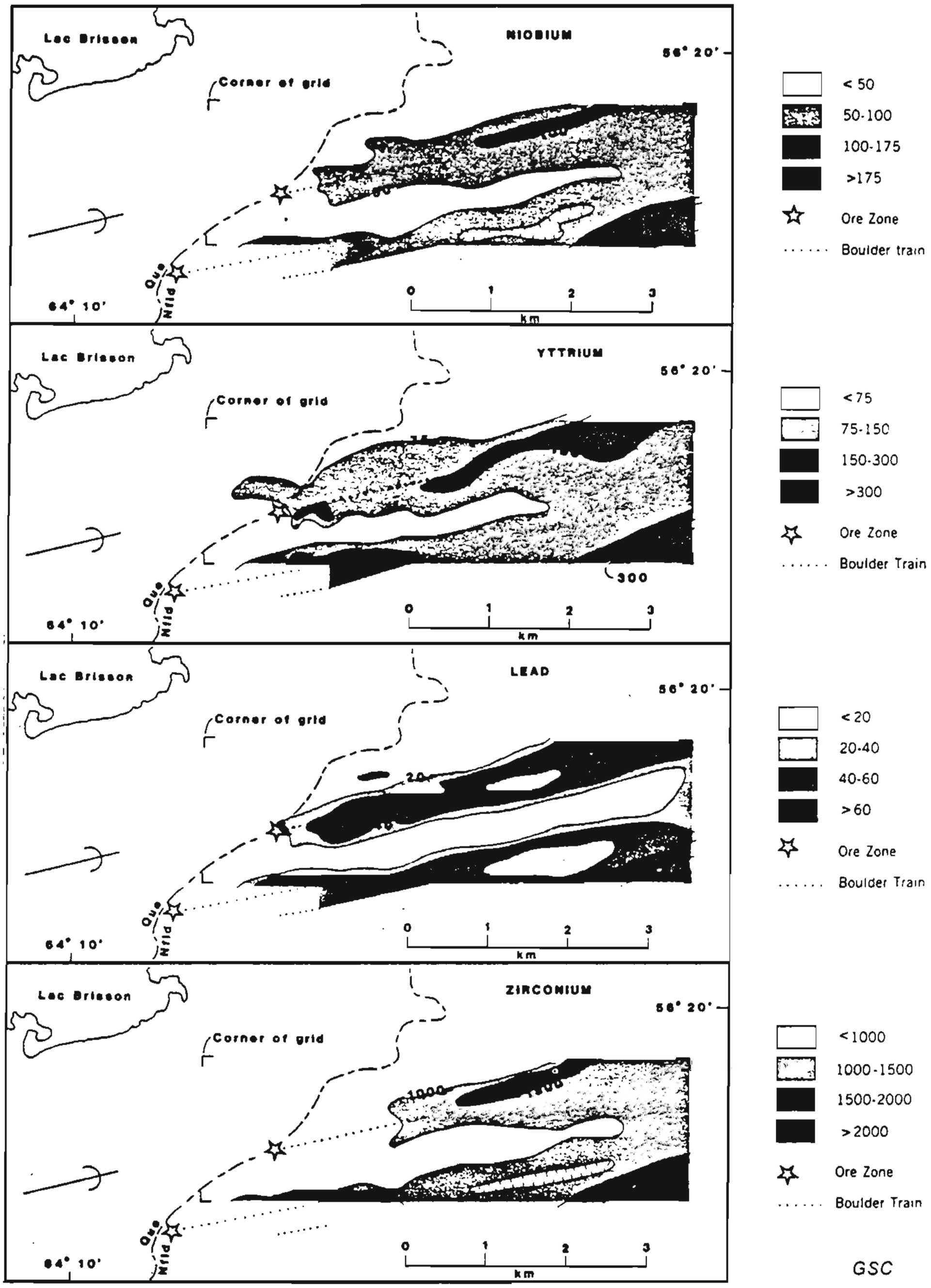


Figure 13. *The Strange lake dispersal train, labrador, mapped by the abundance of trace elements in the <63 μm fraction of till.*

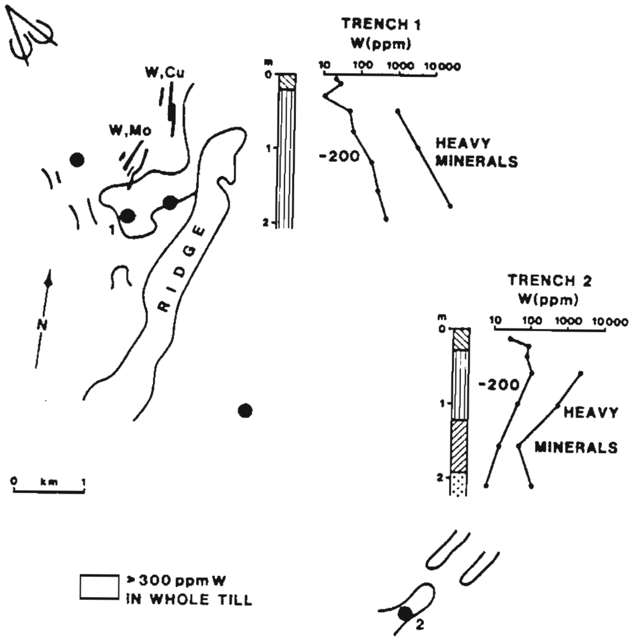
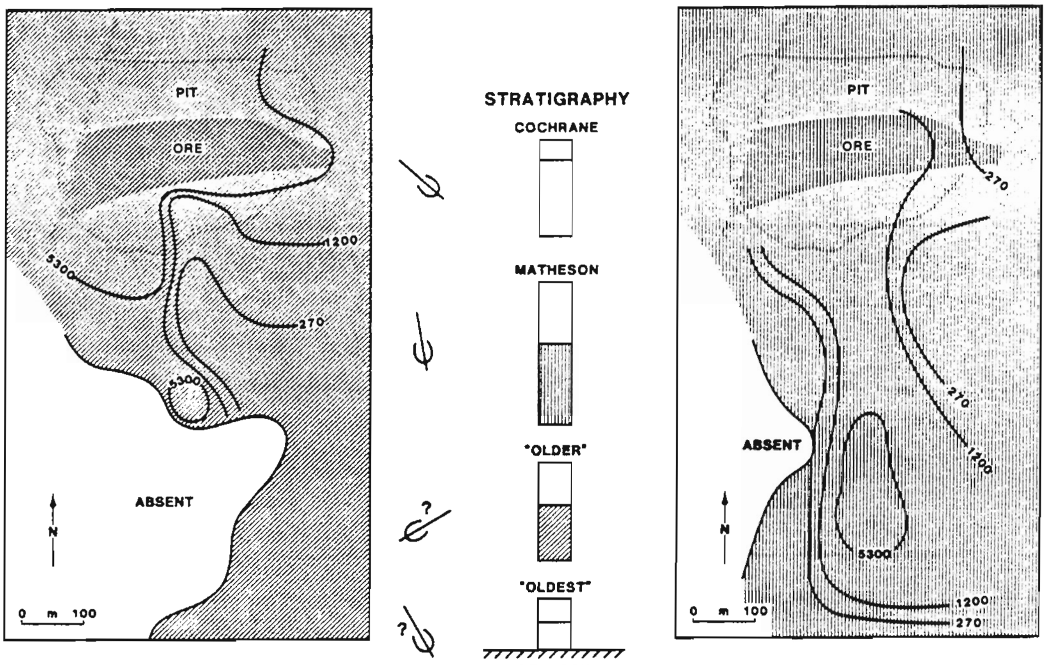


Figure 14. *Tungsten in till at Sisson Brook, New Brunswick (after Snow and Coker, 1987).*

A reverse circulation overburden drilling program carried out at the Golden Pond gold deposit, Casa Berardi, Quebec by Sauerbrei et al. (1987) identified a thin lower till containing anomalous Au and abundant gold grains (see Table 2-#32). Of note was the discovery that glacial dispersal of Au was very limited, in the order of 200 to 400 metres. This was because the ice that deposited the lower till moved subparallel to the strike of the mineralized structure, itself recessive and a bedrock trough, further confining the dispersal train.

In Timmins, Ontario, a reverse circulation and rotasonic drilling program was carried out by Bird and Coker (1987) at the Owl Creek gold mine (see Table 2-#45). This revealed a deep and complex overburden stratigraphy with up to four glacial sediment packages, each with different ice movement directions (Figure 15). In the lowest (Older) till, on bedrock, dispersal is very local being truncated against a bedrock ridge. The highest Au levels in till are adjacent to the subcropping Au mineralization. The overlying till (Matheson), has not been in contact with mineralization or bedrock, and has derived its Au from the lower (Older) till. This dispersal is longer, approximately 600 metres, and the area of maximum Au in till is displaced some 300 metres down-ice from the subcropping Au mineralization. Again, the effect of bedrock topography on glacial dispersal, and the importance of understanding the glacial stratigraphy and ice movement directions in an area are emphasized.



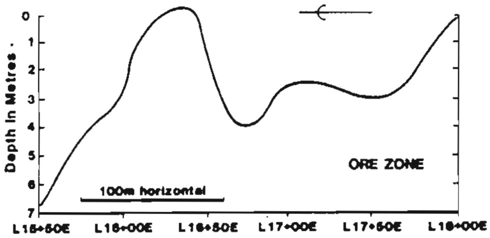
GOLD (ppb)
"OLDER" TILL
HEAVY MINERALS

GOLD (ppb)
MATHESON TILL
HEAVY MINERALS

Figure 15. *Gold levels in heavy mineral concentrates from the "Older" and Matheson Tills at Owl Creek Gold Mine, Timmins, Ontario (after Bird and Coker, 1987).*

In the Hemlo area, at the Page-Williams gold deposit "A" zone, Gleeson and Sheehan (1987) sampled the till using percussion drills with flow through bits (see Table 2-#47). They found that the upper exotic calcareous till gave little indication of the Au mineralization (Figure 16). The underlying locally derived limonitic till gave good response in all size fractions and HMCs, in Au, As, Sb, Mo, Hg, W, and Ba, to the Au mineralization (Figure 16). Once again, dispersal was short (i.e., 200 metres), partly because the deposit lies in the lee of a bedrock high and is protected, and partly because dispersal is truncated against a bedrock high down-ice.

	Gold (ppb)		
Horizon	-50 mesh	-250 mesh (0.063 mm)	Heavy Minerals SG + 2.9
Humus (0.1 m)	10-22		
Upper Ablation Till (0.5 m)		3-73	3-422
Lower Calcareous Till (1 m)		3-20	2-15
Lower Calcareous Till (0.5 m)		19-53	3-39
Old Limonitic Till (0.5 m)		25-300	35-285
Gossan (1.0 m)		+ 15000	+ 15000



Metal Values In Basal Till (-250 mesh)		L15+50E	L16+00E	L16+50E	L17+00E	L17+50E	L18+00E
ppb	Au	12	13	45	300	+15,000	11
	Hg	70	155	790	1,390	297,000	30
ppm	As	2	3	11	25	700	4
	Sb	2	<1	7	46	804	<1
	Mo	3	3	6	7	98	1
	W	2	4	6	4	34	<2
	Ba	560	8,413	1,420	788	1,404	572

Figure 16. *Williams gold deposit - "A" zone Hemlo, Ontario: Range of gold values in humus, exotic calcareous till and local limonitic till from four pits over the mineralization; and, bedrock topographic profile and geochemistry across the mineralization (from Gleeson and Sheehan, 1987).*

A rotasonic overburden drilling program carried out by Averill and Zimmerman (1986) in northern Saskatchewan, located a dispersal train in which the HMCs from the till contained abundant native Au, Au-Ag and Cu, as well as galena, chalcocite, and pyromorphite, which led to discovery of the EP gold zone at Waddy Lake (see Table 2-#59). This classic dispersal train is ribbon shaped with sharp edges (Figure 17). Of note is that the trend of the glacial dispersal train is 15° off the direction for ice movement indicated by glacial striae in the area.

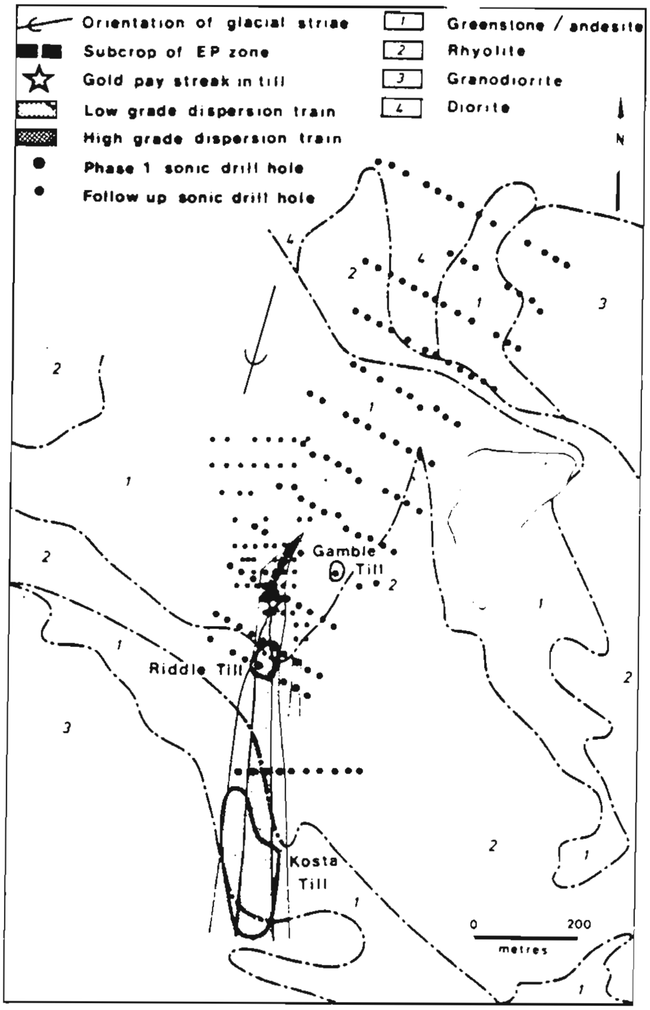


Figure 17. *Glacial dispersal train from the EP gold zone, Waddy lake, Saskatchewan (from Averill and Zimmerman 1986)*

Several countries have started to carry out regional reconnaissance till sampling programs in order to aid mineral exploration and to provide baseline data for environmental, agricultural, geomedical and other disciplines. The outstanding example is the Nordkalott Project carried out by the Geological Surveys of Finland, Norway and Sweden (1986a, b, c, d, e, f and 1987) north of 66° N in these countries (Table 3). Several sample media, including till, were collected and analyzed (<62 µm and HMC >62 <500 µm). Single element, principal component analysis and various types of interpretative and auxiliary data (i.e., geology, magnetics, mineral deposits, etc.) maps were produced. As an example, the regional distribution of Cu (HMC) primarily depicts areas of granulites, areas of mafic to intermediate intrusives and volcanics as well as areas of Cu mineralization (Figure 18).

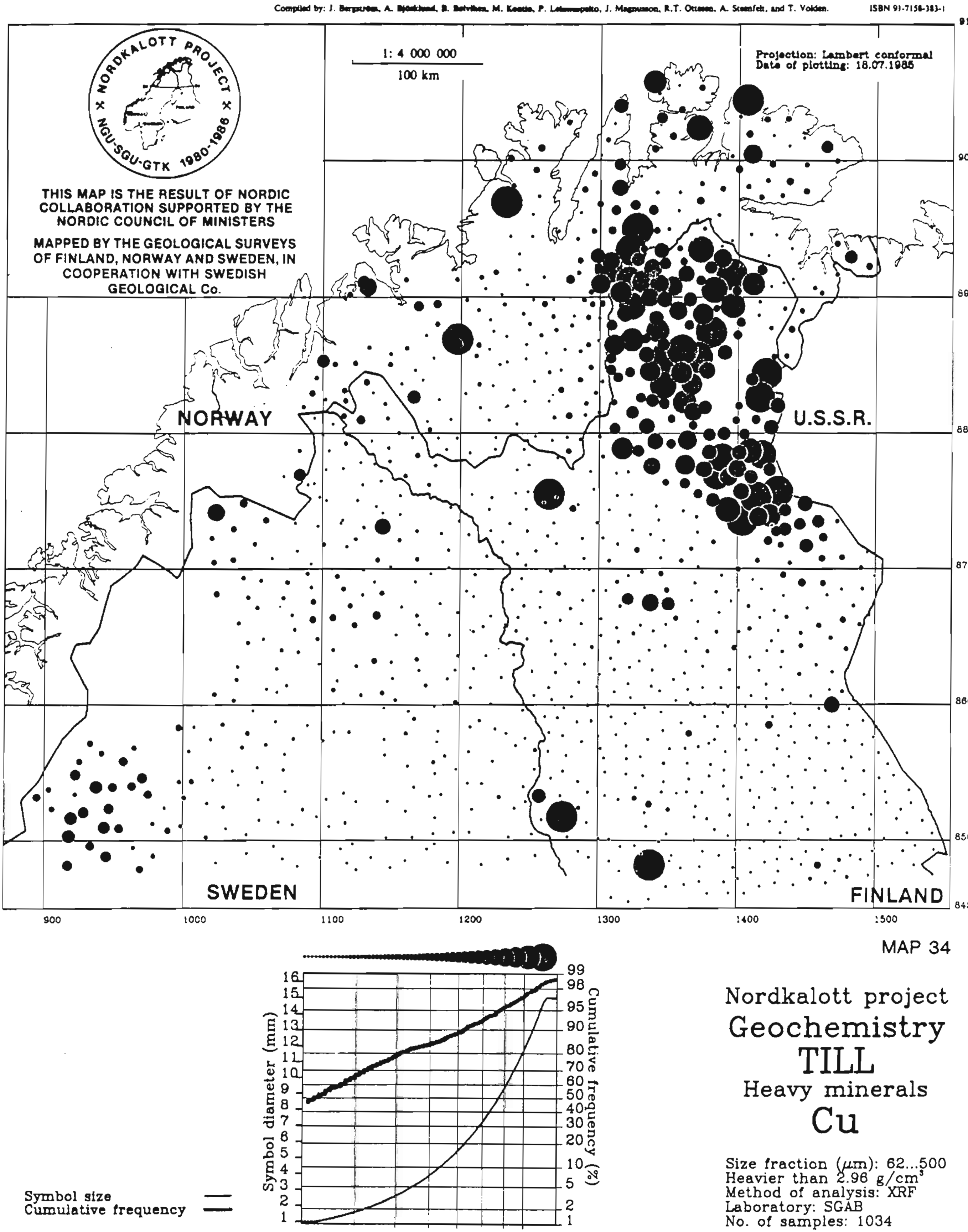


Figure 18. *The distribution of Cu in the heavy mineral fraction of till in the Nordkalott Project area (Geol. Surv. of Finland, Norway and Sweden, 1986f)*

A regional till sampling and surficial mapping program was carried out by Kaszycki and DiLabio (1986a, b) in northwestern Manitoba (see Table 2-#51). The distribution of Zn in the <2 μm fraction of the till clearly depicts the Lynn Lake greenstone belt and other similar geologic features. However, the regional distribution of Zn is controlled by the westward limit of dispersal of carbonates from Hudson Bay, as shown by western limit of carbonate dispersal (i.e., CaCO3 content of tills, Figure 19, Kaszycki, 1989).

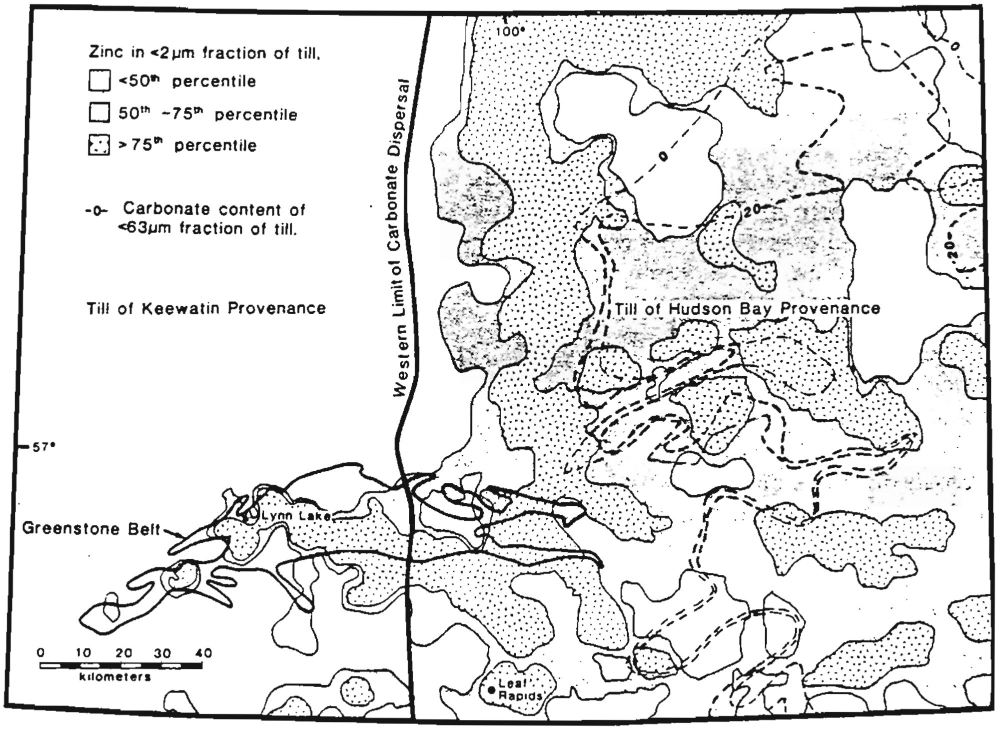


Figure 19. *Anomalous zinc levels in till in relation to bedrock geology and to the presence of exotic calcareous debris in till in the Lynn Lake-Leaf Rapids area, Manitoba (Kaszycki, 1989).*

Another glacial sediment type sometimes used in mineral exploration is esker sediments. The gravel and sand found in eskers can be considered as the sorted coarse sediment that remains when the mud is washed out of till by subglacial and englacial streams. Esker sediments are thus second-cycle sediments (second derivatives of bedrock of Shilts, 1976) and have been shown to reflect the geochemistry and lithology of till where the indicator rocks and minerals survive transport in the esker system. Because eskers are widely spaced and samples from them represent small areas along their length, they are best used in reconnaissance sampling or in detailed sampling where they cross favourable geological structures. Some examples of the use of esker sediments in mineral exploration include work by Lee (1965, 1968), Shilts (1973b, 1984b), Baker (1981, 1982), and Martin and Eng (1985).

APPLICATIONS TO ENVIRONMENTAL ISSUES

Geochemical and lithological data on glacial and postglacial sediments have been used recently to estimate the sensitivity of terrain to acid precipitation and to identify areas that are naturally enriched in potentially noxious trace elements. For example, Coker and Shilts (1979), Rencz and Shilts (1980), Shilts (1984c) and Kettles and Wyatt (1985) all demonstrated how data collected for mineral resource evaluation, to aid bedrock mapping, and to delineate natural regional geochemical trends also could be used to detect existing or potential environmental disturbances.

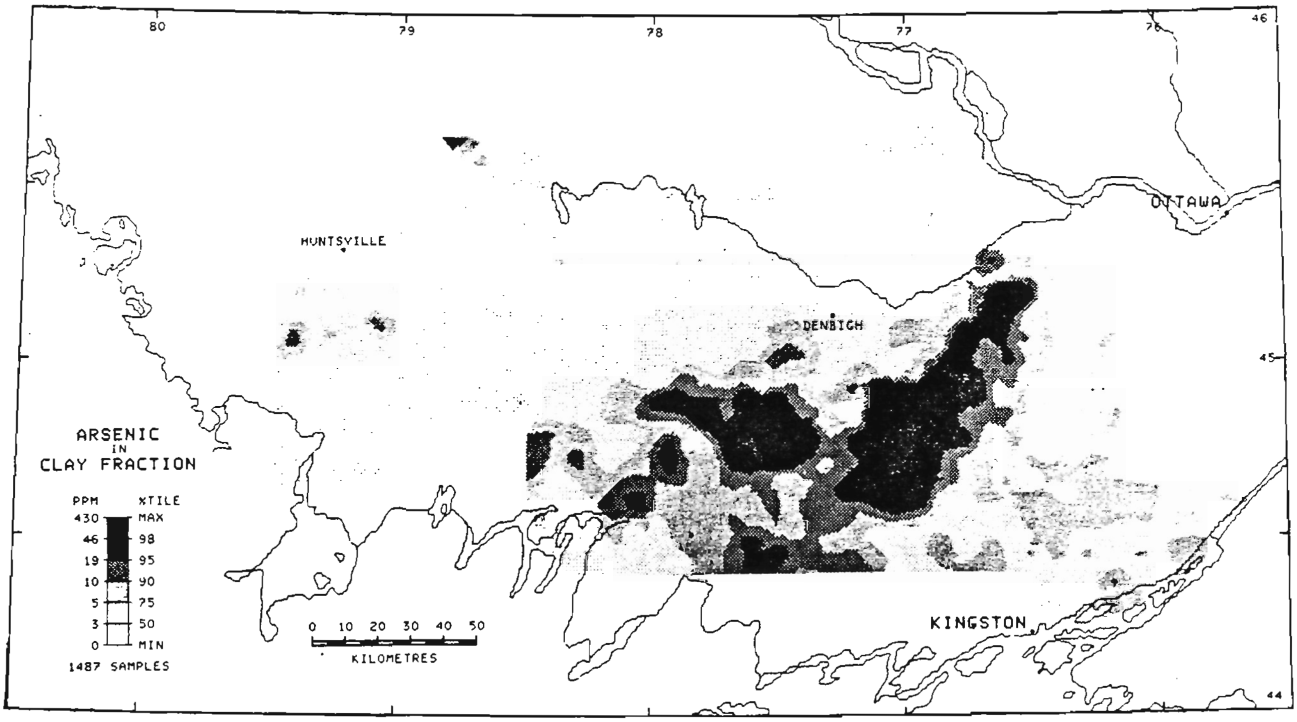


Figure 20. *Arsenic content of till on the Frontenac Arch, southwestern Ontario (after Kettles and Shilts, 1983).*

In a study designed primarily to identify areas that might be sensitive to acid precipitation, Kettles and Shilts (1983) sampled till and other glacial sediments over an area of 15,000 km^2 covering the Frontenac Arch of southeastern Ontario. This area lies within the plume of acid precipitation in eastern North America. The arsenic content of the samples (Figure 20) is one example of data on a potentially noxious element that was mapped in this survey (Hornbrook et al., 1986). Anomalous arsenic levels outline one of the original gold mining areas of Ontario, within the Grenville metasedimentary belt in the eastern part of the Frontenac Arch, and are also found along the southern edge of the exposed Precambrian bedrock. These anomalous levels highlight areas in which arsenic might be remobilized into surface water and groundwater if soil acidity was increased by acid precipitation. The anomalous levels are also significant in terms of mineral exploration. Arsenic is a common pathfinder for gold, and consequently, elevated levels outline areas of known gold occurrences as well as defining similiar targets untested for their gold potential.

Geochemical data are increasingly used in geomedicine and agriculture to outline areas of natural enrichment, or depletion, of noxious trace elements or essential micronutrients (Bolviken et al., 1980). These examples show the multiple uses for geochemical data on surficial sediments, uses which might not have been considered when the surveys were originally designed.

CONCLUSIONS AND FUTURE TRENDS

A number of points have been emphasized in this paper. Many are areas in much need of further work and research. These include the need for:

(1) Regional studies of till provenance, including the effects of exotic drift on local geochemistry.

(2) Correlation of tills in areas of complex stratigraphy and assignment of ice-flow directions to tills.

(3) Investigation of the comminution and weathering behaviour of ore minerals, particularly Au and PGE, in order to design better sampling and analytical schemes.

(4) Demonstration of the use of till geochemical data as a base for other data sets such as biogeochemistry and environmental studies, etc.

(5) Development of more cost effective drilling systems, particularly in areas of intermediate overburden thicknesses (i.e., 10 - 20 metres).

(6) Education and training of geologists in geochemistry and Quaternary geology and a committment by senior explorationists and exploration managers to the use of qualified people to carry out till surficial geochemical and overburden drilling programs.

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PAPER #4

THE APPLICATION OF LAKE SEDIMENT GEOCHEMISTRY IN MINERAL EXPLORATION

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Abstract

Only during the past twenty years or so has a concerted effort been made to examine the role of lake sediment geochemistry in mineral exploration. Since then, numerous studies have described applications not only to regional and property scale mineral exploration, but also resource appraisal, bedrock mapping, public health and environmental studies.

For mineral exploration lake sediment geochemistry is particularly well suited to regions of low relief with indefinite and disorganized drainage systems. This is characteristic of the Precambrian Shield area of Canada. Major provincial and federal surveys have covered extensive parts of this area, providing a wealth of publicly available regional lake sediment data. In addition to these surveys, provincial and federal agencies are also undertaking considerable work designed to refine and enhance the lake sediment technique.

The paper focuses on several aspects of lake sediment geochemistry relevant to mineral exploration. The objectives are: 1) to describe in some detail the methodology for lake sediment surveys, from sample collection to chemical analyses; 2) to briefly review some of the factors affecting element distribution in lake sediment and how these may effect data interpretation including - composition of source material, dispersion processes, scavenging, and anthropogenic input; 3) to show some examples of lake sediment geochemistry applied to mineral exploration including - the Hemlo area in northwestern Ontario, the Strange Lake area in Labrador, and the East Kemptville area in Nova Scotia; and, 4) to provide an appropriate list of references as a guide to further studies.

Résumé

Ce n'est que depuis à peu près 20 ans que des travaux concertés ont été effectués pour évaluer le rôle de la géochimie des sédiments lacustres dans l'exploration minérale. De nombreuses études ont ainsi décrit ses applications non seulement à l'exploration minérale d'une région ou d'une propriété mais également à l'évaluation des ressources, à la cartographie de la roche en place et à la réalisation d'études sur la santé publique et la protection de l'environnement.

En exploration minérale, la géochimie des sédiments lacustres est particulièrement bien appropriée lorsque les régions sont à faible relief et que les réseaux hydrographiques sont indéfinis et non organisés. C'est le cas des territoires du Bouclier précambrien au Canada. D'importants levés provinciaux et fédéraux ont couvert de vastes étendues de cette immense région; ils ont permis de recueillir une très grande quantité de données régionales sur les sédiments lacustres, lesquelles sont accessibles au public. En plus de ces levés, des organismes provinciaux et fédéraux effectuent actuellement des travaux pour affiner et améliorer les techniques d'analyse des sédiments lacustres.

Le présent rapport porte sur plusieurs aspects de la géochimie des sédiments lacustres appliqués à l'exploration minérale. Les objectifs visés sont les suivants : 1) décrire en détail la méthodologie utilisée dans les levés des sédiments lacustres, allant du prélèvement d'échantillons aux analyses chimiques; 2) examiner brièvement certains facteurs influant sur la répartition des éléments dans les sédiments lacustres et la façon dont ils peuvent biaiser l'interprétation des données. Ces facteurs comprennent notamment la composition des matériaux d'origine, les processus de dispersion, le phénomène d'absorption et les effets anthropogéniques; 3) montrer quelques exemples où on a appliqué la géochimie lacustre à l'exploration minérale, par exemple dans les régions de Hemlo dans le nord-ouest de l'Ontario, celle du lac Strange au Labrador d'East Kemptville en Nouvelle-Écosse; 4) fournir une bibliographie pertinente pour orienter les études ultérieures.

1.0 INTRODUCTION

Only during the past 20 years or so has a concerted effort been made to examine the role of lake sediment geochemistry in mineral exploration. Since then, numerous studies have described applications not only to regional and property scale mineral exploration, but also resource appraisal, bedrock mapping, public health and environmental studies.

For mineral exploration the technique is particularly well suited to regions of low relief with indefinite and disorganized drainage systems. This is characteristic of the Precambrian Shield area of Canada, where with some exceptions, most of the lake sediment surveys have taken place (Figure 1.0a). Recently the use of lake sediment cores, which provide stratigraphic and temporal data, has expanded the application of lake sediment to pollution and global climatic change investigations.

It is not the intent of this paper, nor would it be possible given the limited space, to cover all aspects of lake sediment geochemistry relevant to mineral exploration. The objectives of this review are: 1) to describe in some detail the methodology for lake sediment surveys, from sample collection to chemical analyses, an aspect not particularly well documented in the literature 2) to briefly review some of the factors affecting element distribution in lake sediment and how these may affect data interpretation 3) to show some examples of lake sediment geochemistry applied to mineral exploration 4) to provide an appropriate list of references as a guide to further studies.

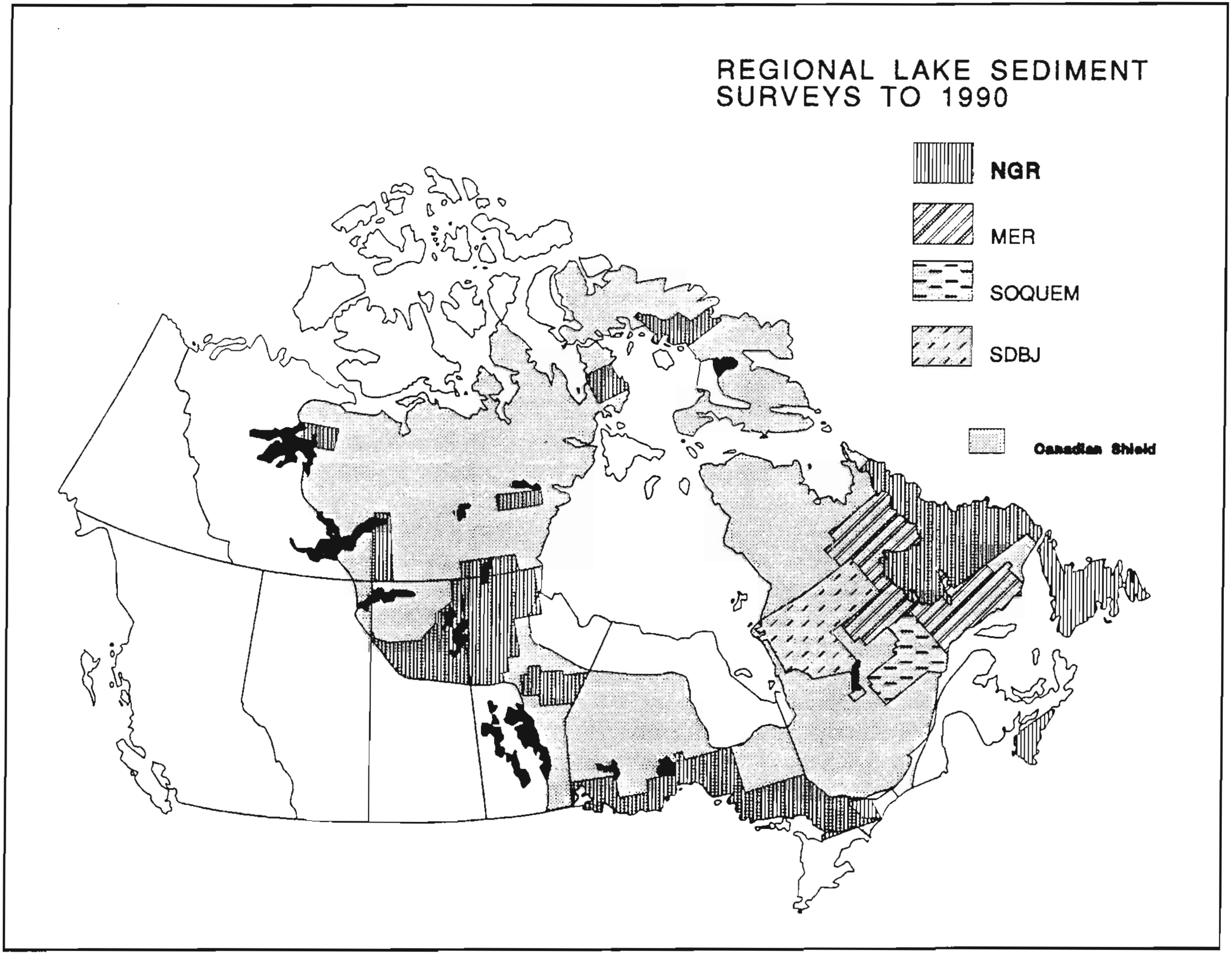


Figure 1.0a. Selected regional lake sediment coverage in Canada to 1990.

2.0 METHODOLOGY FOR LAKE SEDIMENT SURVEYS

2.1 Sample collection design

Before any geochemical survey is undertaken it is essential that a sample collection strategy be set in place to monitor and control sampling and analytical variance. Without it, analytical data generated from the survey will be of considerably less value. For all lake sediment surveys conducted by the GSC, samples are collected adhering to a basic sampling design that incorporates field duplicate, blind duplicate and control reference samples (Figure 2.1a).

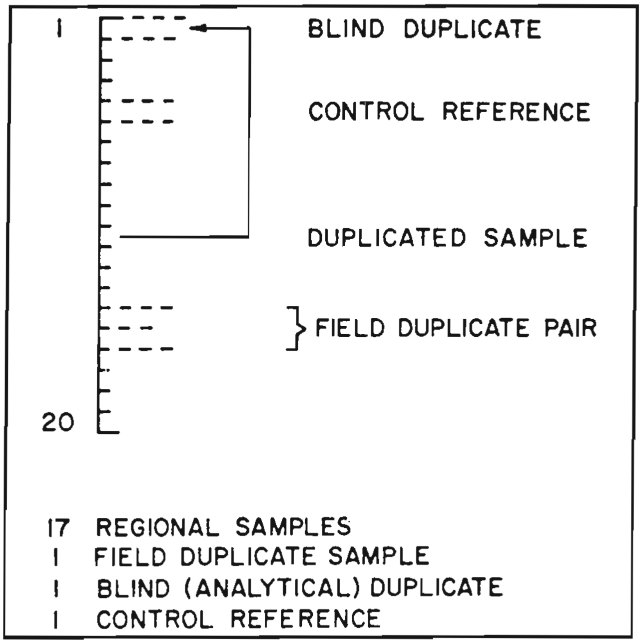


Figure 2.1a. Sample collection design used by the GSC in its stream and lake sediment surveys.

Samples are collected in 'blocks' of 20 consecutive field numbers (e.g., 001...020, 041...060, 061...080). Within each block of 20 there are 17 routine field samples, a control reference sample, a blind (analytical) duplicate sample, and a field duplicate sample. The field duplicate sample is a separate sample collected at one of the 17 routine sites. The choice of which site to duplicate is random and left to the judgement of the sampling team.

The blind duplicate is a reserved number for the second member of a blind duplicate pair. This reserve number is always the first field sample number in a block (i.e., 021, 041, 121, 341,...). The sample preparation laboratory selects a sample in the block to duplicate in this reserved slot, preferably one of the field duplicate samples. Another number in each block is reserved for the control reference sample. GSC standard reference materials (usually 3 different ones with a similar matrix to the material being analyzed) are later inserted into these slots. By using this type of collection design, sampling and analytical variance can be monitored and controlled.

2.2 Sample collection

2.2.1 What to sample and where to find it

Lake sediment material can be broadly classified into three groups: inorganic sediments, organic sediments or organic gels (Timperley et al., 1973; Jonasson, 1976). Inorganic sediments are characterized by various mixtures of sand, silt, clay and hydrous oxides with little organic matter. These tend to exist near the shore of lakes, near inflow and outflows and in lakes where surrounding vegetation is sparse (e.g., above the treeline). Often they represent reworked tills. Organic gels, referred to as gyttja, are generally found in the deeper, less active parts of the lake environment. These gels, which can be considered as mature sediments, are thixotropic, organic-rich, and commonly greenish brown to grey in colour. Organic sediments can be viewed as blends of organic gels, inorganic sediment and immature organic debris. They occur in most Shield lakes usually near shores or inflows. Compared to organic gels they represent immature sediments.

Of these three different lake sediment materials the organic gels (gyttja) are the preferred sample medium for lake surveys, because:

1) element concentrations tend to be higher and more consistent in the gyttja compared to the other media.

2) the somewhat high and consistent LOI content of the gyttja reduces the influence of this factor on the distribution of elements in lake sediment.

3) the relatively deep water environment of the gyttja, represents a chemically more stable environment than shallow water sediments that are subject to seasonal redox shifts.

Maps (e.g., Figure 2.2.1a) created from acoustic subbottom profiles, of Big Turkey Lake in northwestern Ontario (Shilts and Farrell, 1982), illustrate the typical distribution of gyttja in Shield lakes. The material is not uniformly distributed but is concentrated in the profundal basin(s). Thicknesses of more than 10 metres are not uncommon, thinning laterally away from the basin towards the shoreline. The gyttja may be underlain by glacial deposits such as till or lie directly on bedrock.

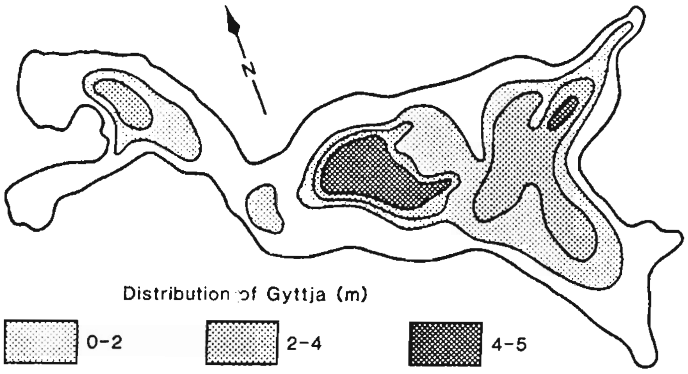


Figure 2.2.1a. Distribution of gyttja at Big Turkey Lake, Ontario (modified after Hornbrook, 1989).

2.2.2 How to collect samples and other survey considerations

An important preliminary task in any lake sediment survey is selecting tentative sample locations on suitably scaled (usually 1:50 000 or 1:250 000) NTS map sheet(s). These are gridded to form 'cells' corresponding in area to the selected sample density. For reconnaissance surveys (sample density usually 1/6 km^2 to 1/13 km^2), an ideal sample is taken from a lake less than 5 km^2 in size and greater than 3 metres deep, with a single central basin that is the focus of drainage in the area surrounding the sample site. A lake with active inflow-outflow drainage is sampled in preference to a stagnant lake in a given cell. Round lakes with one central basin are preferable to lakes with several arms and deep bays. Large lakes are not sampled in their central basins where grid cells are entirely over water, along smooth shorelines or amongst islands in the middle of the lake, although deep bays of such large lakes can be sampled. Small peat bog or string bog ponds are not sampled. Similar considerations need to be given to sample site locations for all types of lake surveys, even the most detailed. Sample density is largely controlled by the objectives of the survey and can vary from 1/13 km^2 or greater for reconnaissance surveys to multiple sampling of every available lake for property scale investigations.

Some of these sample site selection factors can be determined directly from the topographic maps, e.g., lake size, presence or absence of inflow-outflow drainage, lake shape etc. Others are best determined while on traverse. For example, determining the exact sample site within a chosen lake is readily apparent from the helicopter as a lake is approached. The extent of the profundal basin is defined as a relatively darker coloured area of the lake, and the presence of multiple basins indicated by dark patches separated by lighter coloured shallow areas.

Sampling is carried out using float-equipped helicopters manned by two crew members plus the pilot. A Bell Jet Ranger 206B is preferred because of the relative ease of mounting an external winch and attaching a working platform to the floats, in addition to the large interior working space. The senior sampling crew member (navigator) is responsible for recording all pertinent field data, determining the actual sample site on the traverse maps and, with the pilot, for navigation along a traverse planned and filed before flight time. The junior crew member (sampler) is responsible for sample collection and noting various field information which is relayed to the senior member.

To collect the lake sediment material the GSC uses a hollow-pipe, bottom-valved sampler (Figure 2.2.2a), attached to an external winch and rope system on the fuselage of the helicopter. Alternatively the sampler can be hand-lined. Variations of this method have been developed and used by other provincial agencies and private companies. When the helicopter lands on the lake and becomes stationary the sampling apparatus is released and allowed to sink unimpeded to the lake bottom. Generally, the full length of the sampler will penetrate the bottom sediment. The sample obtained, extending from the butterfly valves to several centimetres below the triangular port, represents a 30-35 cm section of lake sediment from several tens of centimetres below the water-sediment interface. The material is retrieved from the sampler by inserting a plastic scoop into the barrel through the triangular port, inverting the sampler and then 'thumping' the sampler on a wood plank screwed onto a plywood platform attached to the helicopter float. The sediment samples are then placed in high wet-strength paper bags, approximately 10x15x15 cm with a double fold top, and put into a partitioned aluminum tray specially designed to fit in the back of the helicopter. It is important to collect a full bag of sample material. One to two kilograms of wet lake sediment will shrink to a hard, dark brown to black lusterless 'brick' about the size of a golf ball weighing 50 to 100 grams depending on the LOI content of the sample. Field observations such as lake size and depth, and local relief are recorded on standard field cards (Garrett, 1974) at the site.

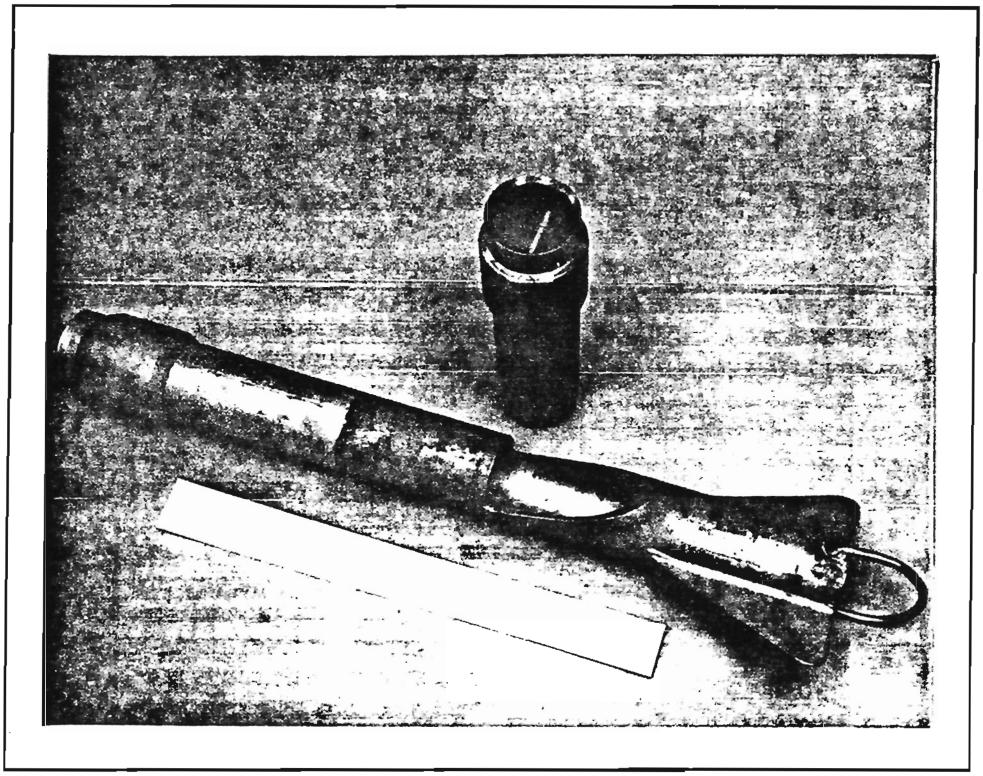


Figure 2.2.2a. Geological Survey of Canada lake sediment sampler. Bar is 46 cm long.

Other sampling devices being used include gravity corers and clam bucket type devices. The advantage of the gravity corer is that it can supply stratigraphic information. However, this benefit comes at the cost of sampling rate of about 8 samples per hour (Fortescue, 1988) versus 15 or better with the GSC sampler. Whatever sampling device is used, it must be capable of collecting a sample in which the upper 10 cm or so of the lake sediment column is not included. This material can contain significant input from anthropogenic sources (refer to section 3.3) resulting in spurious data. For this reason a clam bucket or other sampling device that takes a grab sample from the sediment/water interface is not recommended.

2.3 Sample preparation and analyses

Sample preparation begins in the field. After each work day, collected samples are checked to ensure that field sample numbers are correct relative to the location maps and that they match 'one for one' with the field cards. They are then dried in a vented and heated drying area. For most surveys this is a floored tent with propane or fuel oil heaters capable of outputting up to 250 000 BTU's. Constant adjustment is required between venting off hot moisture-laden air and the heater settings to maintain a temperature of approximately 38°C. Higher temperatures may result in sample bag deterioration or loss of volatile elements. The samples will usually take 10 days to dry thoroughly, although longer periods may be required during periods of inclement weather. It is important that the samples are completely dry before shipping. Slightly damp samples sitting in containers for several days will 'sweat' causing bags to disintegrate and sample material to be spilled and cross contaminated.

In the sample preparation laboratory samples are initially crushed or broken down to pieces less than 0.25 cm diameter by pounding the bagged sample with a steel pestle or hammer. The material is further reduced in ceramic ball mills or ceramic shatter boxes (swing mills). The minus 80-mesh fraction is then placed into 16 dram vials. The plus 80-mesh fraction along with any excess material not ball milled is placed in polyethylene containers and stored for possible future use.

A detailed overview of analytical methods used in exploration geochemistry is presented elsewhere in this volume, so only a few comments are given here. In general, there is no one single analytical method that can provide all the required geochemical analyses. Usually a combination of techniques are used that include atomic absorption spectroscopy (AAS), instrumental neutron activation analysis (INAA), inductively coupled plasma spectroscopy (ICP and ICP-MS) and other specific techniques. What combination of these and others methods are used depends on factors such as; elements required, amount of sample required by a method versus amount available, detection limit of a method versus expected background concentration in the samples, accuracy and precision of a method, and cost. However, regardless of what combination of methods is used, data for Fe, Mn and LOI(loss-on-ignition) need to be included as part of any analytical suite (refer to section 3.3).

Table 2.3a summarizes elements determined and methods used by the GSC in lake and stream sediment surveys from the mid-seventies to the present. The changes in elements and methods reflect as much as any other factor improvements and developments in the field of analytical chemistry. At present, INA analysis is the main analytical method used for lake sediments. This method provides data for about 35 elements, of which about 10 are not used because of inadequate detection limits and/or precision. Added to this are several elements determined by AAS and other specific techniques. In total, this combination of methods provides usable data for ~40 elements.

YEAR	MEDIUM	VARIABLES DETERMINED AND METHODS USED
1976	Lake Sediment	Zn,Cu,Pb,Ni,Co,Ag,Mn,Fe(AAS1); As(COL1); Mo(AAS2); LOI(GRAV1); U(NADNC)
	Stream Sediment	Zn,Cu,Pb,Ni,Co,Ag,Mn,Fe(AAS1); Mo(AAS2); U(NADNC); W(COL2)
1985	Lake Sediment	Zn,Cu,Pb,Ni,Co,Ag,Mn,Fe,Cd(AAS1); Mo,V(AAS2); As,Sb(AAS3); Hg(AAS4); LOI(GRAV1); U(NADNC); F(ISE); Au(FANA)
	Stream Sediment	As per lake sediment plus W(COL2); Ba,Sn(AAS2)
1990	Lake Sediment	Zn,Cu,Pb,Ni,Co,Ag,Mn,Fe,Cd(AAS1); V(AAS2); Hg(AAS4); LOI(GRAV1); F(ISE); Na,Sc,Cr,Fe,Co,Ni,As,Br,Rb,Mo,Sb,Cs,Ba,La,Ce,Sm,Eu,Tb,Yb,Lu,Hf,Ta,W,Th, U,Au(INA)
	Stream Sediment	As per lake sediment plus Sn(AAS2)

AAS1: atomic absorption spectroscopy (AAS) with an air-acetylene flame; AAS2: AAS with a nitrous oxide-acetylene flame; AAS3: AAS with hydride evolution; AAS4: cold vapour AAS; COL1: Colorimetry involving use of diethydithiocarbonate; COL2: Colorimetry involving use of dithiol or zinc dithiol; FANA: fire assay preconcentration with neutron activation analysis of dore bead; GRAV1: gravimetric determination at approximately 500 C; ISE: Ion selective electrode; INA: instrumental neutron activation; NADNC: neutron activation analysis by delayed neutron counting.

Table 2.3a. Summary of elements determined and methods used for GSC lake and stream sediment surveys conducted from the mid-seventies to present.

2.4 Survey costs

The cost to undertake a lake sediment survey (expressed as cost/sample), including collection, preparation, analyses and data management, is highly variable and dependent on several factors, including location and accessability of the survey area, number of survey sites, sample density and suite of elements being determined. For example, over the last few years the GSC has undertaken surveys that ranged from southern Ontario to northern Manitoba, involved 1 000 to 3 000 sites at an average density of 1 sample per 13 km^2. The analytical suite determined is outlined in Table 2.3a. Collection, sample preparation and analyses were contracted out. Overall project supervision, data management and Open File production were handled by the GSC. The cost of these surveys varied from $75 to $115 per site. Rogers et al. (1990a), estimate a total cost of $50 per lake sediment sample in Nova Scotia.

3.0 FACTORS AFFECTING TRACE ELEMENT DISTRIBUTION IN LAKE SEDIMENT

Table 3.0a summarizes the distribution of several elements in lake sediment from four geographically distinct regions of Canada. The data are from four GSC Open File releases. The table serves to indicate the range of trace element concentrations that may be encountered in lake sediment and illustrates that there are similarities and differences in the element distribution between areas. There are a number of factors that account for the observed variations. The two most important are; 1) differences in type and composition of the source material from which the lake sediments are derived and 2) differences in the chemical and mechanical dispersion processes that move the material from source to sampling site. Other factors need to be kept in mind as well, and include scavenging by organics, scavenging by hydrous Fe and Mn oxides, anthropogenic input (contamination), in-situ modification, aquatic biology etc. A basic understanding of these as they affect lake sediment composition is necessary to get the most information from a lake sediment data set.

3.1 Variation in type and composition of source material

There are three primary sources from which elements are derived; bedrock, glacial deposits, and mineralization. Elements from these sources may be reworked by several surface processes (i.e., taken-up

AREA	NTS SHEET(S)	Variable	LOI	Fe	Mn	Zn	Cu	Pb	Ni	Co	As	Mo	Hg	Na	Sb	La	W	Au	
		Units	pct	pct	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	pct	ppm	ppm	ppm	ppb	
		Det. Lmt.	1	0.02	5	2	2	2	2	2	1	2	10	0.02	0.1	2	1	2	
		Method	GRA	AAS	AAS	AAS	AAS	AAS	AAS	AAS	AAS	AAS	AAS	INA	INA	INA	INA	INA	
Contwoyto Lake (NWT) N=123	76E		6.0	1.1	67	52	24	3	22	5	2	<2	20	1.4	<0.1	25	<1	<2	5th %tile
			13.0	**2.0**	**107**	**98**	**60**	**5**	**40**	**11**	**7**	**<2**	**34**	**2.1**	**<0.1**	**37**	**<1**	**3**	50th %tile
			25.6	4.1	365	176	146	8	93	30	45	2	68	2.5	0.2	52	3	8	95th %tile
Labrador N=1364	13I,J,K 13N,O		4.6	0.5	50	27	10	<2	4	2	<1	<2	10	.14	<0.1	20	<1	<2	5th %tile
			28.8	**2.2**	**240**	**70**	**24**	**2**	**12**	**9**	**<1**	**4**	**60**	**.72**	**0.1**	**61**	**<1**	**<2**	50th %tile
			48.8	8.7	2195	185	75	9	32	41	6	21	160	2.71	0.5	208	3	6	95th %tile
Ontario N=867	52A,H		9.1	0.4	55	46	18	<2	10	3	<1	<2	50	0.06	<0.1	5	<1	<2	5th %tile
			41.8	**1.4**	**220**	**96**	**54**	**3**	**21**	**9**	**<1**	**2**	**120**	**0.21**	**0.2**	**18**	**<1**	**3**	50th %tile
			64.5	4.6	855	194	181	11	45	23	4	5	230	1.40	0.6	46	1	9	95th %tile
Saskatchewan N=1151	73O,P 74A,B,C		9.4	0.8	185	38	6	<2	6	3	<1	<2	24	0.08	<0.1	9	<1	<2	5th %tile
			41.6	**2.8**	**520**	**82**	**17**	**<2**	**15**	**8**	**<1**	**3**	**60**	**0.33**	**0.1**	**58**	**<1**	**<2**	50th %tile
			72.5	17.0	2318	160	40	4	32	19	5	7	125	1.60	0.3	190	2	4	95th %tile

Table 3.0a. Variation of selected elements in lake sediment from four regions of Canada. Data taken from recent GSC Open File releases; GSC Open Files **2179** (Ontario), **1636** (Labrador), **1644** (Saskatchewan) and **(In preparation)** Contwoyto Lake.

by vegetation, moved by ground and surface water, mechanically dispersed) before final deposition in lake bottom sediments. The most important of these three is bedrock, although locally either of the other two may dominate and overprint the chemical signature related to the underlying bedrock.

Most elements are preferentially concentrated in certain rock types because of igneous or sedimentary processes. Numerous studies have shown that the geochemical distribution patterns of elements in lake sediments, particularly regional trends, are largely related to, and reflect the variations in the chemical composition of the underlying bedrock (c.f., Hornbrook and Garrett, 1976; Jonasson, 1976; Cameron and Ballantyne, 1977; Maurice, 1977; Friske, 1985a; Kerr and Davenport 1990; Garrett et al., 1990).

Detailed work by Johnson et al. (1986) showed that loading of metals into sediments of the Turkey Lakes area reflected the elemental composition of the surrounding bedrock. Reduced variability for several elements in the lake sediment relative to bedrock was also noted, illustrating the integrating effect of weathering and sedimentation. Fortescue and Vida (1990) also demonstrate, at a detailed survey level, the close correlation between bedrock and lake sediment composition.

Although the size of a given mineral occurrence is small relative to the total area of a catchment basin, it can exert a significant influence on the sediment composition of a nearby lake because (1) trace elements such as Cu, Pb, Zn, Ag, Mo, etc., usually occur in mineralization in concentrations that are several orders of magnitude greater than in surrounding bedrock, and (2) mineralization most often occurs as, or is associated with sulphides that upon exposure undergo rapid oxidation, releasing the chemical components into the secondary environment.

Most areas in which lake sediment surveys are undertaken are covered to a greater or lesser extent by glacial deposits, of which till is the most common. These deposits are generally composed of material that has been transported only a relatively short distance (Shilts, 1976) and have a chemical composition similar to the underlying bedrock. The absence of any significant displacement or obstruction of regional geochemical lake sediment patterns in areas covered by extensive glacial deposits is evident from a number of studies (Friske, 1985a,1985b; Davenport and McConnell, 1988; Rogers et al., 1990a). However, on a local scale, possible down-ice dispersion of material is an important consideration in interpreting any lake sediment data set. Often the dispersion from a point source, such as mineralization, extends over several catchment basins. On the plus side, this increases the size of the exploration target. However, it complicates interpretation and follow-up of data because the source of the anomaly is outside the catchment basin from which the sample was collected. As described below (refer to section 4.3), a good example of a large multi-catchment-basin anomaly is the dispersion train associated with the Strange Lake deposit, Labrador.

Other types of glacial deposits, including lacustrine, outwash and eolian are not likely to reflect the composition of underlying bedrock or mineralization. The adverse effects of these types of transported glacial material on lake sediment surveys have been well documented by Gleeson and Hornbrook (1975), and should be considered as a possible influence on element distribution in lake sediment. Still, areas covered by these deposits should not be ruled out as potential lake sediment survey areas. It is possible that movement of elements to the lake sediment site by ground water and/or through vegetation uptake followed by erosion, can develop geochemical signatures reflecting nearby bedrock and mineralization.

3.2 Dispersion processes

Input into the lake environment is largely controlled by surface weathering processes: lake sediments are the result of a mixture of hydromorphic and mechanical weathering effects.

Traditionally it has been assumed that within the low energy environment typical of lake sediment survey areas mechanical dispersion is somewhat less important than chemical (hydromorphic) processes. Recent work has shown however that in some instances mechanical dispersion can be a significant factor, particularly in the generation of anomalies related to mineralization. Rogers and Garrett (1987) describe the presence of angular and discrete grains of cassiterite in a sample collected from Moosefly Lake in Nova Scotia, which they interpret as having been mechanically transported into the lake from the nearby tills (refer to section 4.4). Other heavy mineral investigations have revealed discrete gold grains in centre-lake sediment (Rogers, 1988). In general it appears that elements (e.g., Sn, gold, REEs ...) commonly tied up in refractory grains may to a significant extent be mechanically dispersed, more so than grains susceptible to weathering, such as sulphide minerals.

Chemical dispersion of an element is largely controlled by its ability to go into true solution (i.e., free ion or soluble complex), or form soluble colloidal complexes. Once in solution, either in surface or ground water, its ability to stay in solution and disperse from its source is controlled by the stability of the compounds it forms with other components in solution. Coker et al., (1979) have emphasized that in flat-lying tree-covered terrains, typical of large portions of the Shield, the incidence of organic matter is high and metal-organic interactions predominate. Organic matter can enhance trace-metal mobility by forming soluble or colloidal metal-organic species, or retard it by the precipitation of insoluble organic complexes or sulphides. Other components in solution such as carbonate, chloride, sulphate and hydrous metal oxides can also play an important role in trace-metal migration.

Because there is little quantitative data on the combined effects of these factors, qualitative estimates of the relative mobility of elements are often cited. Such estimates for several different surficial environments are given by Rose et al. (1979). Under oxidizing conditions and pH between 5 and 8, the order of relative mobility is given as: Mo>F~Zn~Ag~U~As~Hg>Mn~Pb~Cu~Ni~Co >Fe. This order is a generalization, and will vary considerably in response to changes in the chemical environment. Still, it serves as a general guide and illustrates the difference in the mobility of elements, an important consideration in evaluating any geochemical data set, particularly detailed surveys.

Cameron (1977) studied the geochemical dispersion in lake sediment and water around massive sulphide mineralization in the Agricola Lake area of the Northwest Territories. He determined that Pb, Ag and Hg from the mineralization are relatively immobile in the surficial environment and are largely retained in the soils close to the mineralization. In contrast Zn, Cd and to a lesser extent Cu are very mobile, with anomalous concentrations found 7 km down drainage, and possibly further. Besides the obvious conclusion that the more mobile elements are better indicators of mineralization because they form larger halos and targets, the data illustrates that the distribution of anomalous concentrations of elements can be used as a guide to proximity to source. In the case of Agricola Lake, anomalous concentrations of Pb, Ag or Hg in lake samples indicate a proximity to mineralization.

3.3 Other factors affecting lake sediment composition

Iron and Mn oxides and organic-matter are noted for their ability to sorb (scavenge) trace elements, often resulting in anomalously high concentrations of elements unrelated to elevated source levels, resulting in 'false anomalies'. The relation between organic content (approximated by loss-on-ignition (LOI)), Fe, Mn and several selected elements are shown in Table 3.3a and Figure 3.3a (next and following page). Several features are evident.

1) Not all elements exhibit a significant linear correlation with either Fe, Mn or LOI. The only

	Loss-on-ignition				Iron				Manganese				
	Lab	Cont	Ont	Sask	Lab	Cont	Ont	Sask	Lab	Cont	Ont	Sask	
LOI													*LOI*
Fe									*	***	*	*	*Fe*
Mn					*	***	*	*					*Mn*
Zn		–			*	–	–	–				–	*Zn*
Cu		*				–							*Cu*
Pb						**				*			*Pb*
Ni		–											*Ni*
Co					***	***	**	–	**	**		*	*Co*
As						*	–			–			*As*
Mo					–	–		*					*Mo*
Hg	**	**		–		–							*Hg*
Na	(***)	(***)	(**)	(***)		(–)							*Na*
Sb													*Sb*
La		–			*	*	–	*					*La*
W													*W*
Au						–							*Au*

– .30–.40
* .41–.55
** .56–.70
*** >.70

Table 3.3a. Summary of pearson correlation coefficients for Fe, Mn, LOI and selected elements. Data as per Table 3.0a.

relatively strong positive associations are Hg with LOI, and Co and La with Fe and Mn. Arsenic, Mo and Zn exhibit relatively weak associations with Fe while the other elements, Au, W, Cu, Pb, Ni and Sb, show no distinct trend.

2) Some elements show an association in some regions but not in others. Mercury with LOI is a particularly good example. These variables are strongly correlated in the Labrador, Contwoyto Lake and to a lesser extent, Saskatchewan data sets, but not within the Ontario data set.

3) Even for elements that strongly correlate, e.g. Co with Fe, there are many cases where samples with high levels of Fe have only background levels of Co, and vice versa. There would appear to be other significant factors controlling the distribution of Co other than scavenging by Fe and Mn.

Based on these observations it is evident that no anomaly should be rejected out of hand simply because it has a high Fe, Mn or LOI content, as is often done. It is possible that the anomalous element(s) do not correlate with these three variables. And even if they do, the anomalous levels likely represent the sum total of several factors, potentially including nearby mineralization.

Anthropogenic input (man-made contamination) can significantly affect element concentrations in recent lake sediment. Besides obvious sources directly identifiable within the catchment basin (e.g., mining activity, roads, camps, etc.) trace metals can be derived from sources tens or even hundreds of kilometres away through atmospheric deposition. Johnson et al. (1986) determined that in the Turkey Lake area, north of Sault Ste. Marie, Zn, Pb, Cd, and Hg consistently showed enrichment in the upper 5 to 10 cm of lake cores. Surface (~upper 10 cm) to background (below upper 10 cm) concentration ratios averaged 21.4, 2.81, 2.72 and 1.76 for Pb, Cd, Hg and Zn respectively (Figure 3.3b). These increases were interpreted as the result of atmospheric input. Al, Cu, Ni, and Cr showed no significant increase.

Results of a study (Chan et al., 1986) that monitored precipitation and air concentrations of trace metals in Ontario in 1982, suggest that no areas are totally immune from the effects of anthropogenic input. Although there are distinct decreasing gradients from north to south, concentrations of trace metals, including Pb, Zn and Cd, were detected in air and

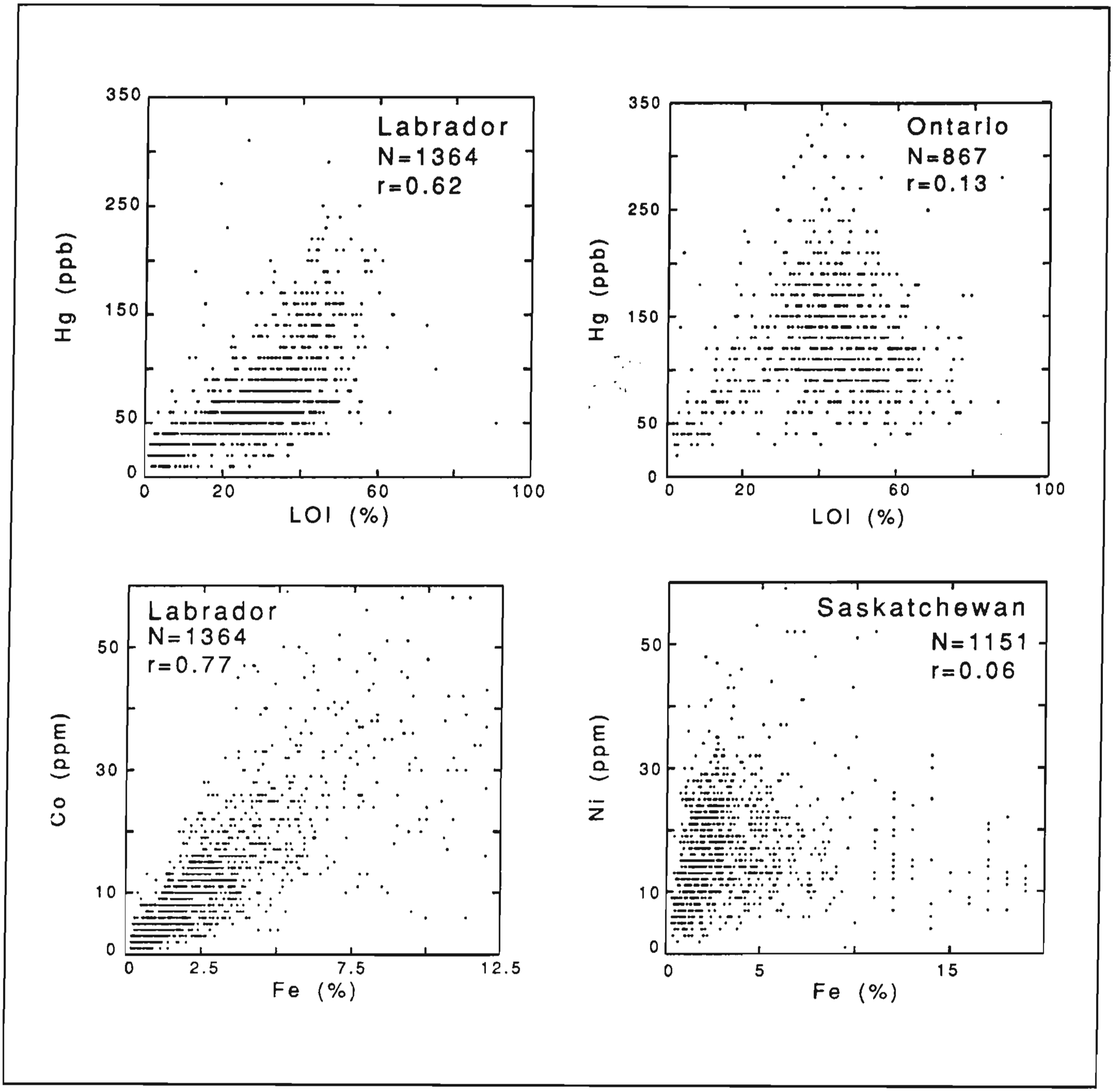
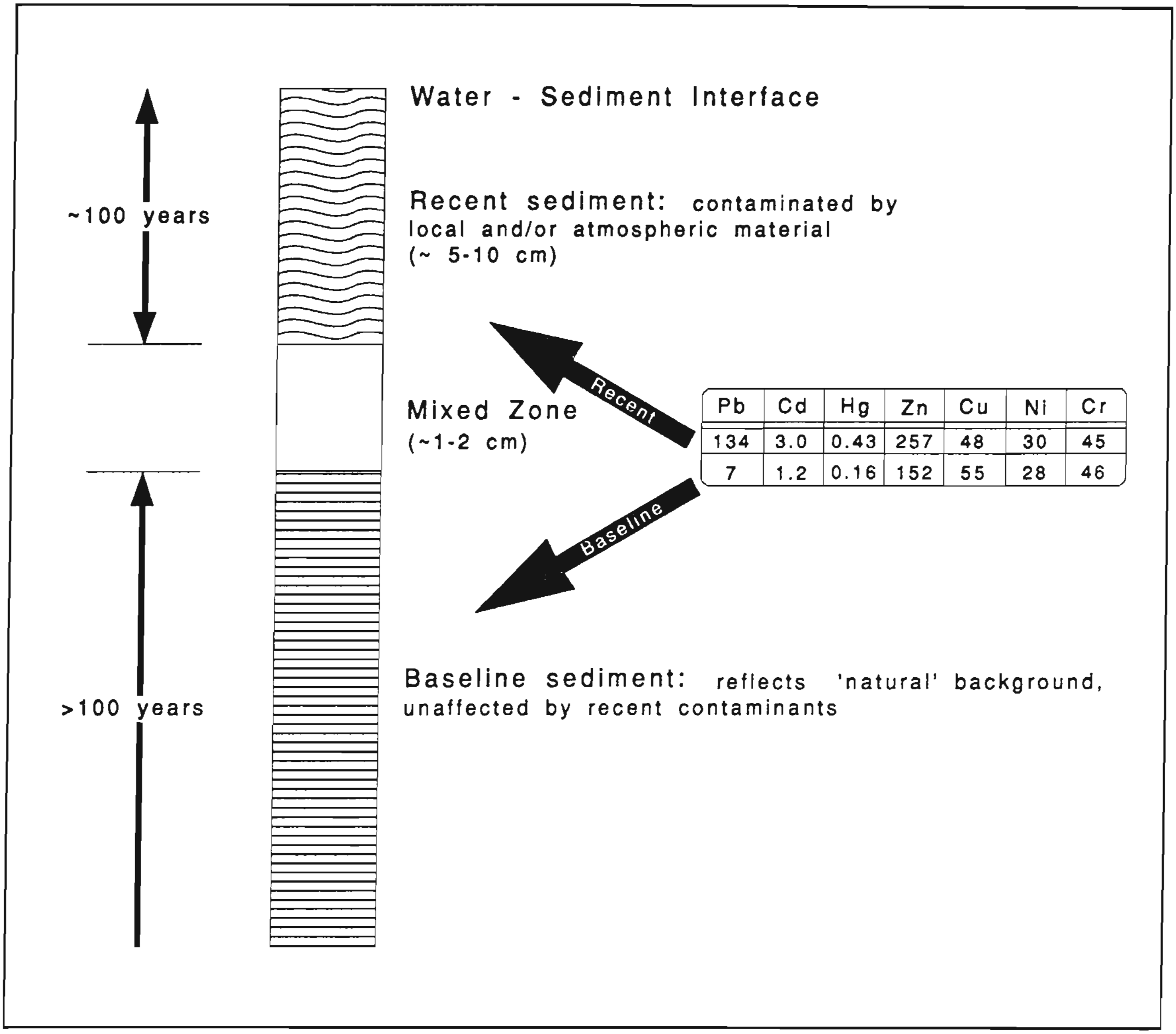


Figure 3.3a. Scatter plots of Fe and LOI with selected trace elements. Plots based on same data set used for Table 3.0a.



Pb	Cd	Hg	Zn	Cu	Ni	Cr
134	3.0	0.43	257	48	30	45
7	1.2	0.16	152	55	28	46

Figure 3.3b. Schematic representation of a typical lake sediment section showing trace element data from Turkey Lake, northwestern Ontario.

precipitation in even the most northern monitoring station (Winisk, Latitude 55°). Therefore during sampling, this contaminated recent portion of the lake sediment column must be excluded from the collected sample (refer to section 2.2.2).

4.0 LAKE SEDIMENTS IN ACTION

4.1 Hemlo, northwestern Ontario

The Hemlo area of northwestern Ontario is one of several areas that the GSC has examined recently as part of a study of precious metals in lake sediment. Figure 4.1a shows Au, Mo, and Sb results for some of the 150 lake sediment samples taken in the Hemlo area. Sediments from Moose Lake, adjacent to the mineralization, are distinctly anomalous in these three elements. The Au concentration of 6 ppb compares to a local background level of <1. Antimony exhibits an even more pronounced response, 8 ppm in Moose Lake compared to a background of <0.2 ppm. The 14 ppb gold value northwest of Moose Lake appears to be a flyer. Subsequent reanalysis failed to repeat the anomaly. A factor that quickly became evident in the Hemlo gold study was the problem of reproducing Au values. This is not only the case for lake sediments but occurs with all geochemical media, and is the result of unique chemical and physical properties of gold, including; common occurrence in native form,

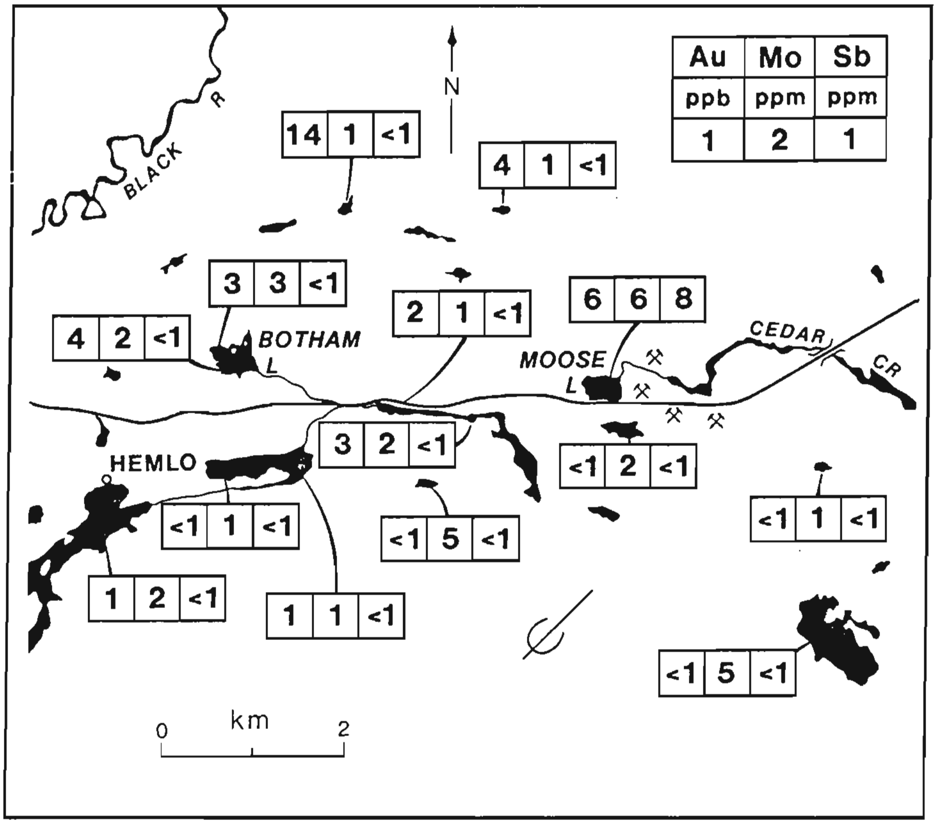


Figure 4.1a. Distribution of Au, Mo and Sb in selected lake sediments from the Hemlo area, northwestern Ontario.

chemical and physical resistance, high specific gravity and low concentration levels (Harris, 1982). These factors result in a particle sparsity effect in which very low concentrations of Au are heterogeneously enriched in the surficial environment. The effect is illustrated in Figure 4.1b, a plot of field duplicate data from 55 Ontario sites (source of data as per Table 3.0a). The Figure also illustrates that most other elements do not suffer this problem. For these reasons interpretation of any gold data should include a close look at commonly associated pathfinder elements (e.g., Sb, W, As, Hg), reanalysis of anomalous samples, and if possible, re-sampling of the site.

The gold reproducibility problem is less pronounced as the organic content of the lake sediment increases. This is illustrated in Figure 4.1c, a generalized plot of 50 replicate Au analyses from the Hemlo study. Of the 22 samples with less than 11% LOI, 5 have replicate Au analyses where the value changed from background to anomalous or vice versa. Between 11 and 20% LOI, 2 changed, compared to LOI levels greater than 20% where no pairs changed. This suggests that high LOI samples are more likely to reproduce their initial Au values, and provide more reliable data than low LOI samples. The increased variability in low LOI samples probably reflects the largely clastic character of the sediment and the greater possibility of containing detrital gold (Hornbrook, 1989). A similar trend was noted by Chapman et al. (1990) in their follow-up of a lake sediment gold anomaly in Saskatchewan, that led to the recent discovery of the Bakos Deposit.

4.2 Contwoyto Lake, N.W.T.

A detailed lake sediment survey was recently carried out by the GSC in the Lupin gold mine area of Contwoyto Lake, N.W.T. The purpose was to evaluate this exploration technique for gold mineralization in a tundra environment. Some of the data is summarized in Table 3.0a and Figure 4.2a. Lakes in the immediate Lupin Mine area and down-drainage from the tailings pond were not sampled.

Figure 4.2a shows that the Lupin gold mine and other gold occurrences are clearly identified. The anomalies are displaced up to several kilometres in a down-ice direction (to the northwest), reflecting the transport of mineralized material. Associated pathfinders, notably W, Br, As, Sb and Cu, reinforce the gold distribution patterns and would be useful in defining the gold potential of the area.

To establish the reliability of the initial gold data, considering the possible adverse impact of the nugget effect, gold determinations were repeated twice more on different aliquots. Figure 4.2a shows that there is a distinct clustering, in the area of the Lupin Mine, of samples that repeated their anomalous gold values; 11 of 16 samples where the gold analyses were anomalous 2 of 3 times, 3 of the 7 samples where all 3 analyses were

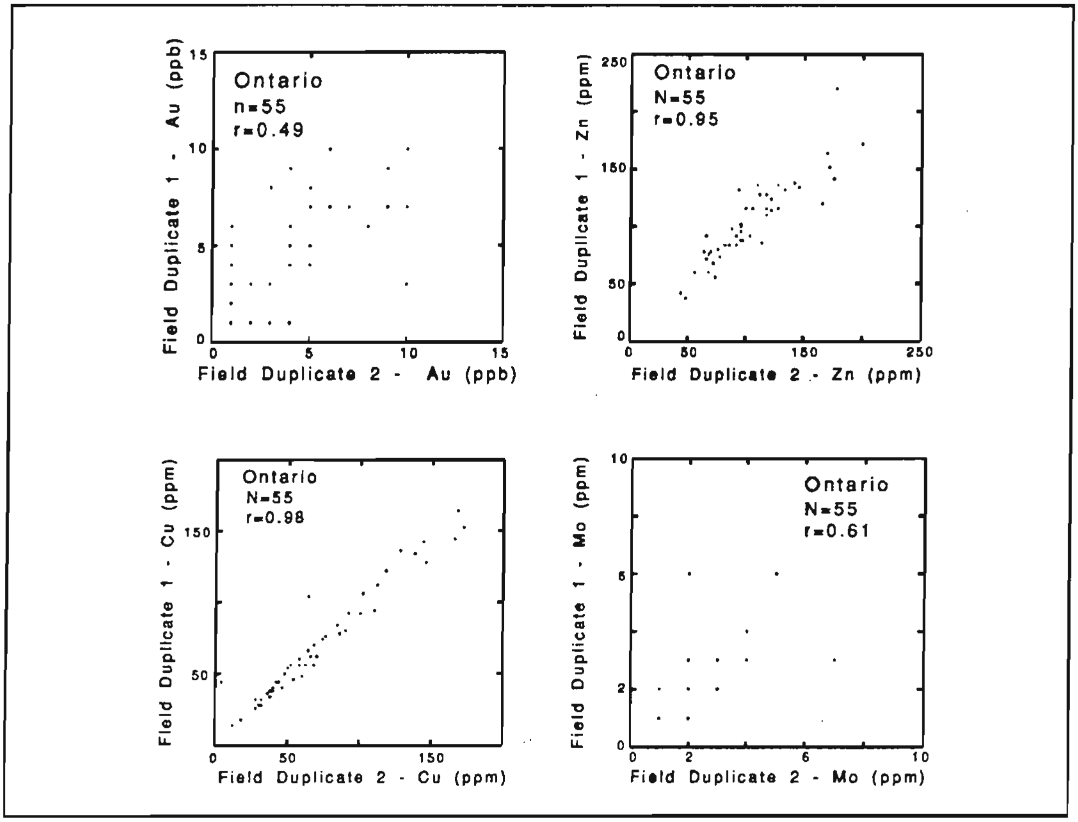
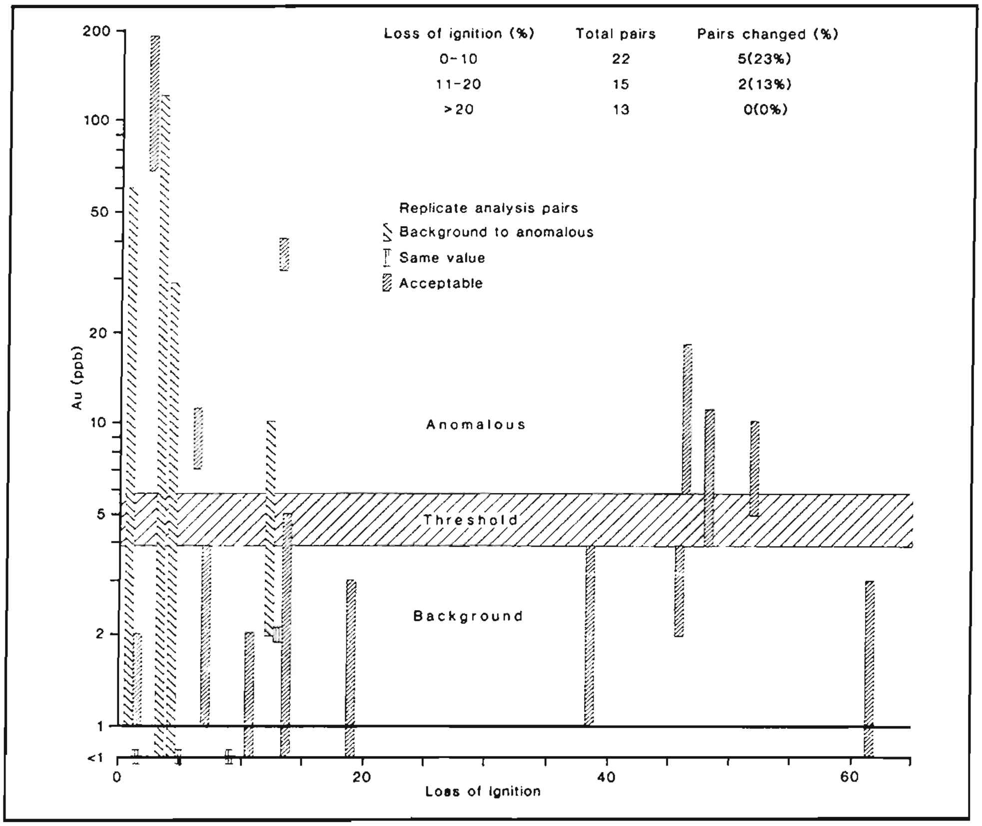


Figure 4.1b. Scatter plots of Au, Cu, Zn and Mo data from 55 Ontario field duplicate sites. Plots based on same data set used for Table 3.0a.



Loss of ignition (%)	Total pairs	Pairs changed (%)
0-10	22	5(23%)
11-20	15	2(13%)
>20	13	0(0%)

Figure 4.1c. Replicate gold data from 50 lake sediment samples from northwestern Ontario.

anomalous. Comparison of contour plots of the three individual gold data sets indicated that the regional anomalous patterns did not change significantly from one data set to the next.

As a test, to obtain more reliable gold data, several samples were ashed at 450°C and analyzed by an INA method. It was hoped that ashing would produce more reliable gold data because 1) ashing would increase the concentration of gold in the ash and 2) the ash would have a higher specific gravity resulting in greater sample weight being encapsulated and used for the analysis. Preliminary observations include:

1) Some elements, e.g., Na, Th and Sm increased their concentration in the ashed material (on average) by a factor of ~1.15 compared to the unashed material. This concentration factor is consistent with the average loss-on-ignition (LOI) of 15% for the samples (Table 3.0a).

2) Some elements, notably Br, showed a marked decrease in concentration in the ashed material, by as much as 80%.

3) There is a loss of gold from some samples during ashing. For example, the gold content in ash for one standard (LS05) was consistently about 8 ppb compared to 10 ppb in the unashed samples. This occurred despite a LOI content of ~45%. Overall gold losses were not consistent, varying from nil to almost 50% as in the case of standard LS05.

These and other observations suggest that ashing of lake sediment should not be undertaken (as is often done in vegetation and humus surveys) to pre-concentrate trace elements.

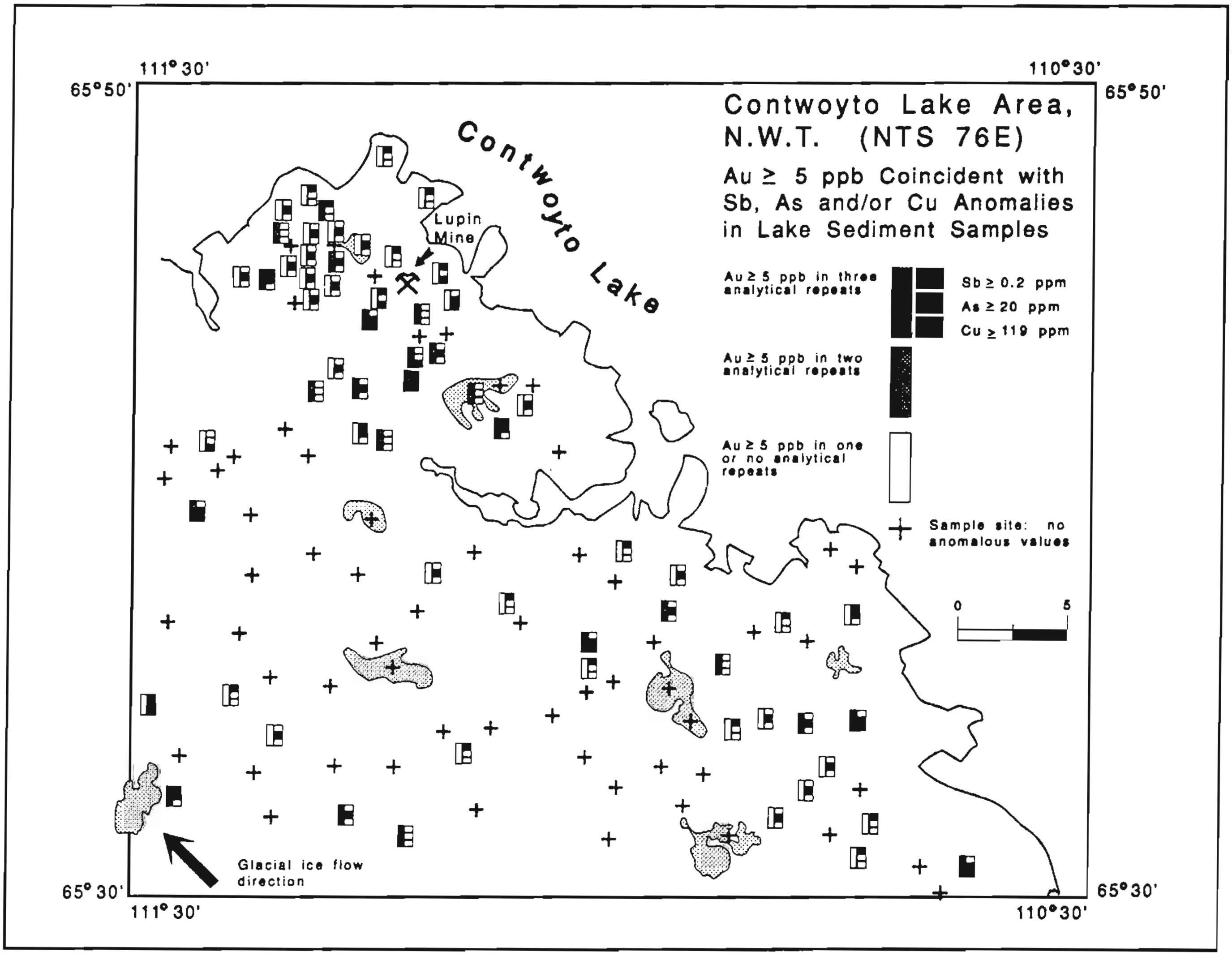


Figure 4.2a. Au, Sb, As and Cu distribution in lake sediment samples from the Contwoyto Lake area, N.W.T.

4.3 Strange Lake, Labrador

The Strange Lake area of northwestern Labrador hosts a large deposit of Y-Zr-Be-Nb-REE mineralization within a peralkaline granite. The initial discovery was made in 1979 by the Iron Ore Company of Canada during a follow-up of a lake sediment and water anomaly outlined by a Canada-Newfoundland Uranium Reconnaissance Program Open File release (Geological Survey of Canada, 1979). The Open File data defines a 40 km Pb dispersion train in the lake sediment and 25 km F train in the lake water, in a down-ice direction from the mineralization.

Subsequent follow-up work (McConnell and Batterson, 1987; McConnell, 1988) involved detailed sampling of till, stream and lake sediment, and water. Samples were analyzed by a variety of techniques including ICP and INA methods resulting in a much wider range of elemental data than in the original GSC Open File. The presence of strong linear anomalies were defined in all media, extending up to forty kilometres down-ice from the deposit. The lake sediments provided the broadest anomalies, followed by streams and then tills. Elements that were particularly enriched in lake sediment and defined distinct down ice dispersion patterns included: REEs (Figure 4.3a), Be, Pb, Th, Y and Zr. The heavier REEs provided more distinct dispersal patterns relative to the light ones.

Element associations, as defined by a correlation matrix for the Strange Lake data set, exhibit some characteristics similar to that defined by Table 3.3a and discussed earlier (refer to section 3.3). The strongest association is a negative correlation between Na and LOI. To a lesser extent Rb, Ba, Nb and Zr and other elements are similarly affected. Fe and Mn exert relatively little control on the distribution of elements, with the strongest

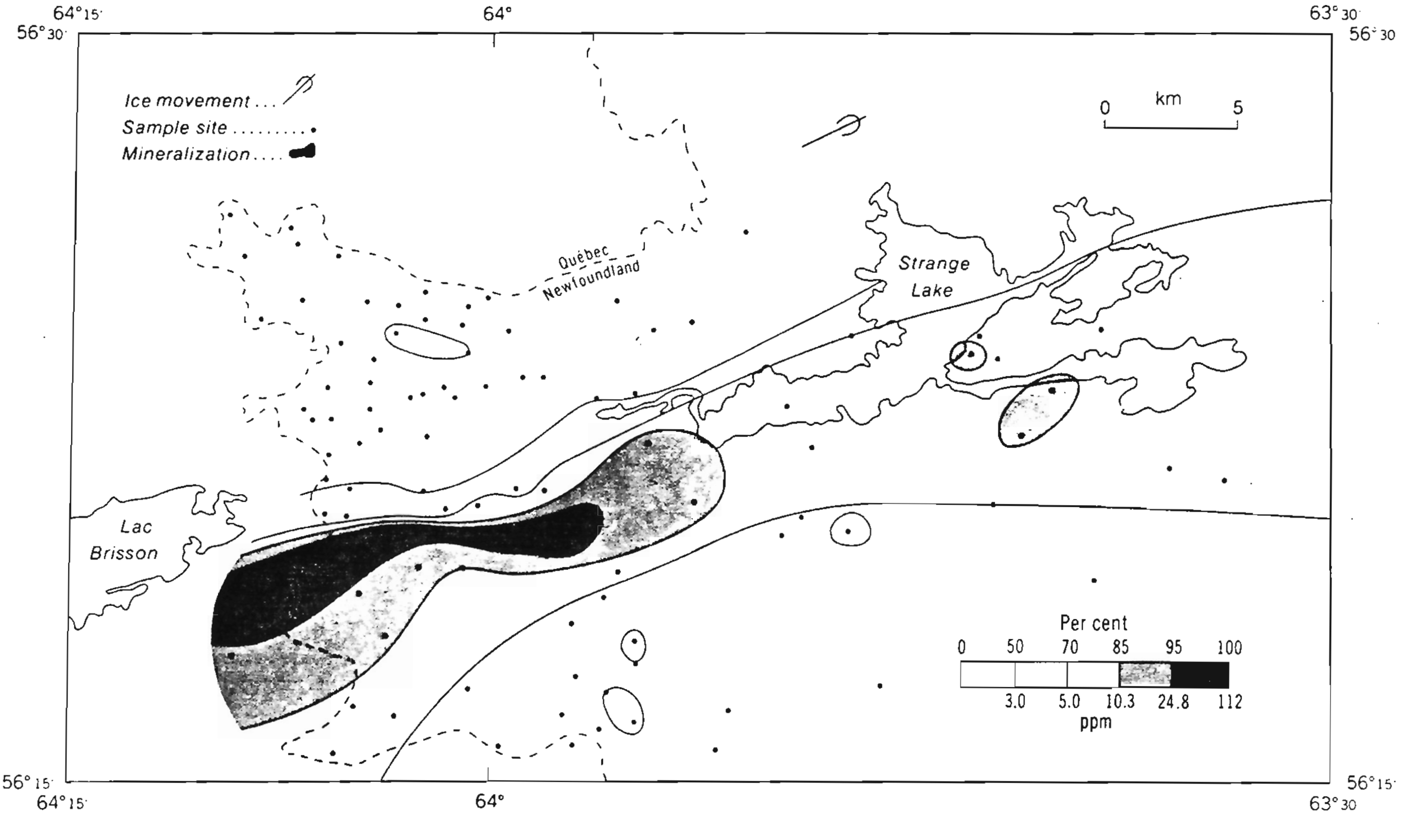


Figure 4.3a. Distribution of Yb in lake sediment, Strange Lake area, Labrador (modified after Hornbrook, 1989).

correlations occurring with Co, Cs, F and Li. Arsenic, Cd, Ce, Eu, Mo, Ni, Pb, Y, Yb and others show little or no correlation with Fe, Mn or LOI.

4.4 East Kemptville, Nova Scotia

The East Kemptville Sn deposit in southern Nova Scotia was discovered in 1978 by Shell Canada Resources, Limited. The deposit consists of Sn mineralization with traces of W and lesser Zn and Cu, located in a greisen zone along the contact between granitoid rocks of the Davis Lake complex and metasediment of the Meguma Group.

A government funded lake sediment survey covered the area in the late seventies but samples were only analyzed for a restricted suite of elements. Subsequently, a number of samples were reanalysed (Rogers and Garrett, 1987) for a broader spectrum of elements, including Sn, W, Au, and U. The data defined a radial pattern of anomalous Sn values in lake sediments, southwest to southeast of the deposit (Figure 4.4a) and a similar but weaker W pattern. The radial pattern is interpreted as having been caused by a combination of topography, relief, and the polyphase glacial history of the area.

Rogers and Garrett (1987) also describe the presence of angular and discrete grains of cassiterite (besides numerous zircon, monazite, and magnetite grains) in a bulk sample collected from Moosefly Lake. They noted that the cassiterite grains exhibited a lack of abrasion. This along with the fact that the Sn data showed no correlation with organic material or other elements suggests that the regional tin anomaly is due in large part to the mechanical dispersion of cassiterite from the tills to the lake.

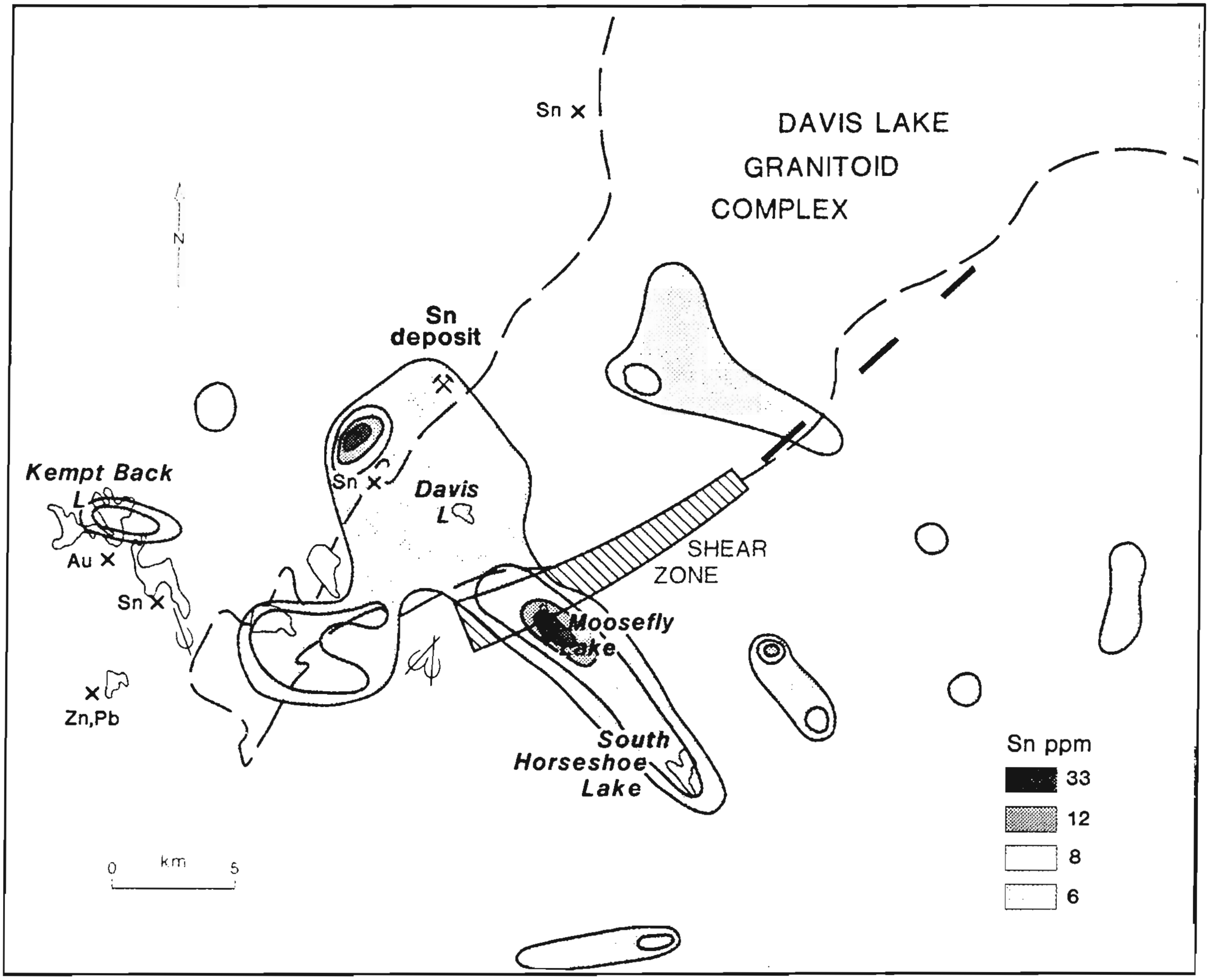


Figure 4.4a. Distribution of Sn in lake sediments, East Kemptville area, Nova Scotia (modified after Hornbrook).

5.0 SOURCES OF LAKE SEDIMENT SURVEY DATA

There exists a wealth of publicly available regional lake sediment data in Canada (Figure 1.0a). Much of it has been collected as part of the GSC's National Geochemical Reconnaissance (NGR) program.

Since the early seventies NGR lake sediment surveys have been undertaken by the Geological Survey of Canada, by the Provinces or jointly under various agreements. To date total coverage is about 1.2 million km^2, representing ~97 000 sites. Sample density varies from 1 sample per 2 km^2 to 1 per 13 km^2, with most of the coverage at the lower density.

These data are available as Open File reports published by the GSC and/or equivalent Provincial Ministry or Department. The data are also available in digital form. A recently released GSC brochure describes the NGR coverage and lists about 135 separate surveys (lakes and streams) available on floppy disks. Digital Nova Scotia data are available through Peter Rogers (Manager, Geochemistry and Quaternary Section, Nova Scotia Department of Mines and Energy). For the Island of Newfoundland all digital data are available through Peter Davenport (Senior Geochemist, Newfoundland Department of Mines and Energy).

In Quebec, available regional lake sediment coverage (Figure 1.0a) includes:

1) Surveys undertaken by the Provincial Ministry (MER) since 1983, generally at a density of 1/13 km^2.

2) Sociétés de Dévelopement de la Baie James (SDBJ) surveys undertaken in 1973 and 1974 at a sample density of 1/7 km^2.

3) SOQUEM's 1976 and 1977 surveys at an average sample density of 1/2 km^2.

All this Quebec data, and more, are available on paper or in digital form. Further information can be obtained from Marc Beaumier, Geochemist, Ministère de l'Énergie et des Ressources.

Besides regional data, Provincial and Federal agencies are making available infill/orientation survey data. These are more limited in aerial extent than the regional surveys, but tend to have a higher sample density. For example John Fortescue (Research Geochemist, Ontario Geological Survey) is in the process of releasing a series of 'broad sheets' (e.g., Fortescue and Vida, 1990) that summarize the results of infill surveys covering the entire Batchawana greenstone belt in northwestern Ontario. Sample density is in the order of 1/1.3 km^2.

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PAPER #5

THE USE OF THE HEAVY MINERAL FRACTION OF STREAM ALLUVIUM: APPLICATION TO LOW-ENERGY GLACIATED ENVIRONMENTS IN EASTERN CANADA

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Abstract

In 1984 the Geological Survey of Canada initiated a regional geochemical mapping project in the Eastern Townships of southern Quebec with the prime objective to produce an alluvial gold distribution map for the region. The sampling method employed was based on the collection of heavy mineral concentrates from large volumes of stream alluvium. The concentrates were analyzed for gold and about forty other elements providing a wide range of data useful in mineral exploration and for bedrock and Quaternary mapping.

This paper examines the pros and cons and the limitations of the heavy mineral approach to geochemical mapping and exploration. It compares heavy minerals with regular stream sediments, which represent an alternative method that could have been used in this project. Guidelines are provided for interpreting heavy mineral data with special attention placed on the significance of absolute concentrations.

Résumé

En 1984, la Commission géologique du Canada entreprenait un projet de cartographie géochimique dans la région de l'Estrie-Beauce au Québec. Le but principal de ce projet était de produire une carte de la répartition de l'or alluvionnaire dans la région. La méthode d'échantillonnage était fondée sur la cueillette de concentrés de minéraux lourds à partir de gros volumes d'alluvions. Les minéraux lourds ont été analysés pour l'or et une quarantaine d'autres éléments ce qui a fourni une gamme de données pouvant servir à l'exploration ainsi qu'à la cartographie des roches et des dépôts Quaternaires.

Le présent document examine le pour et le contre ainsi que les limites de la méthode basée sur les minéraux lourds comme outil de prospection et de cartographie géochimique. On compare les minéraux lourds avec les sédiments de ruisseaux ordinaires, lesquels représentent une alternative que l'on aurait pu utiliser dans ce projet. On présente des directives pour interpréter les résultats d'analyse de minéraux lourds en se penchant particulièrement sur la signification des valeurs absolues.

INTRODUCTION

Heavy minerals can be extracted from different materials and then used for geochemical exploration. We can pan soils, glacial overburden of all kinds, stream alluvium, rocks, marine sediments, beach deposits, etc. Even material that is very fine such as lacustrine clay, which is made up largely of rock powder, has a heavy mineral component. It can be separated, perhaps not easily by panning, but by using other techniques such as a combination of heavy liquids and centrifuge.

In this part of the short course, we will examine why one should choose to sample and analyze heavy mineral concentrates (HMCs) when it is considerably easier and less costly to collect other types of materials such as stream sediments or soils. Under what circumstances should HMCs be collected? What are the advantages and the limitations of this approach?

Before we dwell on these questions, we will examine the rationale that led to the HMC survey in the Quebec Appalachians, conducted by the Geological Survey of Canada in middle and late 1980s.

BACKGROUND

In the early 1830s, gold was discovered in a small creek in the Beauce region, just south of Quebec City. This led to one of the first gold rushes of North America which lasted intermittently until the Klondike at the end of the century. The last placer operation in southern Quebec ended in 1964 and it is estimated that about 4 tonnes of placer gold were extracted from the region.

Over the years, the widespread occurrence of alluvial gold in southern Quebec attracted the interest of many geologists. Most reported on the small-scale mining operations that flourished until the 1920's, but no comprehensive study of the phenomenon was ever carried out. This lack of basic knowledge, combined with a growing interest in gold exploration in the 1980s, is what instigated GSC to undertake a research project on placer gold in Quebec's Eastern Townships.

The primary goal of the project was to produce a map which would show the distribution of gold in modern alluvium. It was hoped that such a map would reveal patterns that could lead not only to exploration targets for concealed economic deposits, but also to a better understanding of the genesis of the alluvial gold in the region.

With these specific objectives in mind, it was thought that HMCs systematically extracted from large volumes of stream alluvium would constitute a very good sample medium. Sample collection was carried out during four field seasons, 1984, 1985, 1987 and 1989 (see the general location map in the Appendix). Sampling in the field was carried out using a portable suction dredge and the HMCs were analyzed for about 40 elements by a variety of techniques including neutron activation, atomic absorption, XRF, and others (see Maurice 1988, for a description of the sampling and analytical procedures).

In 1984 and 1989, regular stream sediments were collected in addition to the HMCs at the same sites, allowing comparisons in the geochemical response of both media. The 1984 stream sediments, however, were analyzed only for gold, but there are plans to reanalyze them for some of the other elements in the near future. The 1989 HMCs and stream sediments were analyzed for the same elements except Ti, Nb, Sn, Sr and Y (the XRF suite), S, and Pt and Pd, which were not analyzed in the stream sediments.

The HMC survey described here follows the work by W.W. Shilts of the Geological Survey of Canada who, during the last two decades, conducted an exhaustive study of the region's Quaternary geology including extensive work on the geochemistry of the glacial deposits. The wealth of information contained in Shilts' reports have proven invaluable in interpreting the HMC survey data because, as it will become obvious in this report, the glacial processes that have acted upon the region are largely responsible for the present geochemical landscape.

GOLD DISTRIBUTION

Figure 1 is a compilation showing the distribution of gold in modern alluvium in the area covered by the four surveys. It was produced from approximately 1600 HMC gold analyses at a site density of one per 10-12 km^2. The map also shows the location of stream placer drainages that have been worked or at least were known to contain alluvial gold from the historical records (Boyle, 1979). At the majority of these sites, alluvial gold was found on the beds of existing (modern, postglacial) streams but the richest paystreaks were mined in Tertiary placers buried in paleochannels tens of metres beneath the Quaternary cover.

There is generally a good correlation between the known (historical) alluvial gold occurrences and HMC gold anomalies, although the gold anomalies tend to occupy a much wider proportion of the land than do the known auriferous stream segments. This supports the common belief among Eastern Township geologists and many area residents that *"it is difficult to find a stream in the area that has no gold at all"*. In fact, in our survey, 48% of the HMCs had over 1 ppm Au and at many of these sites, native gold particles were seen in the concentrate during their preparation (i.e. with minimal searching).

The gold distribution as shown on figure 1 appears to reflect widely scattered sources throughout the region combined with a thorough redistribution of the metal by glaciation. Auriferous regoliths and paleoplacers probably covered most of the source areas prior to glaciation.

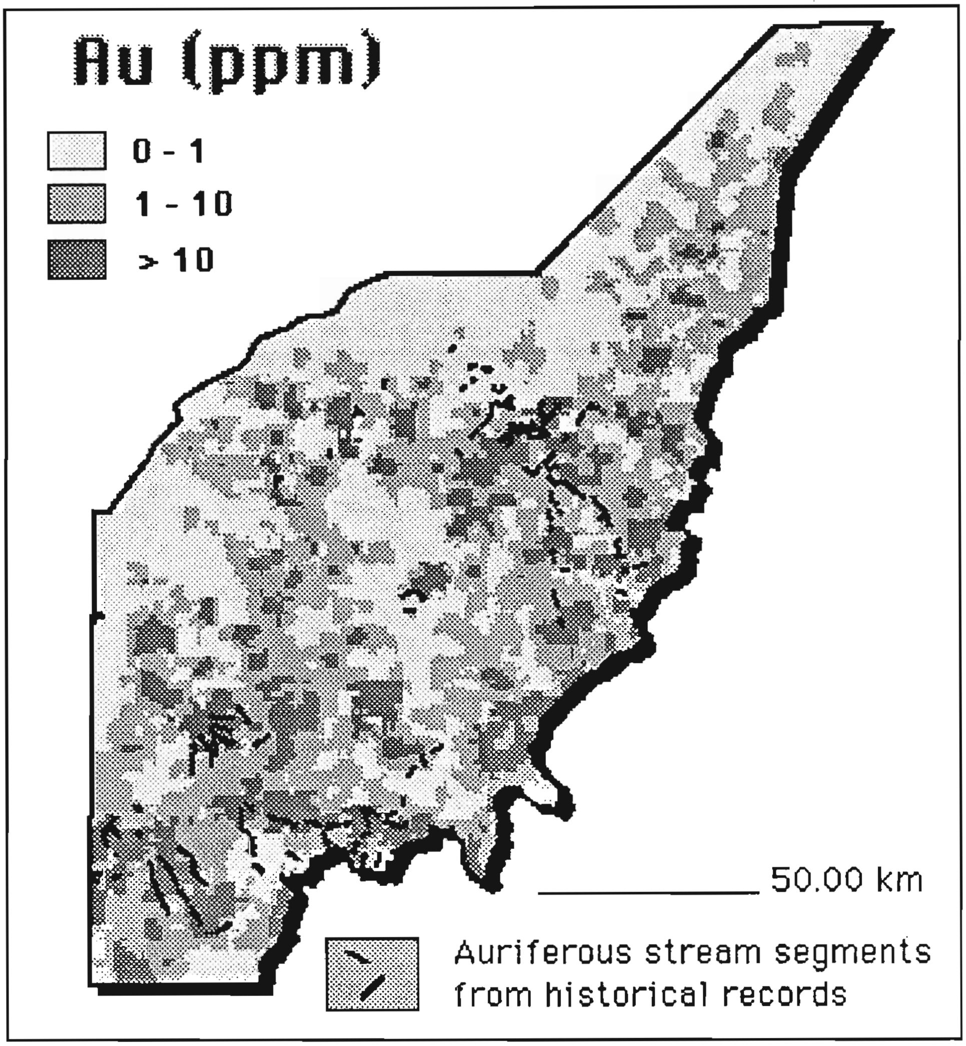

Figure 1 Gold distribution in southern Quebec from alluvial heavy mineral survey and location of known auriferous stream segments from historical records

In most instances, the source rocks are thought to have been simply sedimentary and volcanic rock units with abundant pyrite containing several hundred ppb (up to a few ppm) Au. In some rarer cases, gold-bearing mineral deposits have been identified as the likely source of the alluvial gold. Figure 2 shows an example where gold anomalies occur down-ice from a group of auriferous sulphide deposits in the Sherbrooke-Coaticook area. Associated elements in the deposits, Cu and Ag, also form dispersal trains that coincide with the gold anomalies. It is interesting to note that alluvial gold has long been known to occur in Moe River but until this survey was carried out, everyone who had spent any time studying the question believed the source to lie to the south-east of the anomalies (up-drainage) rather than to the north-west (up-ice) as the geochemical pattern suggests. One observation that strongly supports a glacial rather than alluvial origin for these anomalies is that not only the main channels of the Moe, Coaticook and Ascot rivers are enriched in gold, but also their tributaries which points to the glacial till as the source of gold.

HEAVY MINERALS VERSUS REGULAR STREAM SEDIMENTS

The concentration factor

Would the dispersal patterns, shown in figures 1 and 2, be recognizable in regular stream sediments data? Figure 3a, depicts the gold distribution in -100µm stream sediments in the 1984 survey area. It shows

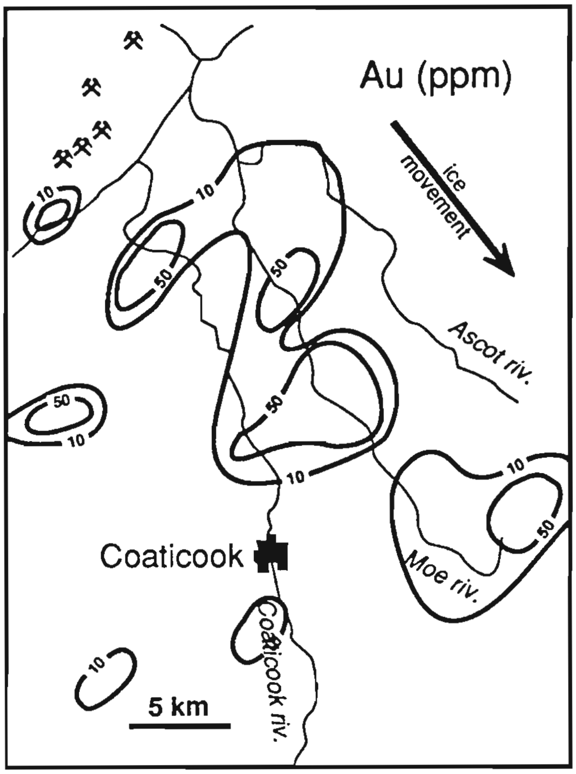

Figure 2a *Gold distribution in alluvial heavy mineral concentrates, Sherbrooke-Coaticook area (Eastern Townships), Quebec (see location map in Appendix)*

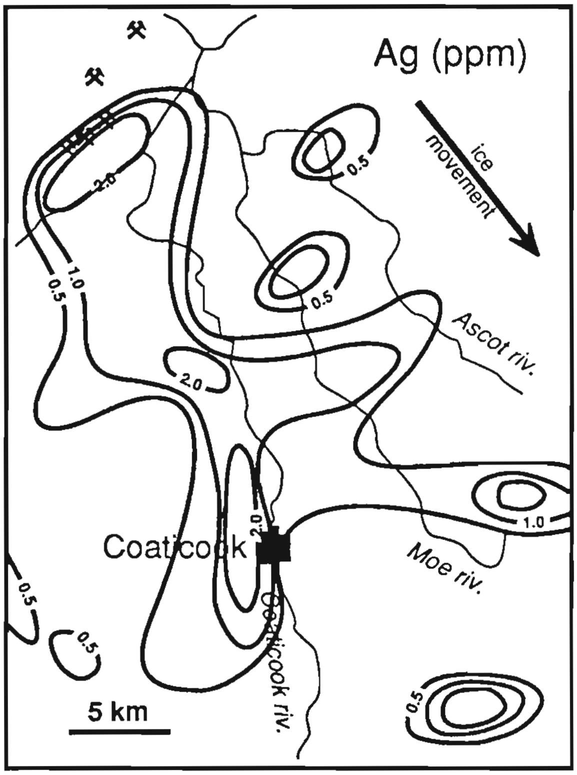

Figure 2b *Silver distribution in alluvial heavy mineral concentrates, Sherbrooke-Coaticook area (Eastern Townships), Quebec (see location map in Appendix)*

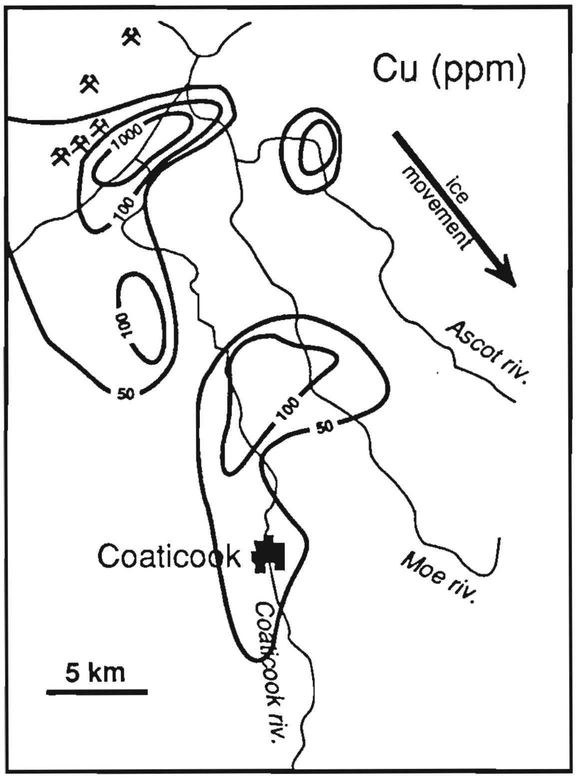

Figure 2c *Copper distribution in alluvial heavy mineral concentrates, Sherbrooke-Coaticook area (Eastern Townships), Quebec (see location map in Appendix)*

punctual anomalies but few interpretable patterns. This is hardly surprizing since about 82% of the stream sediment values are below the analytical detection limit of 5 ppb Au (compared to only 14% for the HMCs). Furthermore, with a HMC median of 1.34 ppm Au, gold is of the order of 500 to 1000 times more concentrated in the HMCs than in the stream sediments (depending on what value we assign to the median in the stream sediments).

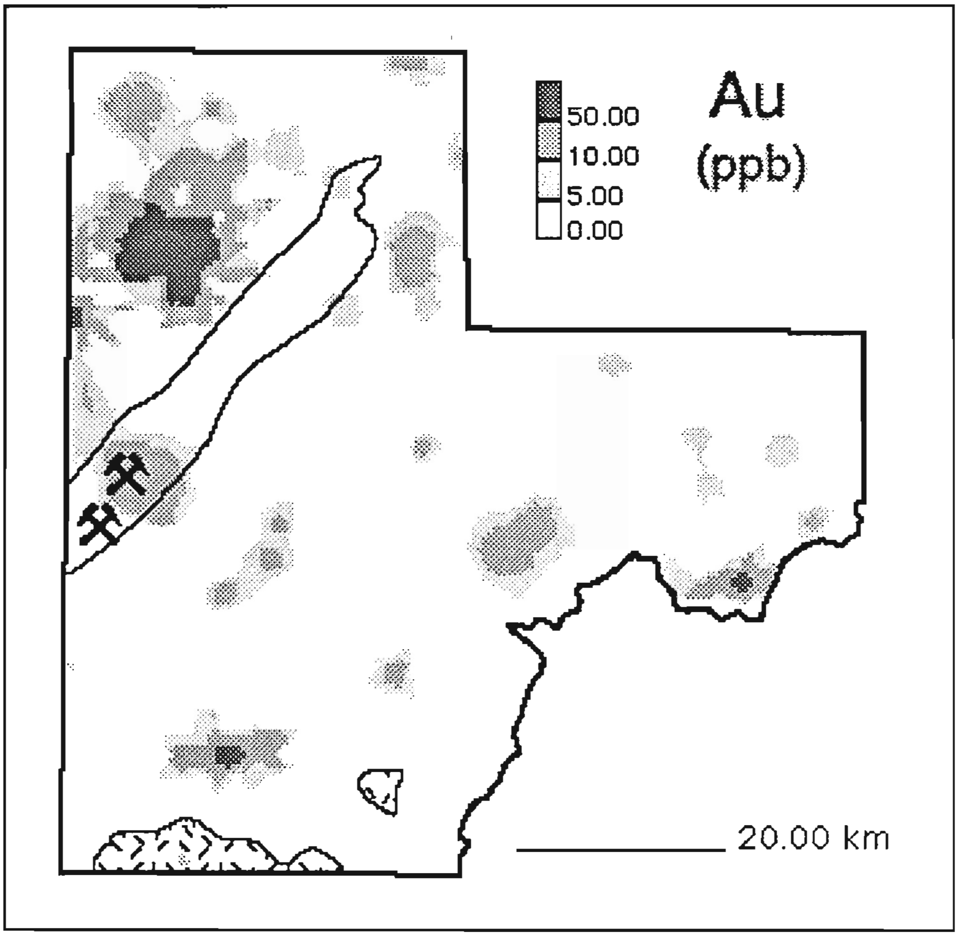

Figure 3a Gold in regular stream sediments, 1984 survey area

For comparison, the gold distribution in the HMCs is shown at the same scale for the same area in figure 3b. Note that the peaks of the anomalies for the two distributions do not generally coincide. In fact, the strong stream sediment anomaly in the northwestern part of the area does not have an equivalent HMC anomaly. This may be very significant because the stream sediment anomaly, which involves four sample sites, could reflect very fine gold, too fine for the HMC technique.

Therefore, one major difference between using heavy minerals and other more conventional sample media may be stated as follows:

Because of the concentration factor, HMCs result in a substantial improvement in our ability to detect the elements that make up the heavy mineral suite;
this allows:

- **better detection of rare elements, particularly precious metals (gold and PGEs)**
- **more revealing patterns**

The amount of improvement is a function of the concentration factor, or the proportion of heavies in the original sample medium. This varies not only from area to area, depending on the mineralogical composition of this medium, but it is affected also by the method used for separating the heavies because this determines which type of heavy minerals end up in the concentrates. For example, if the separation method allows lower density heavy minerals, such as pyroxenes and amphiboles, to be extracted and included in the concentrates, these will dilute the heavier minerals and may reduce their concentration significantly, thus reducing the advantages of using HMCs.

In southern Quebec, a few measurements have shown that the heavy fraction (d ≥ 3.6) represents from about 0.1% to about 2% of the alluvium by weight. This translates into improvements in detection of 50 to 1000 times.

This is useful for two reasons:

1. It allows us to detect elements that are almost always too "low" to be detected in unprocessed samples. Gold and the PGEs are obvious examples, but other elements including Ag, W, Sn and several REE also fall in this category; and,
2. For many elements, it increases substantially the number of samples above the anomaly threshold so that the patterns that emerge contain more detail, which makes interpretation easier.

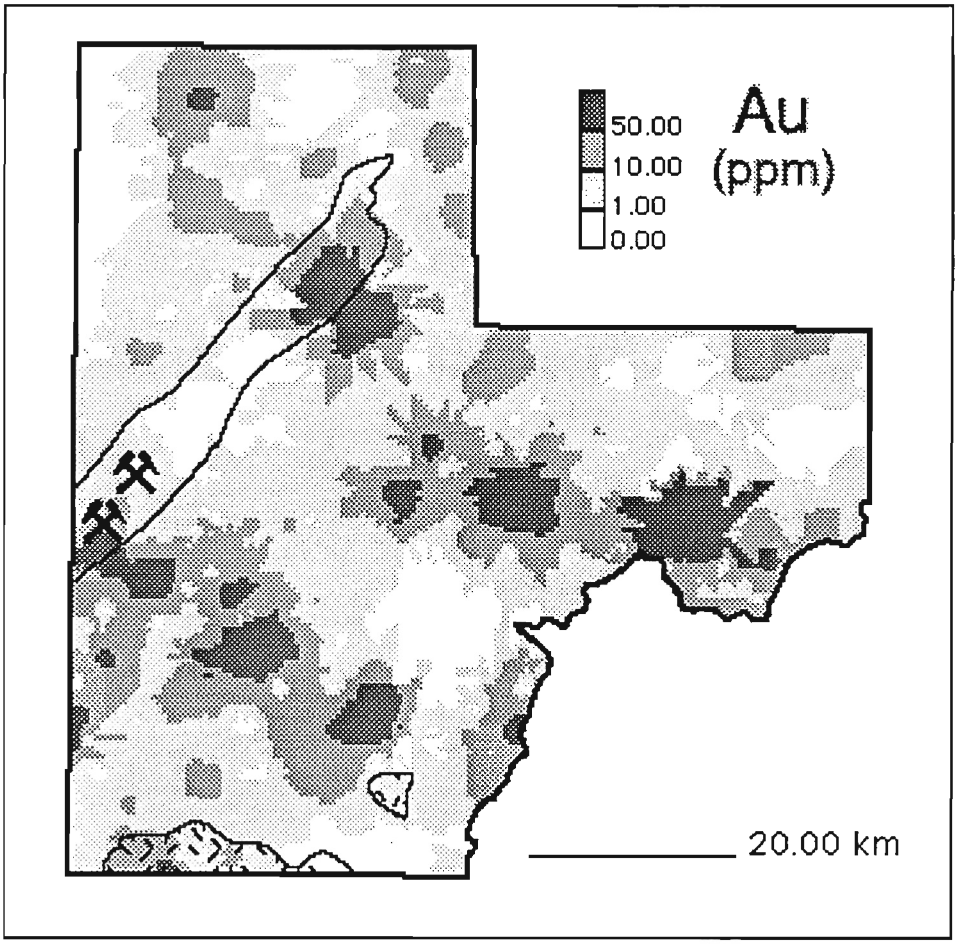

Figure 3b Gold in heavy mineral concentrates, 1984 survey area

This last point is illustrated in figure 4 which depicts the distribution of tungsten in the center of the survey area, dominated by a group of Devonian granite intrusions.

The map shows a series of

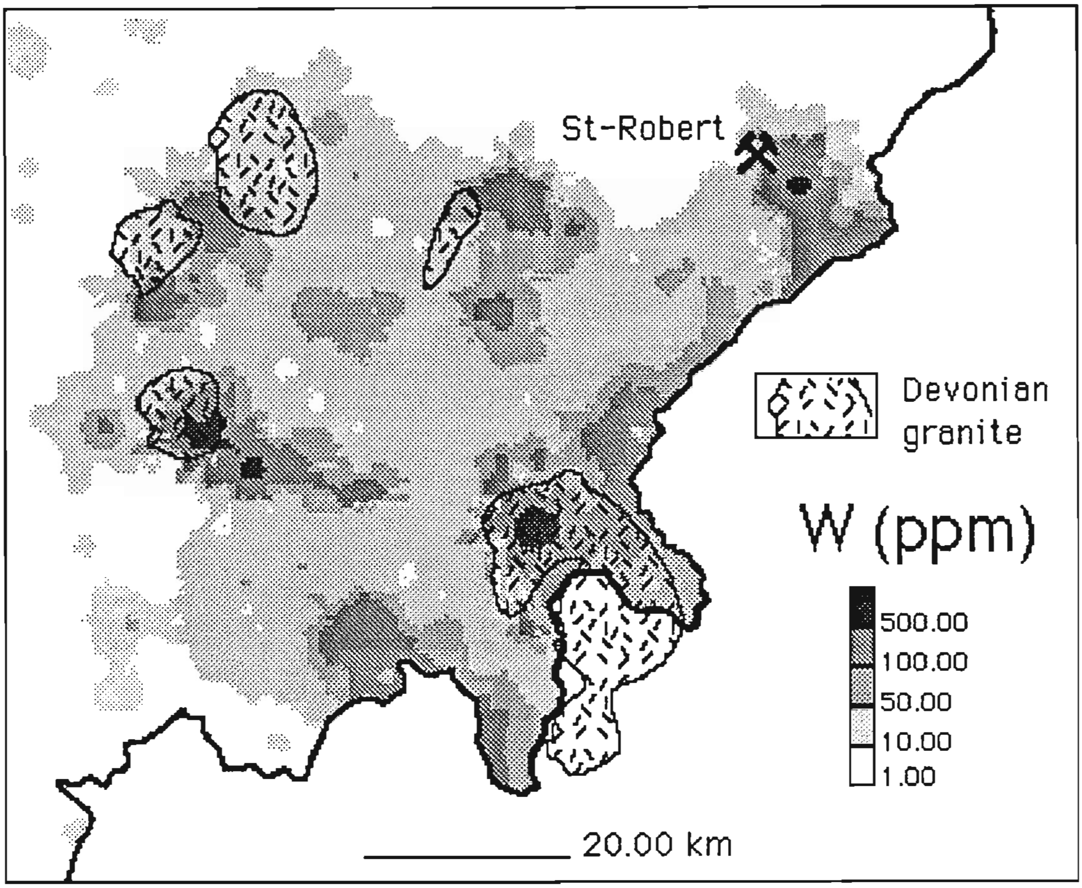

Figure 4 *Glacial dispersal illustrated by the tungsten distribution in alluvial heavy minerals in parts of the Eastern Townships, Quebec (see location map in the Appendix)*

well-developed glacial dispersal trains originating from the intrusive bodies or known tungsten mineralization (i.e. St-Robert). Although some of the tungsten peaks that reach several thousand ppm would probably generate anomalies in unprocessed stream sediments, the amount of detail provided by the heavy mineral data is without doubt superior.

All this is very useful, not only for mineral exploration but also in the study of the glacial history of the area. The amount of new information on glacial processes that was extracted from these data is remarkable.

Overcoming the "nugget effect"

Figure 5 shows the chromium distribution in the central part of the region and data for three PGEs: Pt, Pd, and Ir. The most prominent features are the massive chromium dispersal trains originating from two bodies of ultrabasic rocks, one near Thetford Mines (#1 on figure 5) and another, smaller, near St-Joseph-de-Beauce (#2). Both trains were previously mapped in detail by W.W. Shilts (Rencz and Shilts, 1980) using chemical analyses of the fine fraction of glacial till.

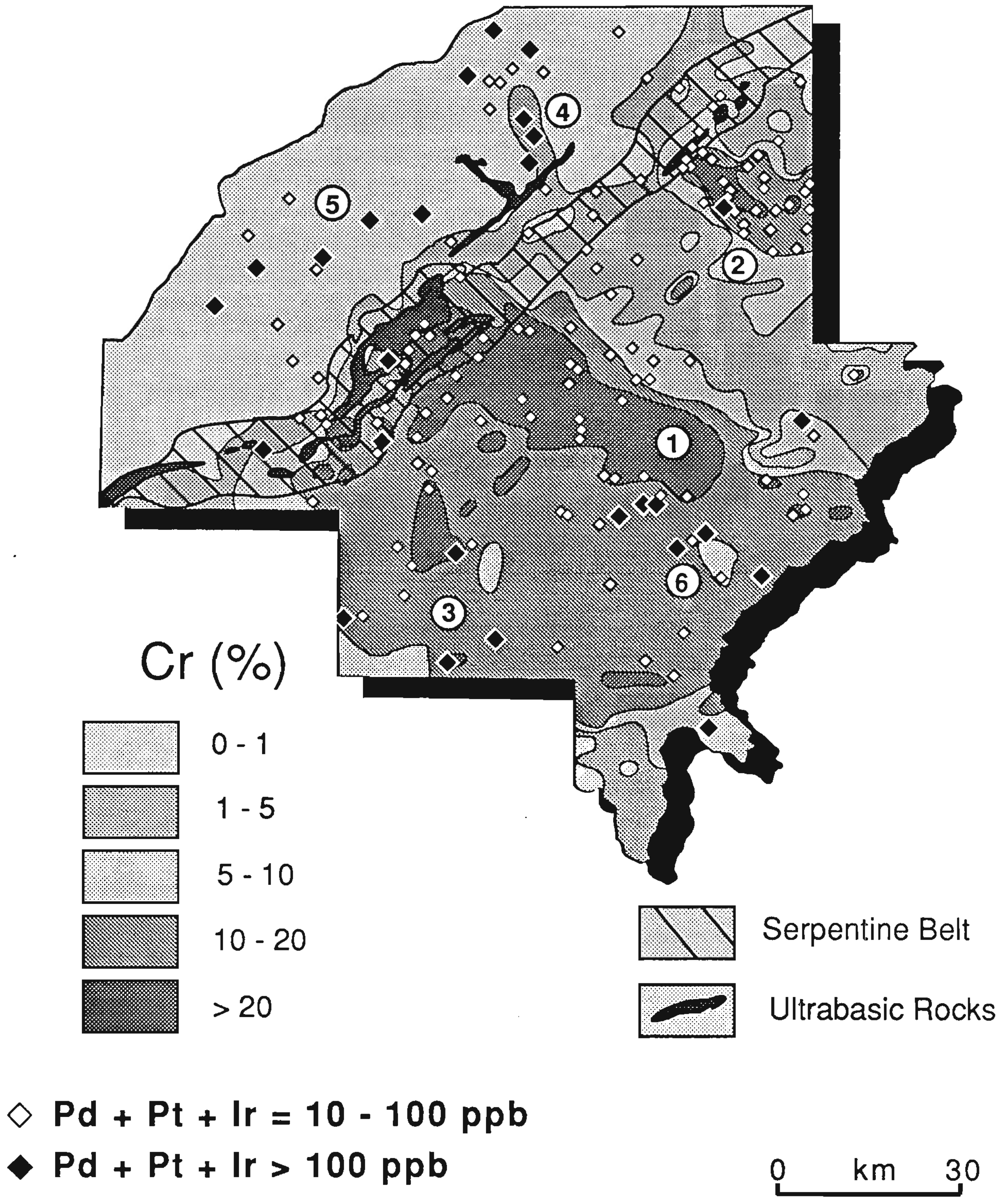

Figure 5 Chromium and PGE distribution in alluvial heavy minerals, 1985 and 1987 survey areas, Eastern Townships, Quebec (see location map in Appendix)

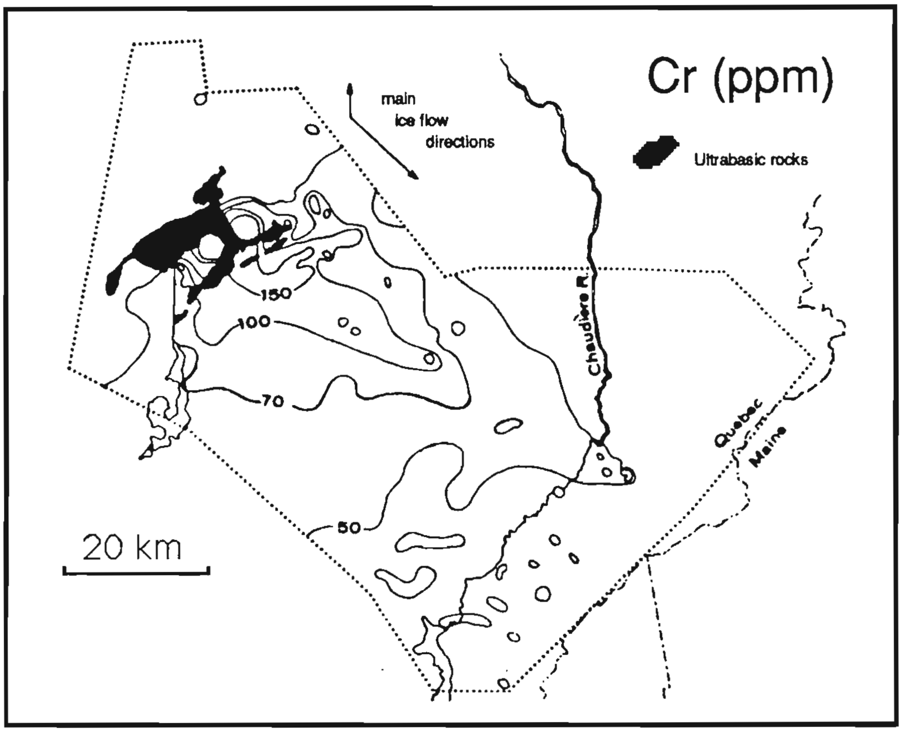

Figure 6 Chromium distribution in the silt and clay size fractions (≤63 µm) in glacial till, Eastern Townships Quebec (from Rencz and Shilts, 1980)

Note the similarity between the pattern obtained by Rencz and Shilts, 1980 (figure 6) and the one produced from the alluvial heavy mineral data (figure 5). The chromium ratio between the two surveys is about 2000 to 3000. This is much higher than the 500-1000 concentration factor discussed above, but it is probably related to the fact that the -63µm fraction used by Rencz and Shilts (1980) is likely to be depleted in chromite, which occurs mostly as coarse to medium sand-size grains in the source rocks.

The distribution of PGEs follows to a large extent that of chromium. In fact, the PGEs in the two main chromium dispersal trains probably reside in the chromite grains themselves. It is interesting to note that only about half of the samples in train #1 have detectable quantities of the three PGEs whereas nearly all of the samples in train #2 are enriched Pd+Pt+Ir. This seems to reflect different PGE concentrations for the two source areas and may have exploration significance.

Several samples near area #4 in figure 5 contain much higher levels of PGEs than was found in either of the two main chromite trains. The PGEs seem to be associated with a weak northward-oriented chromium dispersal train that is interpreted as having been formed by northward-flowing ice during the last glacial retreat. The train appears to have originated from a small body of ultrabasic rocks known as the Pennington dyke (see figure. 7). Because of the very high PGE/Cr ratio in these samples, it is quite probable that the PGEs occur as particles of native metal. It must be emphasized, however, that the occurrence of native PGE particles in these samples is suspected but has not been confirmed.

Another group of high-PGE samples (#5, figure 5) forms an east-west train that seems to point to the same Pennington dyke source as train #4. The east-west trend corresponds to the flow direction of an earlier ice sheet and there is documented evidence of glacial dispersal in that direction (McDonald and Shilts, 1971). However, the glacial landscape generated by this earlier ice flow was largely obliterated by the more recent southeastward flow. Thus, the suggestion that train #5 represents dispersal from the early flow has to be regarded as tenuous despite the appearance for such in figure 5.

What is less questionable, however, is the facility with which heavy minerals were able to detect precious metals occurring in the surficial environment in the native state. The observed high frequency of detection in our survey, both for gold and the PGEs, is without any doubt related to the large volumes of alluvium from which the heavy minerals were extracted. The need to sample large volumes to maximize the detection of native metal particles (i.e. reduce the "nugget effect") in geochemical exploration for precious metals, is well documented (Day and Fletcher, 1986, 1989).

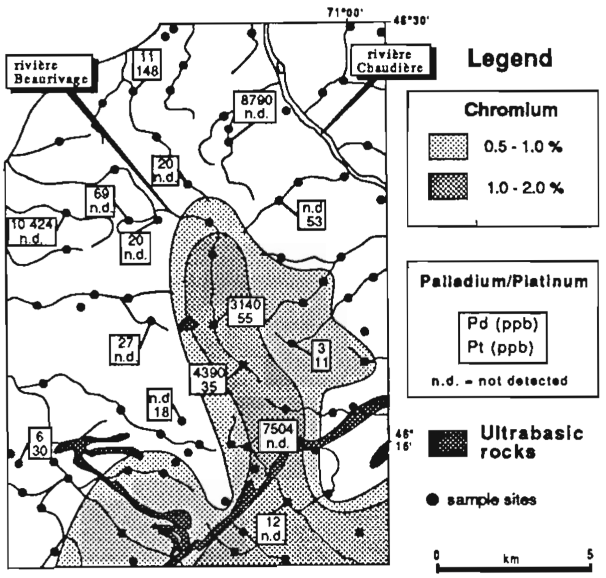

Figure 7 Chromium and PGE distribution in heavy mineral concentrates near the Pennington dyke, Eastern Townships, Quebec (see location map in the Appendix)

Thus, we contend that:

Because they are extracted from considerably larger volumes than regular samples, when exploring for precious metals HMCs

- **are more representative than untreated samples;**
- **data reproducibility is enhanced; and**
- **the "nugget effect" is greatly reduced**

The capacity of the gold pan is roughly between 10 and 100 times the amount of unprocessed material that would normally be fire-assayed for a gold analyses. The size of the sample and therefore its representativity is further increased if more than one panfull of material is used to obtain the heavies at each site.

In southern Quebec, much larger volumes of sediments than could be practically treated with a gold pan were obtained with a suction dredge. This increased considerably the chances of capturing native metal particles when such particles were present in the alluvium. We suspect that the gold distribution shown in Figure 1 would be considerably more "patchy" had the HMCs been extracted from much smaller volumes of sediments (e.g. using a gold pan).

A geochemically simpler sample

HMCs are made up of relatively coarse clastic grains above a certain specific gravity that depends on the separation and concentration methods used. Thus, HMCs do not retain the hydromorphic component which forms part of the geochemical signature of stream sediments, soils and other materials. This hydromorphic component is mostly present in those materials as ionic species or complexes absorbed by scavenging substances such as clay minerals, organic matter, and precipitated hydroxides. Some precipitated, metal-enriched hydroxides may find their way in HMCs but most form thin coatings on light mineral grains and, under normal circumstances, are not retained in the HMCs.

Neither do the HMCs retain the geochemical signature of metals associated with common rock-forming light minerals. For example barium in feldspar or nickel in serpentine, which can have a strong influence on the geochemistry of regular stream sediments, do not affect the composition of HMCs.

Therefore:

The elimination of the hydromorphic and other geochemical components from the HMCs simplifies the samples and facilitates data interpretation. Because they are generated largely by clastic mineral grains, HMC patterns can be interpreted almost entirely in terms of clastic dispersal processes.

The geochemistry of regular stream sediments is further complicated by the fact that the main constituents (clay, silt, sand, heavy minerals, organic matter, chemical precipitates, etc) occur in highly variable proportions from one sample site to the other. Therefore, much of the variation in a stream sediment survey can be attributed to variations in the proportions of the main constituents of stream sediments.

In the glaciated terrain of southern Quebec, the dominant clastic dispersal process is glacial. This is quite evident in the patterns shown in figures 2, 4, 5 and 7. In this region, clastic dispersal of heavy minerals attributed to alluvial processes is relatively unimportant compared to the glacial processes and appears to have had minor influence on the regional geochemical patterns. In higher energy environments, however, alluvial dispersal may become the dominant dispersal mechanism for heavy minerals.

Table 1 Average concentrations (medians) and correlation coefficients for selected elements in heavy mineral concentrates and regular stream sediments, 1989 survey area

Element	Median HMCs	Median stream seds	Med (HMC)/ Med (S.S.)	Correlation HMC vs S.S.
Cr	1.12%	120	93.3	0.659
Hf	345	16	21.6	-0.026
Ta	20	1	20.0	n.a.
Zr	1.7%	855	19.9	0.002
Fe (NAA)	34%	2.5%	13.6	0.299
Th	38	5.9	6.4	0.200
U	14	2.3	6.1	-0.097
La	130	26	5.0	0.449
Ce	315	64	4.9	0.361
Sm	28	5.7	4.9	0.263
Sb	0.9	0.3	3.0	0.155
Cu	13	8	1.6	0.163
As	9	6	1.5	0.025
Fe (AA)	2.5%	1.8%	1.4	0.087
Hg	26 ppb	30 ppb	0.9	0.073
Zn	22	51	0.4	0.166
Ni	7	17	0.4	0.213

values in ppm except when indicated

n.a. - not available

Differences in the geochemical patterns produced by HMC and stream sediment surveys will be greatest for those elements that have important non-clastic (non-HMC) components. Differences in concentrations will be smallest for those elements because of the added signal from non-HMC components. Table 1 gives the correlation coefficients, the medians and their ratios for a selection of elements analyzed in both HMCs and stream sediments in the 1989 survey area.

The highest median ratio in table 1 is 93.3 for Cr. This indicates that Cr has the least-important non-HMC component of all the elements listed. If the non-HMC component for Cr is insignificant, then the value of 93.3 approximates the concentration factor or the average proportion of heavies in the alluvium.

Note that the ratios in table 1 decrease with increasing element mobility, with Zn and Ni having the lowest values. The ratios are expected to be quite different depending on whether the analyses are for total metal (NAA, XRF) or acid-leachable metal (note Fe in table 1). Some immobile metals may have a relatively low ratio if they are present in significant quantities in rock-forming minerals and other non-HMC phases. This is probably the reason for the large difference in the ratios of Cr and Zr. The latter (and Hf) occur in zircon, a common inclusion in many rock-forming minerals.

Figures 8 and 9 show the distribution of Cr and Zn, respectively the elements with the highest and the lowest median ratios in table 1, in HMCs (a) and in stream sediments (b) in the 1989 survey area. Note the similarity between the distributions of Cr in HMCs and in stream sediments and the much lower concentrations in the stream sediments. In contrast, the Zn distributions is much more dissimilar with Zn concentrations in stream sediments exceeding those in HMCs. Also, stream sediment Zn shows a greater abundance of stronger anomalies. Some of them coincide with HMC anomalies, but many do not. Although one could be tempted to regard the stream sediment Zn as being more useful, the HMC Zn is easier to interpret because its distribution can be attributed to fewer processes. Nonetheless, this example shows that there are important limitations to the usefulness of HMCs for the more mobile elements (see more on this subject below).

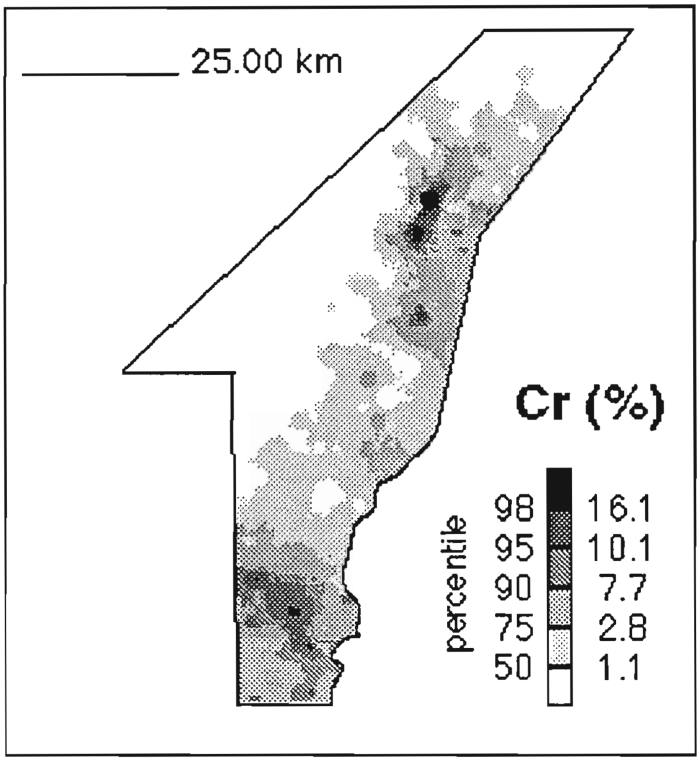

Figure 8a Chromium distribution in alluvial HMCs in 1989 survey area

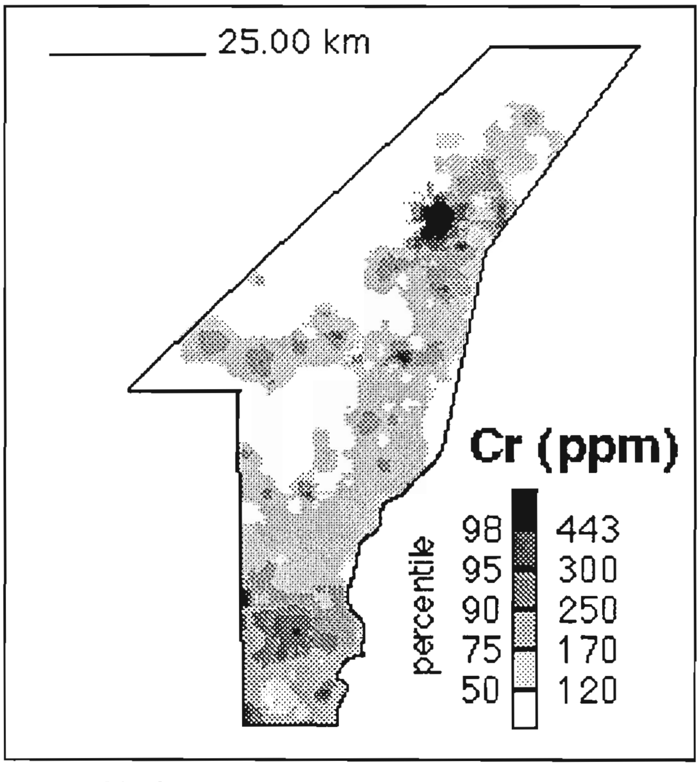

Figure 8b Chromium distribution in regular stream sediments in 1989 survey area

The degree of coincidence in the distributions of Cr and Zn in HMCs and stream sediments are reflected in the correlation coefficients in table 1. In general, however, the correlations between HMCs and stream sediments for most elements in table 1 are low, probably lower than one would expect. Put into words, this simply means that the high non-HMC- and the high HMC-component samples for most elements tend to derive from different sites. The lower the coefficient, the less coincidence there is.

Follow-up procedures

HMCs offer more opportunities to study anomalous samples using a wide range of follow-up techniques based on mineralogy and mineral chemistry.

The usefulness of being able to return to a stored split of an anomalous HMC in order to study the mineral grains that are responsible for the anomaly, cannot be overstated. In southern Quebec, countless observations of HMCs were carried out to help determine a multitude of helpful characteristics relating to the nature of the anomaly, mode of transport, provenance, etc. The following is a sample of observations made during our study:

- Confirmation of ore minerals by XRD and/or SEM-microprobe; ore minerals found include scheelite, cerussite, sphalerite, chalcopyrite, monazite, pentlandite, barite, cassiterite, secondary antimony minerals, etc;

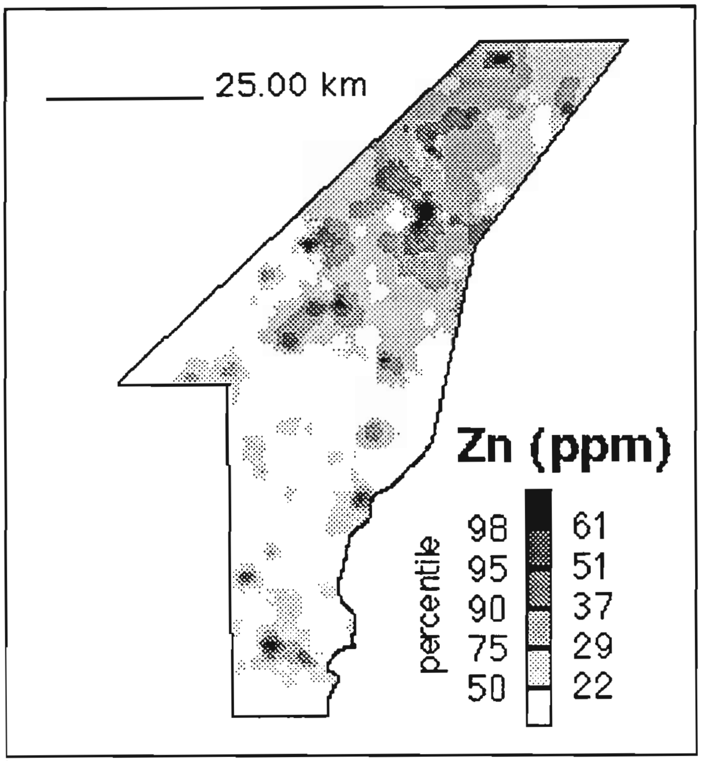

Figure 9a Zinc distribution in alluvial HMCs in 1989 survey area

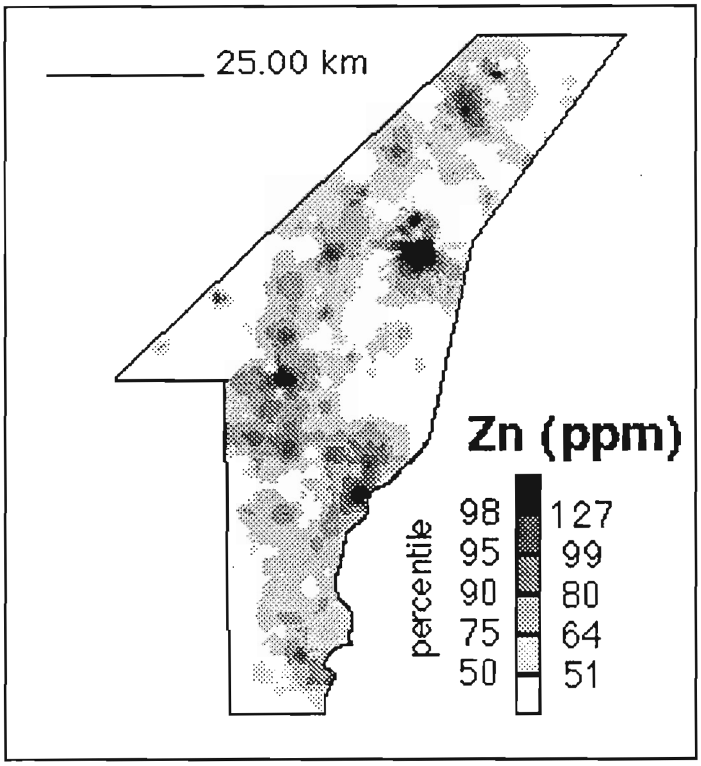

Figure 9b Zinc distribution in regular stream sediments in 1989 survey area

- Presence of possible man-made contaminants including metallic lead, metallic tin and alloys;
- Examination of gold grains to determine mode of origin (fineness, crystal outlines), transport mechanism (grain angularity, striations), source type (mineralogy and chemical composition of solid inclusions), etc;
- Other provenance studies: garnet composition and morphology; internal structure of ilmenite;
- Gold content of pyrite; Ta and Nb content of ilmenite; REE composition of monazite, etc.

DISADVANTAGES AND LIMITATIONS OF THE HEAVY MINERAL APPROACH

Sample cost

Heavy minerals cost more per sample to collect than several, more traditional, sample types

Comparing sampling costs in exploration geochemistry can never be considered a definitive exercise. There are many variables involved such as access to sample sites, transportation and other logistical considerations, type and portability of sampling equipment, scale of surveys, level of competition amongst sampling firms, etc. The highlighted statement above is certainly true when comparing sampling cost for alluvial heavy minerals as practiced in southern Quebec with regular stream sediments or soils in the same region. It is much less so when comparison is made between, for example, alluvial HMCs and till sampling, especially when excavating or drilling equipment is used to collect the till samples rather than a hand shovel.

Also, when stream sediments or other easily collected sample medium are used, the tendency is to cover the survey area at a much higher sample density because, once the sampling crew is on site, it is quite inexpensive to collect additional samples. This has been the practice in southern Quebec where the provincial government and private companies have covered most of the region with stream sediments collected at a density averaging 1 sample per 0.4 km^2. This is 25 times the number of sites per km^2 used for GSC's HMC surveys. The additional stream sediment samples may have a marginal effect on the sampling costs, but a considerable one on the analytical costs. No doubt that they provide additional information, but is this required for effective mineral exploration?

Field equipment and sample preparation facilities,

Using HMCs brings about a need for elaborate field equipment and sample preparation procedures and facilities

HMCs are normally extracted in two steps. The first, is a pre-concentration phase that is often carried out in the field using either a gold pan, a suction dredge as in the present survey, or other separating devices such as rockers, jigs, etc.

The second step is the preparation of a final concentrate and this is generally accomplished in a laboratory. It may involve one or two procedures depending on the degree of purity sought and other considerations. Normally, the pre-concentrate is passed on a shaking table followed by heavy liquid separation. This combination produces the best concentrate as it ensures maximum recovery of heavy minerals above a desired specific gravity. However, it is also the most expensive way and many people object to working with heavy liquids without a sophisticated ventilation system because they present a health hazard.

There are several gravity-controlled separators that produce adequate concentrates without using heavy liquids. A rotary spiral concentrator commercially known as the "Goldhound" was used in southern Quebec. It produces a very pure concentrate but heavy mineral recovery is somewhat less than optimum (Maurice, 1988).

Table 2 Comparison between detection limits for neutron activation analyses of heavy mineral concentrates and regular stream sediments for selected elements

Element	Detect. limit HMCs (range)	Detect. limit Stream seds
As	2 - 18	1
Au (ppb)	10 - 40	5
Ce	48 - 72	10
Co	10 - 54	10
Eu	2 - 10	2
Ir (ppb)	100 - 510	100
Mo	2 - 24	2
Ni	20 - 260	20
Sb	0.2 - 1.0	0.2
Tb	1 - 2	1
U	0.5 - 1.6	0.5
Yb	5 - 10	5
Zn	200 - 1500	200

values in ppm except when indicated

An important consideration when choosing equipment is the minimum grain size of heavy minerals desired. The main concern here is the necessity to concentrate precious metal particles at whatever grain size they occur in the sample medium. This minimum size, however, need not be as fine as the dominant particle size in the orebodies. Even if an orebody contains predominantly micron-size gold, there may be parts of the orebody containing coarser gold that could generate anomalies in sand-size heavy minerals. Also, supergene processes may have acted on the ore zones and led to the formation of coarser gold particles near the surface.

The procedures used in southern Quebec were adequate for coarse placer gold recovery. They should, however, be tested in areas where much finer particles are expected. The combination suction dredge — Goldhound successfully extracted gold down to 50μm in our survey.

Analytical interferences

Certain analytical techniques have a lower sensitivity for HMCs compared to other sample types.

Some of the benefits of using HMCs are reduced because of lower sensitivity of some analytical techniques, including neutron activation and XRF, when analysing HMCs. With neutron activation, the problem is that the signal for some elements becomes masked due to high background generated by high concentrations of other elements, particularly the rare earths, with the effect of decreasing the detection limits. Table 2 shows the differences between the detection limits of HMC and regular stream sediment analyses by neutron activation for selected elements from the 1989 survey data. Note that the detection limits for the HMCs vary depending on the concentration of interfering elements in each sample.

For the XRF analyses, it is the accuracy that suffers because of the differences between the matrices of the samples and those of the standards used by the laboratories.

Difficulties in interpreting absolute concentrations

The value representing the absolute concentration of any given metal in HMCs is very dependent on the total amount of heavy minerals "diluting" that metal in the concentrate

The same number of scheelite grains will produce only half the W concentration in a concentrate with twice as much heavy minerals. This dilution factor has a great deal of influence on the absolute concentrations of individual elements in HMCs and to a certain extent also on the patterns that are derived from those concentrations. A similar problem also exists for other sample types. For example, in a regular stream sediment, the contribution to the absolute concentration of zinc or nickel from the metals absorbed onto the clay minerals in any given sample will vary depending on the amount of other materials diluting the clay in the sample. But this dilution effect is more acute in HMCs than in other types of sample materials and can be quite troublesome in extreme cases. For example, it is conceivable that one could encounter a situation where an HMC is collected in an area where the stream alluvium is derived from a bedrock source containing only one type of heavy mineral, say barite. The Ba analysis for that sample would be about 60% Ba which is the amount of Ba contained in pure $BaSO_4$. The very high absolute concentration in this case, does not necessarily reflect higher concentration at the source than a considerably lower value in a HMC derived from a heavy mineral-rich environment. It does indicate that barite occurs in the area and that is what should be investigated; not the high value.

Such extreme cases probably never occur, but even ordinary situations require great care when interpreting absolute concentrations in HMCs. When dealing with high concentrations of any metal, it is prudent to pay much less attention to the actual values and focus more on what mineral species and metal associations are present, what are the trends in the patterns, whether the anomalies correspond to the type of mineralization expected, etc. Variations in the total heavy mineral content of overburden can generate "false" patterns, particularly if the range is wide. Fortunately, these variations tend to be regional and can usually be predicted with adequate knowledge of the glacial and bedrock geology, and can usually be taken into account during interpretation.

One way to overcome the problem described above is to convert the metal concentrations in the HMCs to concentrations in the original sediment. This requires accurate measurements of the mass or at least the volume of the material from which the HMCs are extracted, and of the total heavy minerals contained in this material (no loss allowed). Because these parameters could not be measured accurately in our surveys, this conversion was not done. It is important to keep in mind that while this conversion reduces one problem, it creates new ones that are supposed to be minimized in HMC surveys. For example, the

Table 3 Relative usefulness for mineral exploration of a selection of elements commonly analysed in heavy mineral concentrates. Based on GSC's heavy mineral surveys in southern Quebec

Very useful
- **Au, PGEs → particle size?**
- **Ag, W, (Hg) → low background**
- **Ba, (Sr), Cr → elevated background**
- **Rare - earths, Th, Nb, Ta → higher bkgrd**
- **Sn, Sb, Pb → possible contamination**
- **Ti, Zr, Hf, As → high background**
- **Cu, Ni, Zn, Co, Bi, As, Mo → stability?**
- **Ga, Ge, In, Cs, Tl, Cd → non-minerals**

Not useful
- **Li, Be, F, B, Br → light minerals**
- **Sc, Se, Te, U, V → ????**

converted numbers become affected by local variations in the abundance of heavy minerals in stream alluvium due to such factors as hydraulic processes.

Relative usefulness

> **The usefulness of HMCs in mineral exploration is limited for some important metal types and pathfinder elements**

Our surveys have demonstrated clearly that the heavy mineral approach is an excellent choice, if not the best choice, for geochemical exploration for the precious metals. The most significant limitation concerning the precious metals is the minimum particle size which can be extracted using a given technique. Recovery of very small particles is always possible but the cost will increase accordingly.

Silver and tungsten also produced very clear, high-contrast and easy-to-interpret patterns. One key factor concerning those elements is that their background is usually very low so that any amount of the metals produces a noticeable feature.

By contrast, elements such as the rare earths, Nb and Ta, Cr, Ba, As tend to show high background because they often occur in accessory minerals in bedrock. Niobium and tantalum, for example show concentrations in southern Quebec HMCs ranging from 100 to 300 ppm Nb and 10 to 50 ppm Ta, practically all of it contained in ilmenite, a major constituent of HMCs. Arsenic is enriched in many sedimentary pyrites, resulting in high background levels in pyrite-rich HMCs.

The chalcophile elements are often regarded as having limited usefulness in alluvial heavy mineral surveys because their main clastic phase, the sulphides, is not stable under oxidizing surface conditions. Nevertheless, experience in southern Quebec has shown that the chalcophile elements produce patterns and that these patterns, although weaker than those in regular stream sediments, may be more informative than the latter. For example, the copper in the anomaly shown in figure 2c occurs as chalcopyrite inclusions in pyrite grains. The presence of the ore mineral chalcopyrite in identifiable clastic grains is in itself much more significant from an exploration standpoint than would be a hydromorphic anomaly, even if it were significantly stronger.

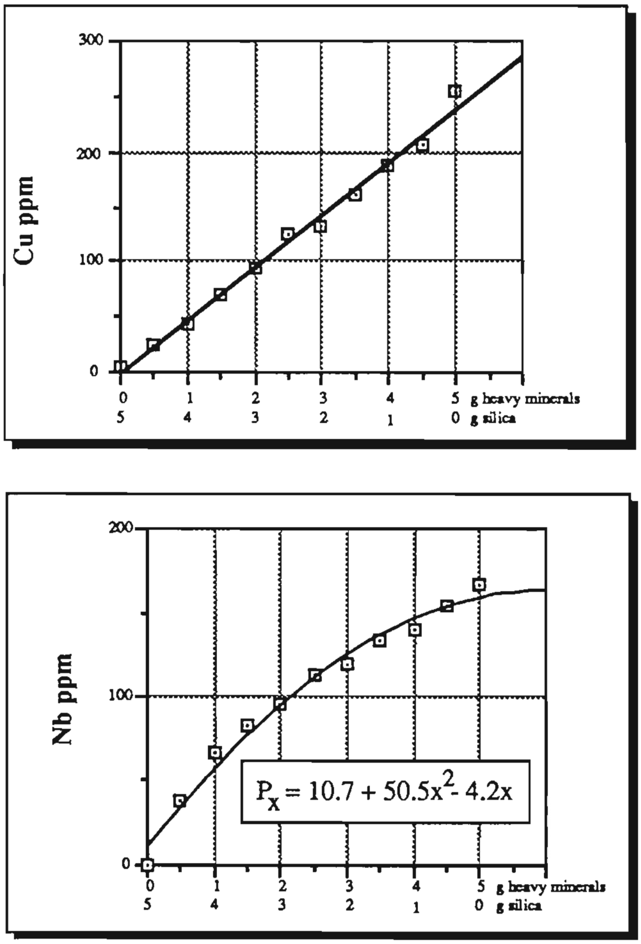

Figure 10 *Results of Cu (AA) and Nb (XRF) analyses of a heavy mineral standard diluted with various quantities of silica, to show linear and non-linear relationships. Second degree polynomials, as the one shown for Nb, were used to apply a correction to diluted samples for some XRF elements.*

Some ore elements, including Pb, Sn and Sb, were found to be very useful as target indicators in southern Quebec, but this is somewhat reduced by the fact that these metals occasionally occur as metallic contaminants in the HMCs. In fact, HMCs are much more sensitive to metallic contaminants than other sample types. On the other hand much of the problem is eliminated by one's ability to return to the sample and examine its mineralogy.

Other elements, mostly obtained as part of the neutron activation 40-element analytical package, produced no clear patterns and are considered to have limited usefulness in heavy mineral surveys, at least in southern Quebec. These include many of the high tech metals (Ga, Ge, In, Cs, Tl) that do not form specific minerals, and elements such as Se, Te and U which form rather unstable or very rare minerals.

The relative usefulness of a range of elements in HMC geochemistry is summarized in table 3.

Problems related to insufficient heavy minerals in the concentrate due to low heavy mineral content of overburden

This has been a problem on occasion, in areas where there is not an abundance of transported overburden and where the local bedrock is sedimentary and heavy mineral deficient. The compressed powder technique of XRF analysis requires a minimum of 5 g of powdered sample material and this establishes the minimum amount of heavy minerals considered acceptable.

This rule had to be broken on occasion. Concentrates weighing less than 5 g and as low as 0.5 g have been used by adding analytical grade silica to "make up" the required 5 g. The final result was obtained by correcting the analysis with the appropriate dilution factor. For most elements, the dilution with silica introduces a linear variation to the results and the correction is made simply by multiplying by the factor. For some XRF elements, however, the variation in the nature of the sample matrix causes a non-linear variation. Those elements are corrected using a polynomial as shown in figure 10b.

CONCLUSION

When used intelligently, heavy mineral geochemistry can be a powerful exploration tool with wide ranging applications. Its strength lies primarily with its ability to enhance hundreds of times the geochemical signal from rare metals, its simplified geochemical make-up which facilitates interpretation, and the fact that the samples lend themselves to direct mineralogical examination and testing.

On the other hand, there are limitations to the technique which have to be well understood in order to successfully interpret the data. Most interpretation problems arise from a lack of understanding of what the heavy mineral concentrate actually represents and how the heavy minerals (or lack of) in surrounding overburden and source rocks affect the signal. Furthermore, simplification of sample geochemistry may have its advantages, but it still means a loss of information. For this reason, heavy minerals should be regarded as complementary to other techniques, particularly when exploring for intermediate- to high-mobility metals.

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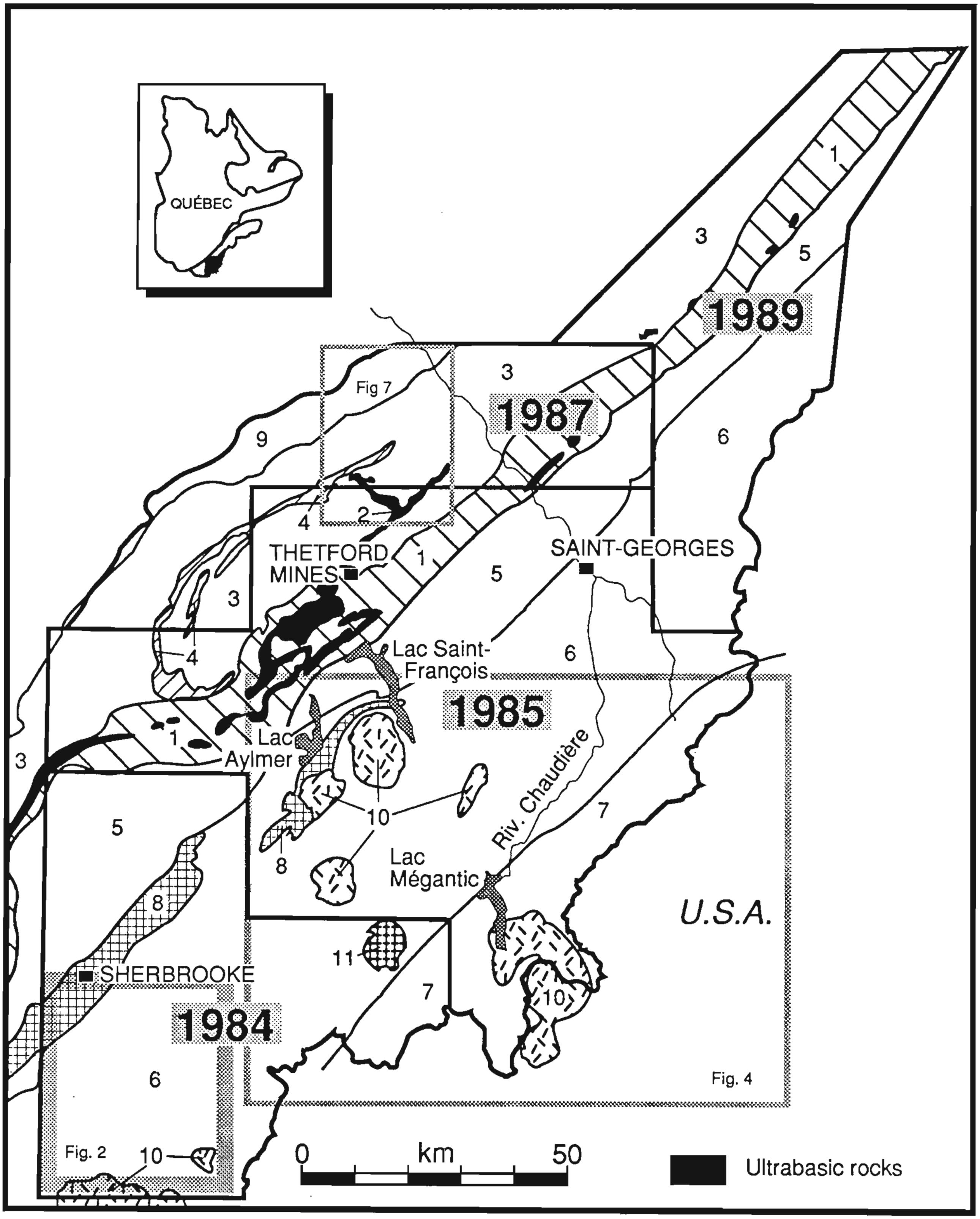
APPENDIX
(regional geology and general location map)



Geology: 1. Serpentine Belt; 2. Pennington Dyke; 3. Sutton/Notre-Dame Belt;
4. Tibbit Hill Metavolcanics; 5. Saint-Victor Synclinorium;
6. Gaspé-Connecticut Valley Synclinorium; 7. Boundary Mountain Synclinorium;
8. Stoke Mountain Belt; 9. External Domain; 10. Devonian Granites;
11. Monteregian alkaline intrusion

PAPER #6

STREAM GEOCHEMISTRY IN THE CANADIAN CORDILLERA: CONVENTIONAL AND FUTURE APPLICATIONS FOR EXPLORATION

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Abstract

Stream drainage geochemical exploration techniques have continued to lead to the discovery of important new mineral resources in the Canadian Cordillera. The variety of metallogenetic, geological and surficial environments found in British Columbia and the Yukon Territory requires the the geochemist-explorationist constantly examine aspects of conventional stream geochemical methodology and refine survey applications in the context of new technology and/or ore deposit models.

The high quality data base of the National Geochemical Reconnaissance (NGR) is examined and the multi-element, multi-media methodology is reviewed. Examples of interpretation of NGR stream sediment and water data are provided.

Detailed follow-up geochemical survey case histories are given which compare and contrast stream sediment and heavy mineral panned concentrate data from different size fractions of stream drainage material. Multi-media (water, sediment and HMC) orientation surveys from the Gataga-Ketchika district of British Columbia are provided to illustrate hydromorphic and clastic dispersion characteristics.

In the Atlin placer gold district the economic interpretation of the diverse heavy mineral suite recovered from active placer gold mining operations is presented. Placer gold grain morphology represents primary gold shapes and grains with gangue are superior exploration material for lode and alteration mineral assemblage identification.

Trace element measurements and gold in water determinations are shown to be a practical exploration and environmental expense early in the exploration and development of precious-metal deposits.

Résumé

L'exploration géochimique par l'analyse des sédiments et des eaux des ruisseaux a continué de mener à la découverte d'importantes ressources minérales dans la Cordillère canadienne. Les différents milieux métallogéniques, géologiques et sédimentaires que l'on trouve en Colombie-Britannique et au Yukon nécessitent de la part du géochimiste qu'il surveille sans cesse les aspects de la méthodologie classique de la géochimie des cours d'eau et affine les applications des levés liées à une technologie nouvelle ou à des modèles gîtologiques.

Nous examinerons la base de données de très haute qualité RGN (Reconnaissance géochimique nationale) et passerons en revue la méthodologie basée sur l'analyse d'éléments multiples en milieux variés. Des exemples d'interprétation de levés de sédiments et d'eau de ruisseaux, contenus dans la base de données RGN sont présentés.

Quelques exemples de suivi détaillés de levés géochimiques sont présentées; ceux-ci permettent de comparer les données obtenues par l'analyse des sédiments de ruisseaux et les concentrés de minéraux lourds (obtenus par lavage à la batée) des sédiments pour différentes granulométries. Les données obtenues lors de levés d'orientation en utilisant divers média (eau, sédiments et concentrés de minéraux lourds) dans le district de Gataga-Ketchika (Colombie-Britannique) sont présentées pour illustrer les caractéristiques de dispersion hydromorphique et clastique. Dans le district aurifère d'Atlin, l'interprétation économique de la suite de minéraux lourds très variée, récupérée durant l'exploitation actuelle du placer aurifère, est également présentée. La morphologie des pépites d'or de placer correspond aux formes primaires de l'or, et les pépites avec gangue sont reconnus comme des matériaux d'exploration supérieurs pour l'identification des filons et des assemblages de minéraux d'altération.

Les analyses des éléments-traces et la détermination de l'or dans l'eau sont considérées comme une dépense pertinente au cours des étapes initiales de l'exploration et de la mise en valeur des gisements de métaux précieux.

INTRODUCTION

Geochemical prospecting techniques have contributed significantly in the discovery and development of several important mineral resource districts and deposits in the Canadian Cordillera.

The first successful geochemical explorationists were the gold prospectors. Many had learned their geochemical methods in the Motherlode District of California. They became acutely aware of the direct relationship of placer gold concentrations and gold-quartz lode sources within the same drainage. One after another, classic gold rushes developed as these 'heavy mineral concentrate' (HMC) experts systematically tested and claimed 'virgin ground' from the Boundary District of British Columbia to the Klondike in the Yukon. Fabulous placer gold riches were extracted. However, gold prospectors soon became disenchanted with the lack of, or, the relatively poor lodes discovered in the Canadian Cordillera compared to their Californian experience.

Because of economic necessity, these men "observed the natural forces at work within a stream or river drainage". They understood bedload and suspended load transport and effectively sampled each and then panned and/or sluiced stream sediment material in the hope of discovering mechanically dispersed gold. They observed the shapes and colours of gold grains while noting diagnostic associated heavy minerals in the concentrate. Gossans and weathered outcrops, as well as 'float' from the stream bed were also crushed, ground and panned for their suspected gold contents. Much of this direct observation process led to questions, and then to the obvious solution that "large gold nuggets grow in creeks". We, as modern geochemists and explorationists, are still struggling to overcome our lack of understanding of mechanical and chemical processes active within the diverse climatic, physiographic regions and environmental landscapes of Canadian Cordillera stream drainages.

It is the purpose of this paper to examine some aspects of conventional stream sediment geochemistry and to review new, or past knowledge in the context of modern technology and earth science research.

HISTORY OF STREAM DRAINAGE GEOCHEMICAL EXPLORATION CORDILLERA

Early Studies

After the initial influx of placer gold geochemical samplers, the modern age of geochemical prospecting, using streams, commenced in 1953 when R.W. Boyle applied water and stream sediment surveys in the Keno Hill area of the Yukon Territory (Boyle, 1958). In 1957, J.J. Brummer of Northwestern Explorations organized the first regional stream sediment surveys in the Cordillera when streams in the Guichon Creek batholith were analyzed for Cu and Zn (Brummer et al., 1987). This successful identification of Cu anomalies, using stream sediment sampling methods, led to its systematic use, and soon survey coverage of large areas in the Canadian Cordillera by other mining companies had begun. At the forefront of this geochemical exploration was Kennco Explorations (Western) Ltd. who, during the period 1959-1970, covered much of British Columbia and Yukon during Cu-Mo surveys (Brummer et al., 1987). Most stream sediment surveys focused on one or two 'ore' elements and they generally were not at a reconnaissance level of sampling design. Detailed sediment sampling of streams and tributaries, on a claim group scale, often led to successful follow-up surveys using soil sampling methods. Many new major deposits were discovered (Brummer et al., 1987).

In the Klondike - Indian River district of the Yukon Territory, heavy mineral studies by C.R. McLeod and C.F. Gleeson were initiated in 1959 and completed in 1962. This survey's impetus was to assist in identifying new placer gold reserves, to test the possibility of recovery of other valuable economic heavy minerals, and to use heavy minerals to locate potential lode gold deposits. This research by the Geological Survey of Canada (Gleeson, 1970) launched the new age of scientific study of heavy mineral concentrates (HMC) and marked a major advancement from the methods used by the original placer gold seekers. Sampling of one cubic foot volumes of material was standardized and uniform recovery of heavy minerals was deemed essential for quantitative study. In the field, screening, washing, portable sluicing and recovery of heavies on riffle fabric was completed. In the laboratory heavy liquid bromoform, size fraction analysis, hand magnet and Frantz Isodynamic magnetic separations and superpanning were conducted. Recovered grains (about 300) were mounted on glass slides and identified and counted with the aid of binocular and petrographic microscopes and X-ray diffraction powders. The grains were checked for radioactivity with a scintillometer and examined under long and short wave ultraviolet light. Gold grains and heavies were then subjected to spectrographic analyses. The survey results and conclusions, which should have an important impact on HMC geochemical prospecting methodology, are as follows:

1) Forty-eight heavy minerals were identified, most coming from local bedrock sources. Some suites of heavies can be shown to be derived from specific types of gold-bearing veins.
2) Placer gold is the best heavy mineral to locate lode deposit possibilities. Placer gold can be detected at concentrations equivalent to 0.00006 3 oz/ton in one cubic foot of sample material.
3) Heavy mineral results indicate that lode gold sources, other than those already known, were, or are still (?) present in the Klondike; thorough prospecting was recommended.

Even to this day, the scope of this HMC research in the Klondike (Gleeson, 1970) has seldom been duplicated in other parts of the Cordillera.

The Modern Age

National Geochemical Reconnaissance (NGR) stream sediment and stream water surveys were initiated in the Yukon and British Columbia in 1976 after preliminary geochemical orientation surveys by the GSC were completed and evaluated. During the period 1976-1978 the Uranium Reconnaissance Program (URP) was the impetus behind this regional geochemical silt (minus 177 micron, -80 mesh ASTM) and water sampling program which was conducted at an average density of about 12-13 square kilometres per sample site. Over the years, funding for the Cordilleran NGR surveys has been provided by a number of programs. These include funding 1) solely by Energy, Mines and Resources Canada, DIAND, 2) jointly under various programs (Canada-British Columbia Uranium Reconnaissance Program, Canada/British Columbia Mineral Development Agreement 1985-1990, Canada/Yukon Mineral Development Agreement), and 3) solely by the British Columbia Ministry of Energy, Mines and Petroleum Resources, (Accelerated Mineral Development Program, 1978). To date, almost two-thirds of the Canadian Cordillera encompassing in whole, or in part, some 85 NTS 1:250,000 map sheets, has been sampled

(GSC, 1990). Sampled areas extend from the Beaufort Sea in the north, to the Okanagan Valley in the south. Over the years, NGR data release dates have consistently led to 'pre-emptive' claim staking (before the release) and also to staking rushes during and after the release of maps and data.

Although most consider NGR data as 'conventional' or 'routine' regional stream sediment sampling, that is not the case. NGR surveys are far from 'dirt bag' programs. During the start up of the URP some members of the industry were strongly opposed to government funded geochemical 'exploration?' surveys. Now, however, majors, juniors, prospectors, consultants and numerous other clients use, and are learning to use NGR maps and data as they would use geologic or aeromagnetic base maps.

Let us examine why the NGR database is 'unconventional' and show why you, as explorationists, should be committed to this reconnaissance scale sediment and water sampling and its spectrum of multi-element determinations and field observations.

NGR program methodology ensures that all aspects of sample collection, data records and field maps, drying, packing and shipping are in accordance with standards which are maintained by the contractor from year to year. Generally, sample collection was restricted to primary and secondary streams having drainage-basin areas less than 15 square kilometres. The belief that sample collection procedures and sample site location criteria are the most important aspects of reconnaissance surveys has probably been the main reason for the success of the program.

Adherence to national standards are also in place during laboratory preparation and analytical determinations. Into each sequence of twenty samples (both water and sediment) there are inserted:

1) a field duplicate, which tests sample site variability;
2) a blind duplicate, which tests laboratory subsampling variability;
3) control reference material which tests analytical variability.

Specific analytical methodology and techniques were established to optimize extraction of each element at its lowest detection limit or at cost effective sensitivities. Consistency between survey times and areas is critical. Analytical results are therefore evaluated to ensure strict adherence to national standards set by GSC-NGR program.

The resultant high quality regional data base was not 'conventional' in its early URP days since it was multi-media (water and sediments) and, as importantly, multi-element (Ballantyne et al., 1976, 1978). Initially, the routine element suite for stream sediments included Zn, Cu, Pb, Ni, Co, Ag, Mn, Fe, Mo and U while stream water analyses provided U, F and pH data. This is a wide departure from 'conventional' stream sediment sampling programs conducted by the mineral industry where, generally, specific exploration targets are identified and sampled, or a few ore elements are utilized to outline anomalies related to mineralization. It became clear early in the NGR program that although results were aimed primarily at assisting the exploration industry's ability to conduct resource assessment, the surveys could also provide an environmental data base that outlined high and low anomalies and background elemental concentrations throughout the diverse regions of the Cordillera.

In 1977, Environment Canada provided one years funding so that mercury could be added to the 'routine' stream sediments element suite. Also, the analysis of uranium in sediment and water provided an improved understanding of its natural concentration levels and factors affecting its migration factors in the surficial environment. This new understanding regarding uranium soon became very important in permitting the development of ore deposits in British Columbia. URP survey data and studies were also used extensively during the 1979-1980 Bate's Uranium Commission reports and recommendations.

Industry's 'conventional' stream sediment sampling usually involved the collection of small quantities of sand and silt from the active stream bed at many detailed sample sites within the drainage being explored. This practice often resulted in samples deficient in fines, and precluded re-analysis or archival of the remaining silts for future use.

NGR methodology requires the collection of 1-2 kilogram fine sands to silts (see sampling section for details). This ensures that ample amounts of the -177 micron size fraction are available for check analysis and for systematic archival. During the URP, specifications dictated that 10 grams of ball-milled minus 177 micron size fraction material have its uranium content measured by neutron activation analysis (NAA). After a "cooling down" period this irradiated sample material was also routinely saved for storage at the NGR-GSC facilities in Ottawa.

The importance of preserving samples for future re-analysis and the use of non-destructive analytical methods (NAA) was quickly tested when industry demands for W and Sn data were forwarded. Samples collected in 1977 (NTS 82F, K, 104N) were retrieved from the archives, analyzed, and the W-Sn data released and added to the original "routine" suite of elements. Before this process was undertaken, detailed orientation geochemical studies concerning W-Sn dispersion characteristics, from known sources, were evaluated. The results clearly showed that NGR sample collection and preparation methodology not only addressed hydromorphic dispersion of elements but also defined anomalies of mechanically moved elements (W-Sn). This would be a major influence on the utility of introducing gold analysis to regional NGR sediment samples collected during the "gold rush" of the late 1980's. These positive results meant that NGR archived samples could also be retrieved and analyzed for gold and other pathfinder elements.

During the history of NGR surveys in the Canadian Cordillera the list of additional elements added to the routine suite has grown steadily. This impetus may be attributed to:

1) clients demanding specific new ore or pathfinder element data;
2) ore deposit and resource studies showed that certain lithologies and/or deposit models contained diagnostic element abundances as haloes or anomalous enrichments;
3) new, cost effective analytical techniques became available thereby reducing total sample analytical costs; additional elements could be added without incurring additional costs;
4) new control reference material became adequately characterized so that high quality data for new and additional elements could be verified;
5) new or additional funding programs for specific NTS map - areas became available so that additional determinations could be added which perhaps were not repeated in adjacent map sheets (see Goodfellow, 1982, for Nahanni map area NTS 105I where the user should be particularly interested in the addition of P_2O_5, F, LOI, V, to the sediment data and the much expanded water chemistry data; see Matysek et al., 1991, for NTS 82G, Fernie map area, and NTS 82J, Kananaskis Lakes map area where the user will be particularly interested in water analysis including Cu, Pb, Zn, As, Cd, Hg and INAA Au plus 25 elements including rare earths in stream

sediments).

The user of NGR data should be aware that in addition to the 'routine' suite of elements for sediments, many map areas contain data for some or all of the following elements: Ba, V, Sb, As, Hg, Cd, Bi, Cr, and F. In both the Yukon and British Columbia, a recently initiated program has used the non destructive method of instrumental neutron activation analyses (INAA) to determine the individual concentrations of 26 elements for an approximately 10 gram sample weight taken from archived sediment collected and stored from previous NGR surveys. Of particular interest to the explorationist will be the gold data as well as gold pathfinder element data including Sb, As, Ba, Cr, Mo and W. Potential users should familiarize themselves with when and where these new map-area or re-releases will take place. This information is available from the Geological Survey of Canada, Ottawa, and the B.C. Geological Survey Branch, Victoria.

Part of the original NGR-URP mandate included identifying potential uranium resources and stimulation of exploration activity in the Cordillera. The present NGR program has clearly evolved and expanded its scope and coverage since initiation in 1976. For those of us who have been involved in its conception, methodology development and evolution it is gratifying to note that this data base has been accepted as the 'conventional' standard and that new uses and clients are being developed.

The program and data have inherent qualities of interest to the explorationist. To date, methods and results have:

1) increased the knowledge of multi-element-trace element dispersion and characterized the primary and secondary chemical and mechanical dispersion haloes and trains related to mineral deposits of variable genetic types in glaciated and unglaciated terrains.
2) identified local-scale anomalies and targets with the positive result that a great number of new mineral prospects have been discovered and old ones re-evaluated.
3) identified high-potential mineral resource areas where existing ore-deposit modelling would not have considered the potential as being significant. This resulted in the stimulation of exploration in neglected areas and markedly increased exploration activity in program survey areas.

4) shown that the data can recognize lithological variation within a geological unit; define geochemical background trace element concentration levels for different geologic units; identify geochemical variations and patterns within geologic-tectonic terrains; define domains and provenance in basin and stratigraphic studies; identify metallogenic provinces and their associated mineral deposits. In the long term as the results are reused and further evaluated the power of geochemical mapping in the Cordillera using stream data will be fully realized.

5) provided leadership in promoting the more effective use of geochemical exploration methods: by conducting orientation and follow-up surveys, by stimulated complimentary geochemical research, by academia and the mineral industry; by training contractors and sampling crews to NGR standard methodologies; and invoking new methods in region - specific surveys; by technical support and transfer of chemical analytical methods to commercial laboratories.

6) provided the high quality background data required to address environmental concerns and issues. The compiled and evaluated data will no doubt become the background or blue print for sustainable development - environmental issues as well as for recreation park proposals and single use land and land status issues.

Stream Dispersion Processes and Sampling Methods

The geochemist-explorationist has learned by practical experience that stream sampling methodologies are an effective means of prospecting in the Canadian Cordillera. However, it also became painfully obvious that different analytical techniques, sampling designs, and methods could drastically alter a geochemical survey's ability to detect mineralized targets. The complex reasons for success and/or failure of programs continues to be problematic. We have all heard statements such as "Geochemistry doesn't work!" Within the context of stream sampling, "Did Mother Nature actually fail to create enrichments and depletions of elements (anomalies) associated with mineralization (the ultimate anomaly)?" Perhaps we should not question either geochemistry of Mother Nature.

The more pertinent question is "Did we recognize those factors that influence element migration which were active in the past and are active today?"

Stream Sediment Sampling

The NGR analytical suite combines elements transported by chemical processes and by particulate dispersion. Sampling methods which optimize this dichotomy are critical to the success of the program. It is assumed that stream sediment samples are representative of upstream catchment material. Of course, sediment can be derived from a variety of sources, including, locally derived or exotic bedrock material. The target material is fine sand to clay-sized particles. It is also assumed that the finer fraction absorbs or complexes more metal ions (chemical dispersion) or that it contains numerous tiny particles of primary and secondary detrital grains in a heavy mineral fraction (clastic dispersion).

Conventional wisdom has dictated that 'active' stream sediment material is best for 'silt' sampling. But what does this word 'active' mean? It can mean bedload, suspended load or a combination of both types of transport of particles. Does the term 'active' impart that sediment must be collected from under water in a flowing portion of the stream? Yes, it could mean underwater collection of particles from either a high or low energy environment today. It could also mean collection of particles from those types of environments which in the past were under water but are now dry and exposed. Considering the variability in topography, physiographic regions, glacial histories and present climate, all of these questions will arise again and again, during sediment sampling programs, throughout the Canadian Cordillera .

A reconnaissance stream sediment survey should collect fine composite sediments from both low energy and high energy sites. Therefore, inner parts of stream bends, tails of bars and pools (low energy) and the outside of bends, upstream ends of gravel bars, obstacles or traps (high energy) are all sites used in the composite collection of sediment, at a single NGR sample site for a given stretch of stream drainage. Sediment samplers should not be encouraged to collect 'good silt' from only one of the forementioned sites; composite sampling will yield much more effective results. The samplers target is to optimize the collection of 'fines'. At any particular sample site these 'fines' may in fact be predominantly silts which have absorbed chemically transported elements or be predominantly clastically dispersed particles or have unknown proportions of each type of transported fine material.

Many stream sediment samplers have been taught to dread organic material and concentrations of iron and manganese (hydroxide). Therefore, they attempt to collect, by hand, silt and clay sized particles from the underwater gravel bedload material. A plume of silt generally quickly floats downstream and one handful of 'good sand' gets put into the small bag of the frustrated 'dirt-bagger'. Even the fine heavy mineral fraction in the bedload can be lost during hand sampling. May I suggest that all stream sediment samplers, whether collecting for 'silt' or HMC analysis, carry and use a large plastic 'bulk-food' or flour scoop and larger sample bags. **DON'T LEAVE CAMP WITHOUT THEM !**

The high walls of a scoop retains fine silt collected from under and behind logs and rocks. Fine silt can be skimmed off the surface of gravel bars, either underwater or on recently exposed bars. Coarse gravel and sand can be decanted off, with the water, before filling the large sample bag with easily collected, different accumulations of fines from several different locations. Black or brown coloured material, which was thought to be organic, can be easily checked for silt and clay content since it is retained in the scoop. Coarse gravel at the heads of bars can be scrapped aside to more easily collect HMC fines. Float gold, trapped in clay 'scum' from the tails of gravel bars, can also be easily collected with a scoop. When the sampler sees that fines and HMC particles are actually being collected and that there is a methodology with observable reasons behind the systematic sampling design, then your survey program has a much better chance of being consistent and therefore, interpretable.

With a scoop and a large sample bag you should be able to collect adequate minus 177 micron material for initial analysis and check analysis. In these days of nugget effects, in both precious and base-metal exploration, 20-40 gms of the final dry sieved material should be the minimum weight target during collection.

Much of the previous discussion described bedload processes and sites for collection. One must also remember that, at various times of the year, clastic dispersion of material includes significant suspended load, over significant stretches of drainage. Inherent in the concept of suspended load is the fact that the particle sizes are small and that their movement and transport downstream is highly dependent on flow velocity and settling factors. Many high energy environment creeks in the Canadian Cordillera have a scarcity of fine-grained stream sediment material in the stream bed. Perhaps the time of sampling or the pre-selected sample site location offered no suitable low energy environment dumping sites. In these situations, during the NGR surveys, high quality and quantity silt samples were collected by targeting suspended load material trapped in moss growing on boulders within the streambed. Our HMC experts, the gold prospectors, systematically panned moss taken from boulders. They were checking for suspended load 'float' gold within a drainage. After discovering that easily obtainable heavies contained gold from moss sampling and panning, prospectors began the laborious task of digging with pick and shovel at the heads of gravel bars. It was there that they hoped to recover coarse gold trapped during bedload clastic dispersion and transport.

Keeping in mind that easily obtainable, consistent quantities of silt is one's target, moss sampling has recently been successfully applied to the NGR-RGS program on Vancouver Island. Abundant annual rainfall in these cool humid regions has flushed the bedload relatively clean of fine silt. Once again, it is the suspended load trapped in moss growing on the top or downstream faces of boulders or logs that ends the samplers frustrations. Results from Vancouver Island verify that fine 'float' gold and other heavy mineral elements are enhanced in the suspended load 'fines' recovered from moss compared to bedload silts. Detailed discussions of results of geochemical orientation surveys using 'moss-mats' is given by Matysek and Day, 1988. Important Cordilleran research, under the direction of Dr. W.K. Fletcher, into the processes active in present day streams, and their effects on element dispersion have been completed or are continuing at the University of British Columbia (see Day and Fletcher, 1986; Fletcher and Day, 1988; Saxby and Fletcher, 1986).

Non-conventional suspensate sampling of stream sediment has been tested by F.R. Siegal in 1982/83. He reports (Siegal, 1990) that stream sediment suspensates ($>0.45\ \mu m$ mineral matter, which is derived from mechanical weathering and from precipitation reactions in the hydrogeological regime) can be collected in situ with a hand operated pump system and then analyzed. His results indicate that suspended mineral matter can be successfully used for geochemical prospecting. Dispersion trains and anomaly contrasts are reported to be enhanced in suspensate (suspended load), compared to bottom sediment bedload material. In the Cordillera in situ suspensate sampling has not been attempted. Only a limited database for a few elements is presently available (Siegal, 1990). However, the method may be applicable since 'suspended load' sediment sampling has a proven record of success (float gold-HMC trapping of sediment by moss).

Heavy Mineral Concentrates in Stream Sediments

Rock and ore forming minerals, when subjected to weathering processes, ultimately form 1) 'freed' resistates (relatively insoluble and therefore stable), 2) new stable forms (native metals such as Au, Cu) or 3) new relatively insoluble minerals and compounds which are dispersed by water into streams as particles (see Table 1, 2). These resistates, native metals, and new minerals or compounds have great variations in size, shape, specific gravity, hardness and magnetic susceptibility. For centuries it has been recognized that collection and identification of stream bourne 'heavy' minerals and insoluble compounds could lead to direct financial rewards. The recovery of placer minerals and gems also led to systematic exploration for their in situ bedrock source. The time honoured practice of heavy mineral 'panning' has, and is still, a prerequisite to the discovery of gold, diamond and precious gem deposits in many parts of the world. Placer gold camps in the Canadian Cordillera could still become 'hard rock' gold deposit districts as exploration for the Motherlode continues.

HMC bedload sampling was preferred since a visual inspection of coarse 'heavies' was normally the result. Bedload transport factors move most heavies down stream to accumulation points where they may 'rest' only to be moved, over time, further down gradient. Suspended load transport of heavies (very fine size fractions) also occurs throughout time. 'Flour gold' (size) and 'float' gold (transport) were sought in mosses (suspended load) for they indicated the possible presence of 'nugget' gold (size and bedload transport). In any event, both bedload and suspended load transport are not static processes.

As reported in the stream sediment sampling section, heavy minerals are dispersed and then collected as part of the silt size fraction of sediment. They are, however, diluted with the many 'light' particles. It is the objective of heavy mineral sampling to remove the light diluting minerals and to concentrate the heavies. Of course by removing the lights one can: a) remove anomalous concentrations of hydromorphically dispersed elements now absorbed onto these clays and quartz particles or b) enhance the anomalous concentrations

PRIMARY MINERALS IN THE ZONE OF WEATHERING: RELATIVE CHEMICAL STABILITY and ORE MINERALS IN THE ZONE OF OXIDATION which contribute to HMC and stream sediment material in Canadian Cordillera.

	VERY STABLE	STABLE	SECONDARY ALTERATION PRODUCTS: STABLE TO UNSTABLE	FAIRLY STABLE	UNSTABLE	SECONDARY ALTERATION PRODUCTS: STABLE TO UNSTABLE
ORE AND ECONOMIC MINERALS	**CHROMITE:** micro element concentrations maybe diagnostic of podiform, layered genisis; PGE inclusions maybe present	**BARITE:**		**HEMATITE:**	**ARSENOPYRITE:**	scorodite = hydrous Fe-arsenate
		CASSITERITE: micro element concentrations diagnostic of deposit type: pegmatite, lode, etc.		**SCHEELITE:** **POWELLITE:**	**PYRITE:** micro element concentrations maybe diagnostics of ore deposits	limonite goethite hematite } oxides siderite ankerite } carbonates jarosite melanterite } sulphates nontronite = silicate
	GOLD AND ELECTRUM: micro element and compositions of Ag, Cu, and Hg may be diagnostic of source and genetic type of mineralization	**GALENA:**	massicot = oxide cerussite = carbonate anglesite plumbojarosite } sulphate wulfenite = other	**WOLFRAMITE:**	**PYRRHOTITE:**	
				TITANITE: Sn composition diagnostic of tin skarns-malayaite fluorescence	**PENTLANDITE:**	annabergite = hydrous arsenate
	BISMUTH: rare but in some skarns **SILVER:** native metals rare **COPPER:** native metals rare **PLATINUM:** inclusions of sulphides may indicate sources	**ILMENITE AND MAGNETITE:** composition and micro element concentrations are diagnostic of deposit type **MONAZITE:** inclusions of ore minerals important			**CHALCOPYRITE:**	native copper metal and copper sulphides cuprite tenorite } oxides malachite azurite } carbonates chrysocolla = silicates atacamite marshite } halides
	RUTILE: when associated with porphyry copper deposits, red in colour; micro element concentrations are diagnostics: high Cu, depletion of Nb and Ta	**NIOBITE-TANTALITE:** **PYROCHLORE:** **GADOLINITE:** **BERYL:**			**MOLYBDENITE:**	ferrimolybdite = oxide powellite wulfenite } molybdates
					SPHALERITE: Cd = micro element diagnostic enrichment in specific deposit types	hemimorphite = silicate smithsonite zincian calcite } carbonate
					FLUORITE:	wurtzite = sulphide

TABLE 1

RELATIVE CHEMICAL STABILITY OF PRIMARY MINERALS IN THE ZONE OF WEATHERING

	VERY STABLE	STABLE	FAIRLY STABLE	UNSTABLE
ROCK FORMING MINERALS AND ACCESSORIES	QUARTZ: CORUNDUM: SPINELS: Sn composition diagnostic of tin skarns-malayaite fluorescence TOPAZ: TOURMALINE: composition micro element concentrations may be diagnostic of deposit type ZIRCON:	ALKALI FELDSPAR: SODIC PLAGIOCLASE: MUSCOVITE: Cr, F, Li, etc. diagnostic of deposit types and source ANDALUSITE: GARNET: composition and micro element concentrations are important in recognizing skarn type KYANITE: SILLIMANITE:	ACTINOLITE: APATITE: enriched chlorine compositions when related to porphyry copper deposits= flourescence diagnostic bright orange FLUORAPATITE: enriched in sedex ? deposits=hanging-wall, Howards Pass, Yukon CHLORITOID: DIOPSIDE: EPIDOTE: STAUROLITE:	AMPHIBOLES(MOST): BIOTITE: CALCIC PLAGIOCLASE: CALCITE: DOLIMITE: FELDSPATHOIDS: GLAUCONITE: GYPSUM: OLIVINE: PYROXENE:

TABLE 2

Data for Tables 1 and 2 from Andrews-Jones, 1968; Williams and Cesbron, 1977; and authors research.

of clastically transported elements. For some elements, (such as zinc), it is possible to <u>miss</u> anomalies if only HMC values are determined since stable clastically transported zinc-bearing minerals may not be present in the heavies.

Normally, however, the concentration factor inherent in HMC sampling ensures that element contents are significantly enriched so that any analytical detection limit problems are overcome.

Active placer mining is now forbidden in the state of California and many other states, but weekend hobby placer gold prospectors can be found 'snipping' for gold in stream sediment. This 'modern gold rush' has produced a whole new 'technological' industry backed by the Gold Prospectors Association of America. Coloured plastic gold pans of numerous sizes, shapes and riffle effects, fully back-packing dredges and micro-sluice boxes, mini shaker tables, gold wheels, spiral and screw pans, various sizing, screening and classifying systems, fine gold recovery matts and of course, gold locating devices (metal detectors) have been developed and marketed - the object to find, separate and concentrate heavy minerals. The gold 'sniper' is generally satisfied with the recovery of very fine gold (flour) and much of the product development has been to enhance the recovery of very fine heavy minerals from <u>numerous</u> test locations. Does this sound like a geochemical exploration sampling program for heavy minerals using portable efficient field separation techniques?

Plastic gold pans have been tested in the Cordillera but generally we have been slow to adapt other separation, classification and concentration methods and equipment. Although most of the equipment was developed solely for gold recovery, the geochemist-explorationist should be able to easily adapt and certainly enhance the total heavy mineral suite recoveries by using this equipment. Since one can and should be using heavy mineral concentration prospecting methods in the search for porphyry copper-gold deposits and for base metal massive sulphide deposits, I believe that improved stream sampling methods warrant much more attention.

F. Marshall Smith Consulting Ltd. reported at the GEOEXPO '86 Conference, Vancouver, at the AEG Heavy Mineral Workshop that small portable suction dredges could be used for sample collection and preliminary concentration of heavy minerals in Canadian Cordillera streams. The back-packing dredge and pump weighed only 9.5 lbs. I have recently seen advertisements for a light weight (15 lb.) gas powered vacuum that "cleans crevices, moss and drywashes of all wet and dry concentrates". The point of using a portable dredge or vacuum is to get to the most suitable site on the stream drainage to be tested. The mechanical dispersion of grains from the source to this site of preconcentration (eliminate the dilution effect of light particles) varies with time (floods, intermittent water flow). The optimum time of collection in any of the various regions of the Canadian Cordillera could be significantly different since the degree of sorting of the stream's bedload material is critical in the enhancing of its HMC contents.

These effects do not hamper a heavy mineral concentrate survey of black sands taken from the sluices or tables of active placer gold mining operations. Mother Nature has already sorted the heavies into the so-called pay-streak or channel and they have been preserved and 'frozen' in time until the placer operator digs them up. The placer operator then sorts and classifies this material, washes it and finally HMC are recovered in a variety of ways. If the heavy mineral explorationist can obtain a portion of HMC particles from the first 5 riffles of the various sizes of sluices in the run then he is assured that this sub-population can yield information of exploration significance (See details in Atlin Placer Gold Section). Most placer gold camps have poor bedrock exposure and thus any detailed data on rock and ore forming minerals within the buried drainage is of assistance.

Today, with modern SEM's and microprobes, accurate mineral identifications of heavy mineral concentrates are possible and greatly improved. Important ore mineral grains (primary or secondary) can be identified on a single grain basis. The micro-geochemistry (majors, minors and traces) of minerals is very important in identifying potential ore deposit models and the sources. (See Tables 1 and 2)

Mineral and/or sulphide inclusions found within heavy mineral grains recovered from streams can be used to suggest the potential for primary buried mineralization within the drainages. Although microprobe and SEM analysis of heavy mineral grains may seem 'unconventional' the diagnostic results can perhaps be more easily interpreted than analytical results. Non-destructive analytical methods (INAA) allow for the mineralogical examination of the grains after analysis and cool down periods. When dealing with HMC analytical determinations the user must be aware of what element concentrations are total, partial or have no reliability because of interferences with other elements that are present in high concentrations. Often HMC chemical analysis can be like complex ore determinations.

Specific chemical attacks may be required, and costly assay determinations must be made by lengthy destructive procedures. In any event, mineralogical micro-geochemistry on selected heavy minerals may be just as cost effective and more specific to a ore deposit model than chemical analysis.

Hydrogeochemistry

Elements which are relatively mobile in the near surface environment (U, Mo, Zn, Cu, Pb, Fe, S) travel in solution either in groundwater or surface water, or both media. Hydrogeochemical sampling is thus particularly applicable to this suite of conventional-elements, but a wider range of elements can be expected to be utilized in the future (see Gold Hydrogeochemical Section). With advancing technology and the necessity of discovering blind ore bodies and/or new environmental requirements it will be in the best interests of the explorationist to define the size and contrast of the aqueous halo around a particular deposit.

The applicability of hydrogeochemical exploration techniques using stream waters is not well documented or well researched (?). During the early days of porphyry Cu exploration, Cu was measured in spring and stream waters. Workers became painfully aware that the wide range of conditions unique to the various terrain types in the Canadian Cordillera could drastically affect exploration programs. Levels of pH were found to be an important factor which influences significantly the concentrations of most elements in aqueous solution. It was found that for most metals there is a considerable decrease in the solubility of the metal, as pH increases from 4 to 7. Now base metals are again becoming of interest to the exploration community. Basic principles to detect a hydrogeochemical anomaly and resultant chemically dispersed stream sediment anomalies must be reviewed in light of past experience. Examples are given in the case history section.

Hydrogeochemical exploration for U is particularly successful. After GSC orientation surveys, U, F and pH determinations in stream waters became a standard medium for NGR-URP surveys in 1976 (Ballantyne et al., 1976, 1978). Hydrogeochemical sampling was expanded for some NGR surveys and today with advances in technology, solution concentrations of elements usually measured in the ppb range are being routinely lowered to ppt levels. It will become more important in the future to initiate, at an early exploration stage, water sampling programs within particular stream drainages. The need for background water data is here to stay; so why not combine future environmental requirements into geochemical exploration programs? The water data will greatly help interpretation of element distribution patterns found in other media. Those explorationists that re-acquaint themselves or start geochemical water sampling now will be better prepared to defend Mother Nature's anomalies as facts of life (during the permitting process) and most importantly, will be able to perhaps discover blind deposits in the future.

All chemical and clastic dispersion processes need water during stream drainage development. Water (surface and groundwater) was very important in the past in creating the specific environment for stable secondary mineral formation during the weathering process (Tables 1 and 2). We must always consider past influences on aqueous haloes. We must often place restraints on the applicability of any particular geochemical sampling methodology used today because of past weathering processes and factors.

For example, exploration for Cu-Au porphyry deposits of the Mount Milligan type are currently an exploration focus in B.C. Hydrogeochemical factors helped during the development of weathered products of these deposits. Perhaps transition zones and/or supergene zones of different copper minerals and liberated gold were formed. Hydromorphic dispersion of copper and sulphur could have been extensive. Glaciation came and removed portions, or all, of the pre-existing weathered profile. During glacial-fluvial processes, resistate minerals, stable secondary Cu minerals, native copper and gold, and primary copper sulphides were mixed in till and or perhaps concentrated in glacial outwash material. Today streams cut through these materials and surface and ground water drainage enters streams. If no sulphides are oxidizing in the 'overburden' the geochemical response to Cu in water will be reduced or negligible even though native copper and stable copper minerals are present in abundance in the glacial material. Native copper metal and/or other copper secondaries may enter the stream during surface run off, bank collapse etc. The 'silt' sampler is collecting material under the assumption that Cu is being dispersed hydromorphically. Analytical methods are also selected under this assumption. Results for 0.2-0.5 g of stream sediment, weakly digested and then analyzed by ICP give low to 'spikey' Cu results. Follow-up fails to reproduce the single site Cu anomalies but it is hard to walk away from the stream drainage because of the elevated and reproducible Au results. Exactly the same problems have arisen during interpretation of soil grids during first stage follow-up surveys. Why?

We have learned about 'nugget' gold effects (analytical sample size) and 'coarse' VG gold (metallic analysis, actual gold size) problems and these have been overcome largely by increasing the sample weights used for a variety of gold analyses. The concept of check and re-analysis of high gold samples by other methods is usually a standard approach to obtaining reliable gold concentration data. However, in our example the native copper 'nuggets', sulphides, stable secondaries etc. were not considered to be present as 'clastic' or resistate grains. Discrete copper grains of variable size and shape (like gold particles), may or may not be present in the tiny sediment or soil sample weight that is usually analyzed. False expectations that copper is present as a product of hydromorphic processes has led to frustration during efforts at interpretation. Hydrogeochemical methods may have worked in the past during the first weathering cycle of the Cu-Au deposit. Now within the context of a transported anomaly removed from the buried 'in situ' deposit, water can only help by the concentration of heavies in the present day stream sediment. In the situation described, the requirements for useful and reproducible Cu analysis are the same as those for Au; beware of nugget effects and analyze large samples by a variety of methods. Heavy mineral sampling is recommended.

The exploration problem described above has been examined and verified at numerous locations within the Quesnel Trough (Ballantyne et al, in press).

The 'power' of water, (past and present), to affect the success or failure of geochemical exploration programs should be better appreciated. We will further examine some case histories involving water (stream-spring) and clastic and hydromorphic transport in stream drainages.

DATA INTERPRETATION - CASE HISTORY EXAMPLES

Regional Data - Discovery of the Unknown

Table 3 provides summary statistics compiled by D.J. Ellwood and S.B. Ballantyne in 1984 for some 31,441 NGR sample sites covering an area of 412,313 square kilometres throughout the Canadian Cordillera. This analytical data, taken from 15 NGR Open File Reports, was compiled as a guideline to explorationists. The survey areas cross all

Table 3 : Summary statistics (31212 samples) for Canadian Cordillera minus 177 micron stream sediments and stream waters from National Geochemical Reconnaissance data set compiled for data released to December 1984, by D.J. Ellwood and S.B. Ballantyne, Geological Survey of Canada.

VARIABLE NAME	UNITS	N	MINIMUM	MAXIMUM	MEDIAN	GEOM MEAN	ARITH MEAN	PERCENTILES				
								1st	2nd	5th	10th	20th
Zn	ppm	31211	2.	12000.	68.	72.3	109.2	15.	18.	24.	31.	40.
Cu	ppm	31212	1.	2850.	22.	21.8	30.1	3.	4.	6.	8.	12.
Pb	ppm	31208	1.	4500.	6.	5.7	12.4	1.	1.	1.	1.	2.
Ni	ppm	31212	1.	2050.	20.	18.7	31.2	1.	2.	4.	6.	9.
Co	ppm	31212	1.	550.	9.	8.8	11.1	1.	1.	3.	4.	5.
Mn	ppm	31212	5.	75000.	420.	432.8	639.1	70.	90.	130.	170.	235.
Fe	pct	31212	.05	32.25	2.10	2.008	2.305	.35	.50	.80	1.05	1.35
Used	ppm	31081	.1	430.0	3.2	3.59	5.97	.5	1.0	1.0	1.4	2.0
Mo	ppm	31213	1.	475.	1.	1.6	2.3	1.	1.	1.	1.	1.
Hg	ppb	20009	5.	99999.	40.	42.6	73.3	5.	5.	10.	10.	20.
Ag	ppm	31206	.1	39.0	.1	.12	.16	.1	.1	.1	.1	.1
As	ppm	12885	.2	1000.0	3.0	3.56	10.29	.5	.5	.5	.5	1.0
Sb	ppm	7152	.1	54.5	.4	.41	.96	.1	.1	.1	.1	.1
W	ppm	27806	1.	1200.	2.	1.9	2.9	1.	1.	1.	1.	1.
Sn	ppm	5192	.5	520.0	1.0	1.72	3.46	.5	.5	.5	1.0	1.0
Ba	ppm	10144	20.	17000.	800.	865.0	1657.4	140.	200.	280.	370.	490.
UWAT	ppb	30345	.01	89.80	.10	.105	.405	.01	.01	.02	.02	.02
FWAT	ppb	30363	5.	9600.	40.	40.4	69.0	10.	10.	10.	10.	20.
pH	pH	30605	2.3	9.1	7.6	7.49	7.52	5.4	6.0	6.5	6.8	7.0

	PERCENTILES											
	25th	30th	40th	50th	60th	70th	75th	80th	90th	95th	98th	99th
Zn	45.	50.	58.	68.	80.	95.	105.	118.	174.	265.	500.	865.
Cu	14.	15.	18.	22.	26.	32.	36.	42.	56.	75.	105.	137.
Pb	2.	3.	5.	6.	8.	11.	12.	15.	24.	36.	60.	96.
Ni	11.	13.	16.	20.	24.	29.	32.	37.	57.	86.	148.	235.
Co	6.	7.	8.	9.	11.	12.	14.	15.	19.	24.	34.	43.
Mn	260.	290.	350.	420.	501.	615.	690.	780.	1100.	1600.	2600.	3800.
Fe	1.50	1.60	1.85	2.10	2.40	2.70	2.90	3.10	3.75	4.30	5.10	5.85
Used	2.0	2.3	2.8	3.2	3.9	4.7	5.5	6.5	14.2	18.2	33.7	51.0
Mo	1.	1.	1.	1.	1.	2.	2.	3.	4.	7.	12.	18.
Hg	20.	30.	40.	40.	60.	70.	80.	90.	130.	180.	290.	410.
Ag	.1	.1	.1	.1	.1	.1	.1	.1	.2	.4	.8	1.1
As	1.0	1.5	2.0	3.0	5.0	7.5	9.0	12.0	22.8	37.2	70.0	105.0
Sb	.2	.2	.2	.4	.4	.6	.8	1.0	2.0	4.0	7.4	10.2
W	1.	2.	2.	2.	2.	2.	2.	2.	4.	6.	14.	25.
Sn	1.0	1.0	1.0	1.0	1.0	2.0	3.0	5.0	8.0	11.0	19.0	32.0
Ba	540.	590.	680.	800.	920.	1100.	1200.	1400.	2250.	3750.	7000.	9999.
UWAT	.02	.05	.05	.10	.14	.24	.30	.42	.84	1.60	3.00	4.60
FWAT	22.	26.	32.	40.	50.	62.	72.	86.	140.	210.	360.	500.
pH	7.2	7.3	7.4	7.6	7.8	7.9	8.0	8.1	8.2	8.3	8.5	8.5

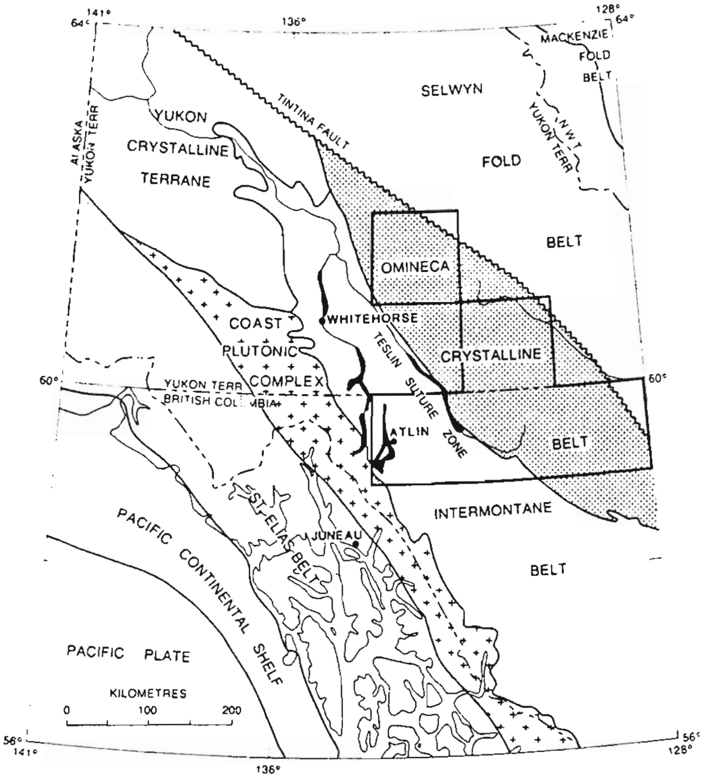

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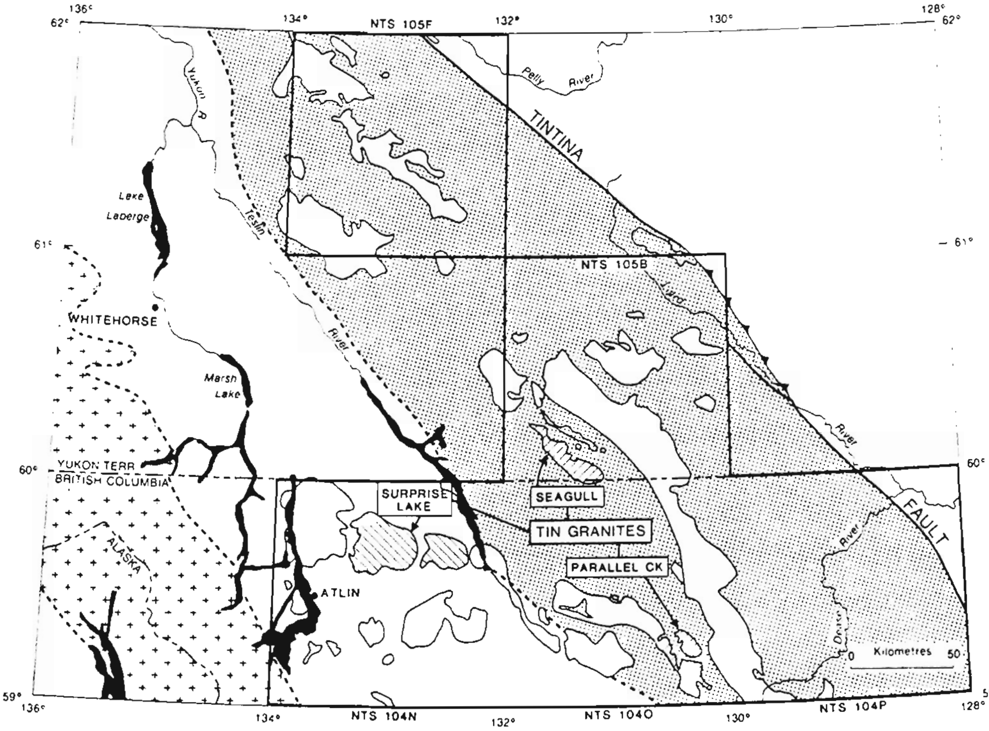
Fig. 1 Tectonic belts of the Cordilleran Orogen, location map NGR study.

Simplified distribution of granitoid intrutions: Specialized plutons are cross hatched.



Cordilleran litho-tectonic assemblages, the Coast Mountain ranges, interior plateaus, the arid Okanagan region and north of 60° N to the Beaufort Sea. Voluminous geochemical data for a large area maybe consolidated, compiled and portrayed by computer generated maps. Single element abundance and distribution maps are often produced with variable colours based on percentile intervals of the entire population. The identification of broad regional geochemical trends or patterns, as well as the characterization of geochemical enrichments, depletions and background concentrations are an obvious result. When attempting to define anomalies the user is cautioned, however, that local geological conditions and environmental factors within a specific local drainage basin are often more important than the absolute concentration level measured for any particular element.

Specialized Granites - Surprise Lake Batholith

As an example of interpretation of NGR regional stream sediment and water data, we will first examine 4400 sample sites in an approximately 62,000 square kilometre area stretching from Rancheria, southern Yukon, to the town of Atlin in northwestern British Columbia. The study area is underlain predominantly by Intermontane Belt, Cache Creek Group Atlin Terrane rocks and Omineca Crystalline Belt, metamorphic-plutonic rocks (Fig. 1). Figures 2, 3, 4, 5 and 6 are 1:3,000,000 scale black and white versions of a method of contouring which filters out minor irregularities and allows ready appraisal of major geochemical trends and patterns.

A simplified distribution of Cretaceous-Tertiary granitoid intrusion is outlined. Of course, the distribution of fluorine in stream water (Fig. 6) represents hydromorphic dispersion. The single element distribution maps for zinc and molybdenum are assumed to be generally chemically dispersed because of their broad patterns (Fig. 2, 3).

Distribution maps for tungsten and tin display confined dispersion patterns closely associated with specific granitoids (Fig. 4, 5). The restricted patterns are typical of mechanically dispersed element and mineral trains.

This suite of NGR elements (Zn, Sn, W, Mo and F) clearly defines the anomalous bedrock geochemistry related to 'specialized' granitoids. Follow-up geochemical surveys defined replacement, griesen and quartz-vein, granite-hosted, mineralization and tin, tungsten and 'wrigglite' skarns related to the 'specialized' granites.

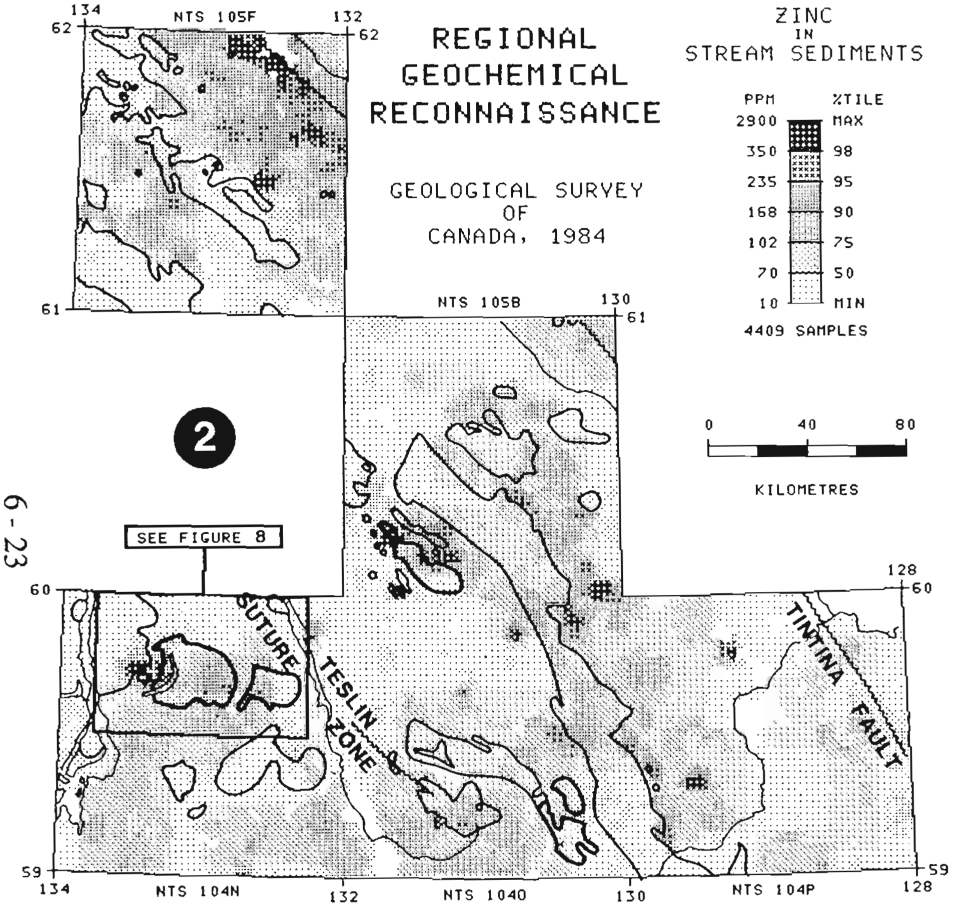


Fig. 2 Distribution of zinc in stream sediments. Granitoids are outlined.

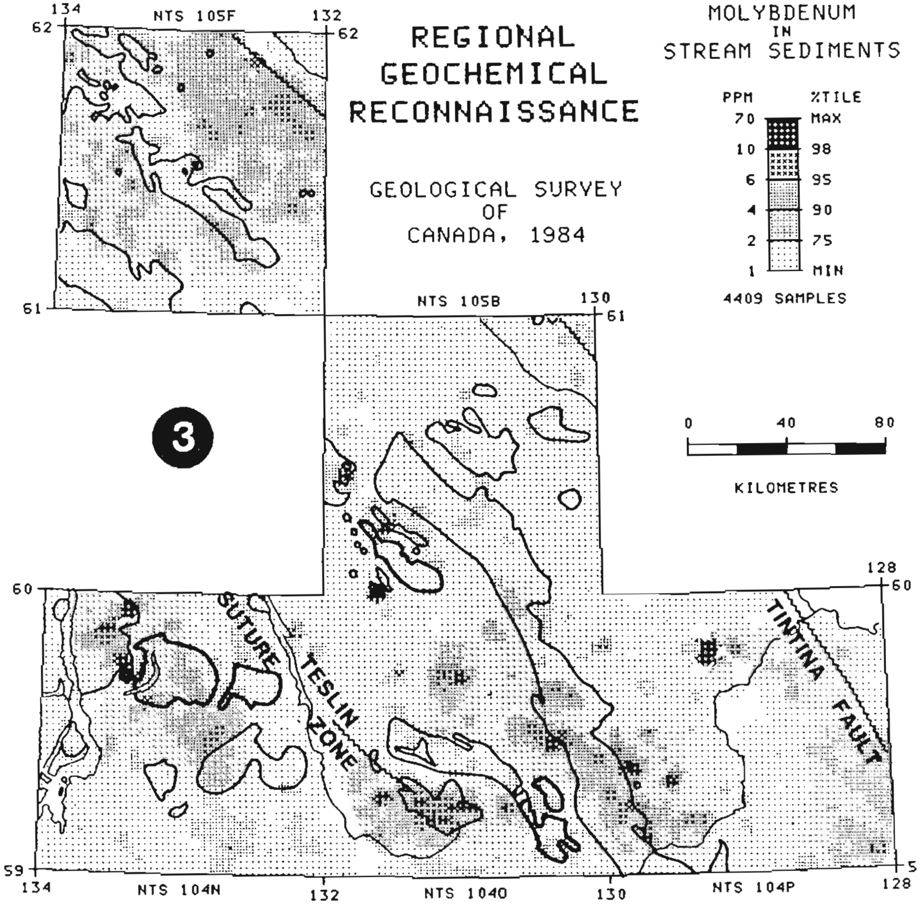


Fig. 3 Distribution of molybdenum in stream sediments. Granitoids are outlined.

Patterns are typical for elements which are hydromorphically dispersed under alkaline conditions.

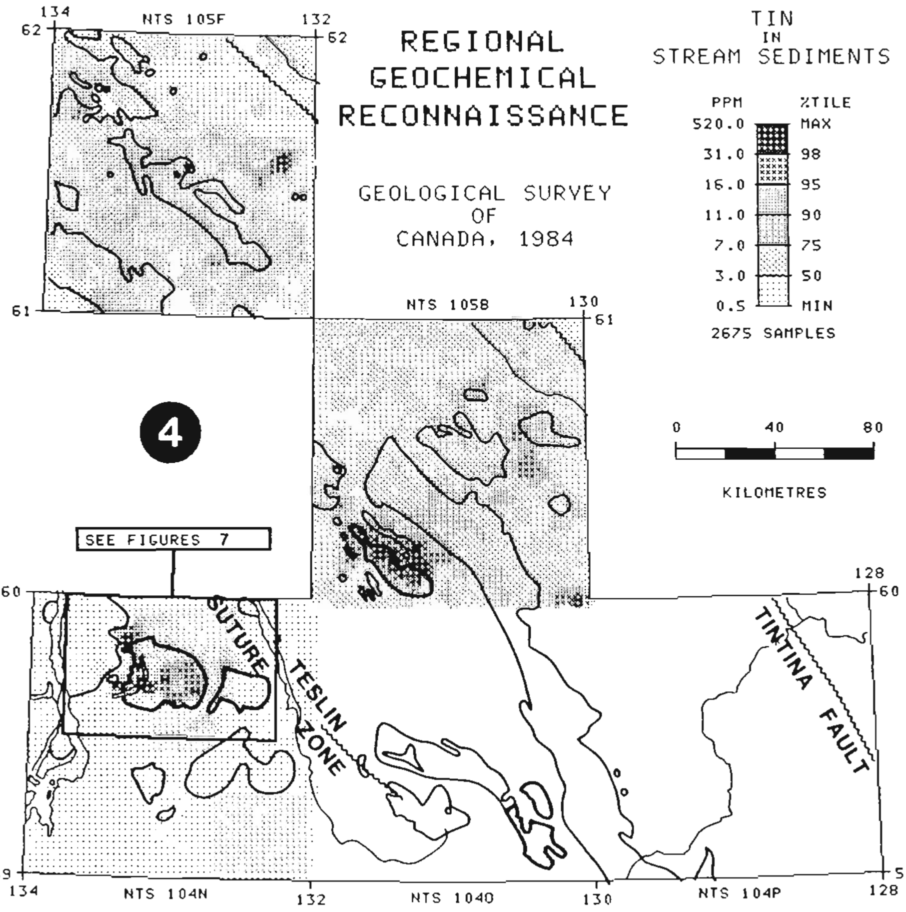


Fig. 4 Distribution of tin in stream sediments. Granitoids are outlined. White areas indicate no data.

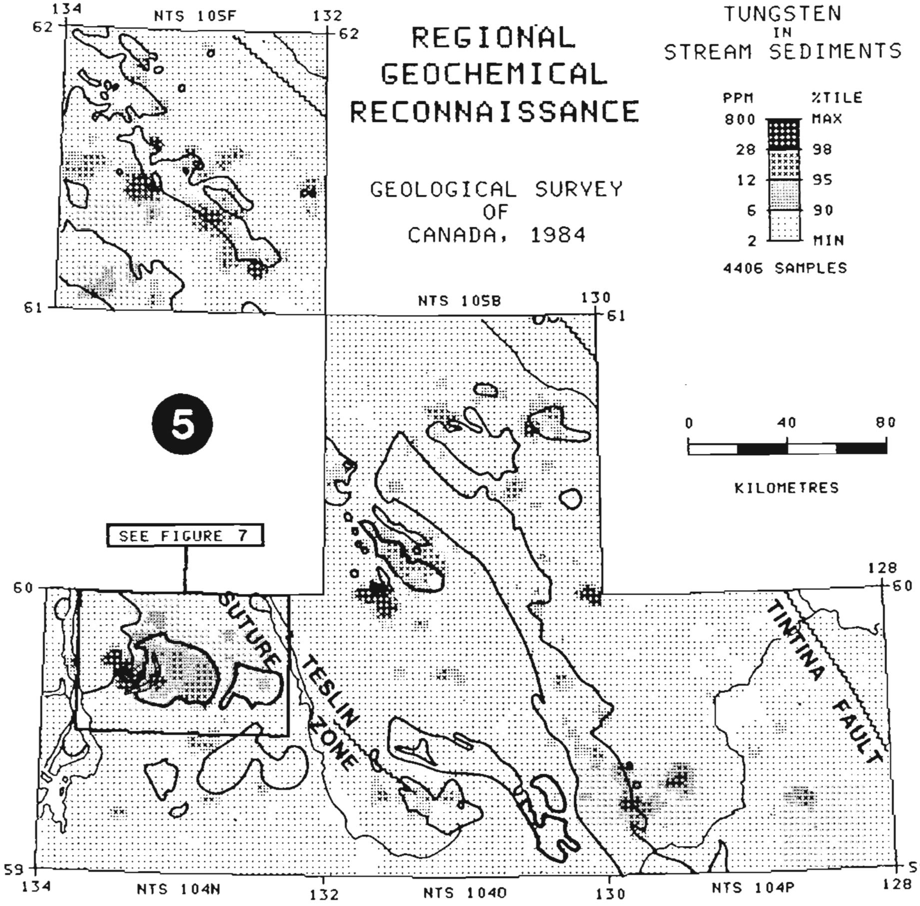


Fig. 5 Distribution of tungsten in stream sediments. Granitoids are outlined.

Patterns are typical for elements which are clastically dispersed.

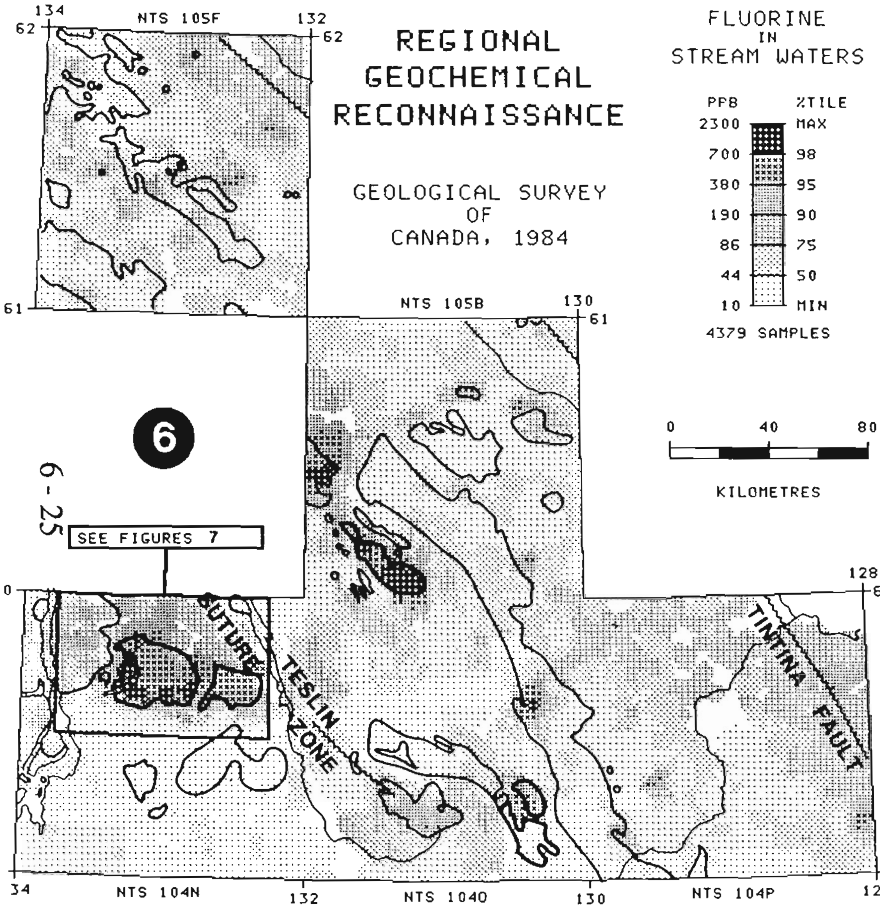


Fig. 6 Distribution of flourine in stream waters. Cretaceous-Tertiary granitoids are outlined; stanniferous plutons are outlined in bold.

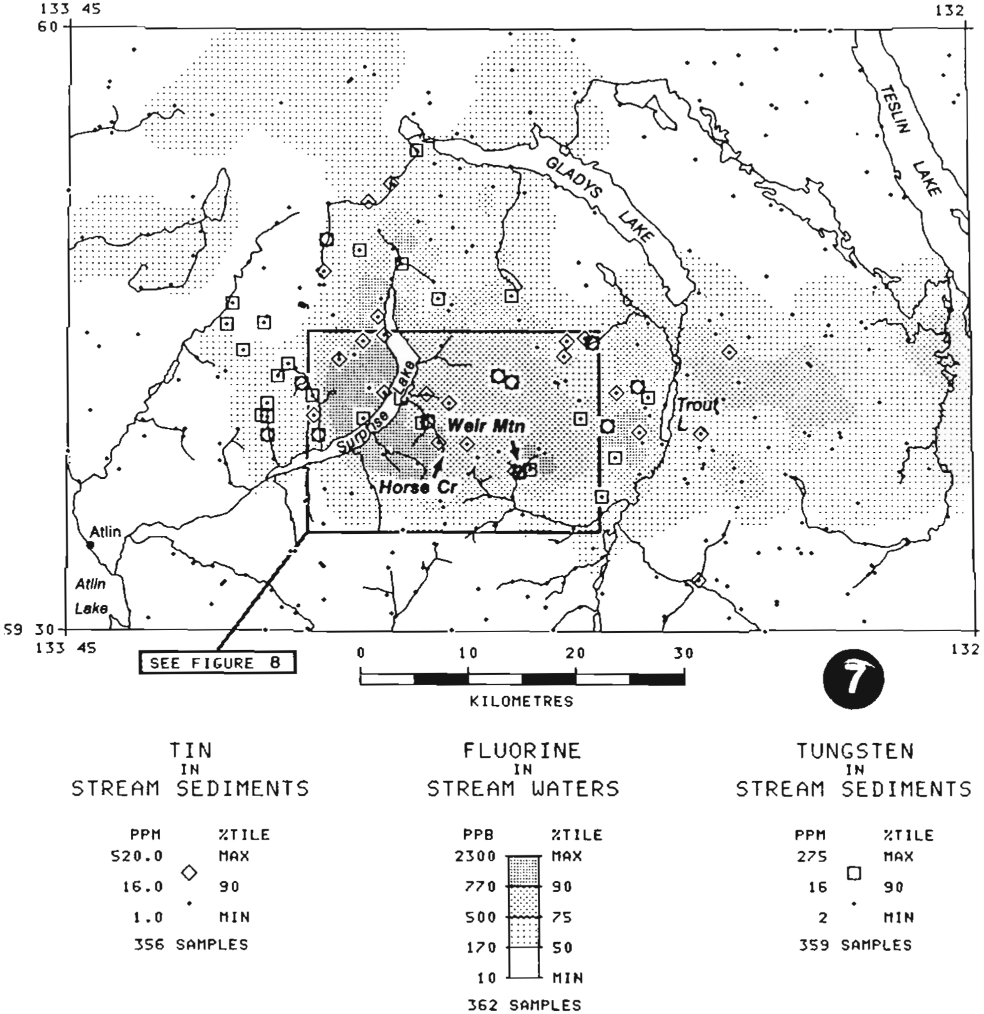


Fig. 7 Distribution of tin and tungsten in stream sediments and flourine in stream waters in the Surprise Lake batholith area, Atlin, British Columbia.

REGIONAL STREAM AND LAKE SEDIMENTS
WEIR MOUNTAIN STUDY AREA

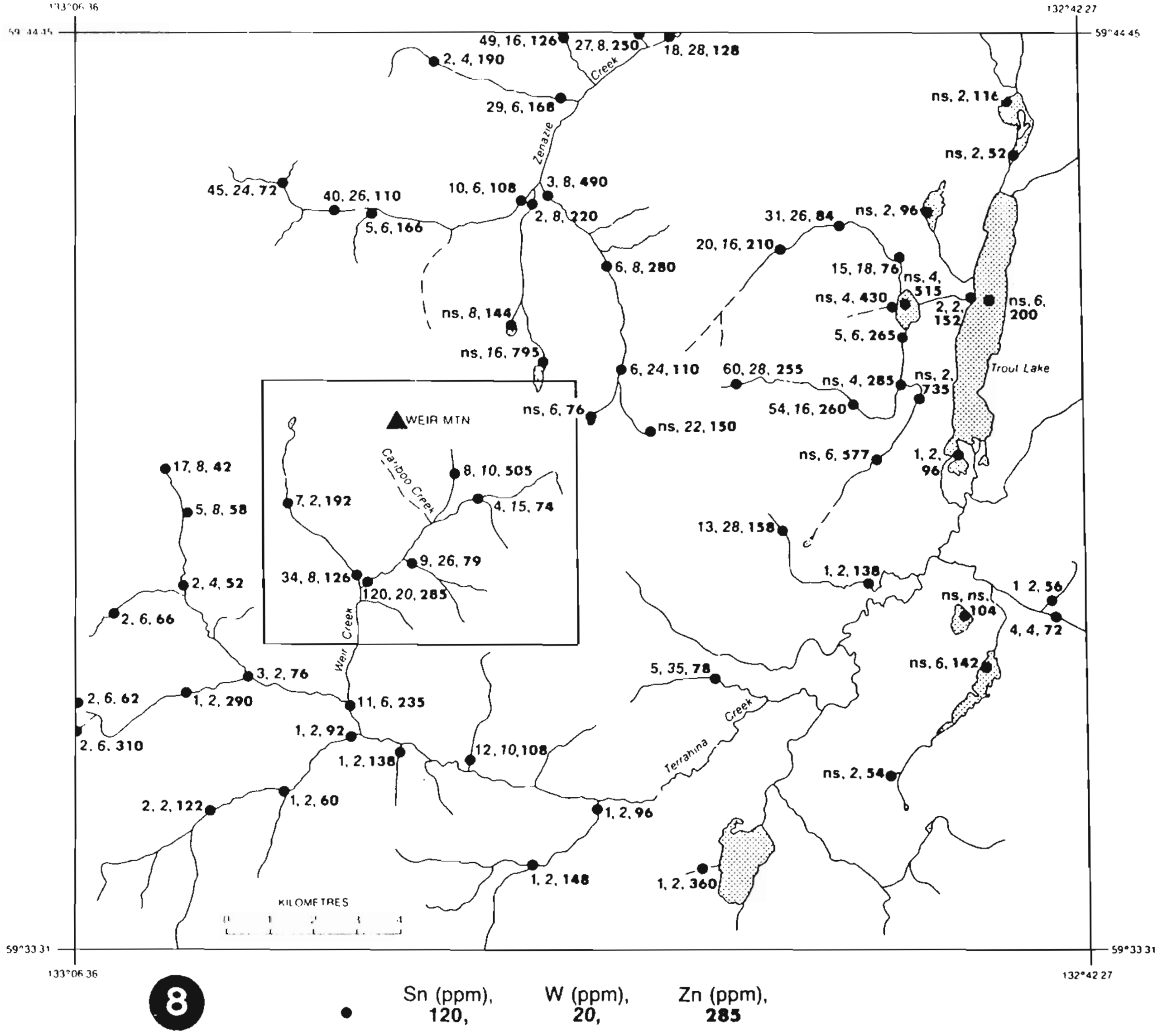


Fig. 8 Concentration of tin, tungsten and zinc in regional stream and lake sediment samples, Weir Mountain study area. Values posted at each site represent tin, tungsten and zinc in that order. Insufficient material for analysis is represented by "ns". Area covered by Figure 11 is outlined.

When outlining targets worth prospecting within a given NGR survey area, it is imperative that associations between the various analytical variables of the multi-element data set be examined. Associations between three elements can be plotted on the same map, two elements as symbols which are proportional to percentile intervals of the data, and the other element underlying as a contoured variable. The Surprise Lake batholith area east of Atlin, B.C. was shown to be a 'specialized' granite within the reconnaissance 1:3,000,000 scale survey area. The fluorine in stream water and tin and tungsten in stream sediment data (Fig. 7) are shown as an example of the application of multi-element plotting. This is an effective way to manipulate sample site data and summary statistics to define element associations and anomalies. It allows easy visual comparisons of three elements at, and between, each sample site. It is not based on correlation statistics of the whole data set which commonly do not establish obvious multi-element associations or coincident element anomalies at single sample sites. Figure 7 and 8 illustrate examples of enrichment, depletion and apparent zoning of zinc, tin, tungsten and fluorine within the Surprise Lake batholith. The distinctive stream geochemistry for the Weir Mountain and Horse Creek drainage systems were examined by detailed follow-up surveys. The study included size fraction analyses of stream sediment and heavy mineral panned concentrate material.

Horse Creek

Horse Creek is a relatively fast flowing stream with steep relief and a major break-in-slope at its mouth. Results and sample locations are illustrated in Figures 9 and 10. Heavy mineral panned concentrate and stream sediment sampling were conducted at suitable locations within the drainage. Wherever possible, sites were selected so that direct comparisons of the sample media and various size fractions could be made. Regional NGR sample concentrations are given for comparison to the detailed survey (Fig. 9). Previously unknown tin-tungsten mineralization found during the survey is marked by the crossed hammer symbol. Detailed interpretation of the results are given in Ballantyne and Ellwood, 1986, however, the geochemical prospector should note that:

1) the greatest concentrations of the elements tin and tungsten and therefore their heavy minerals is found at the mouth of the Horse Creek. However, the magnitude of the anomalous regional NGR contents was not repeated in

HORSE CREEK STUDY AREA

9

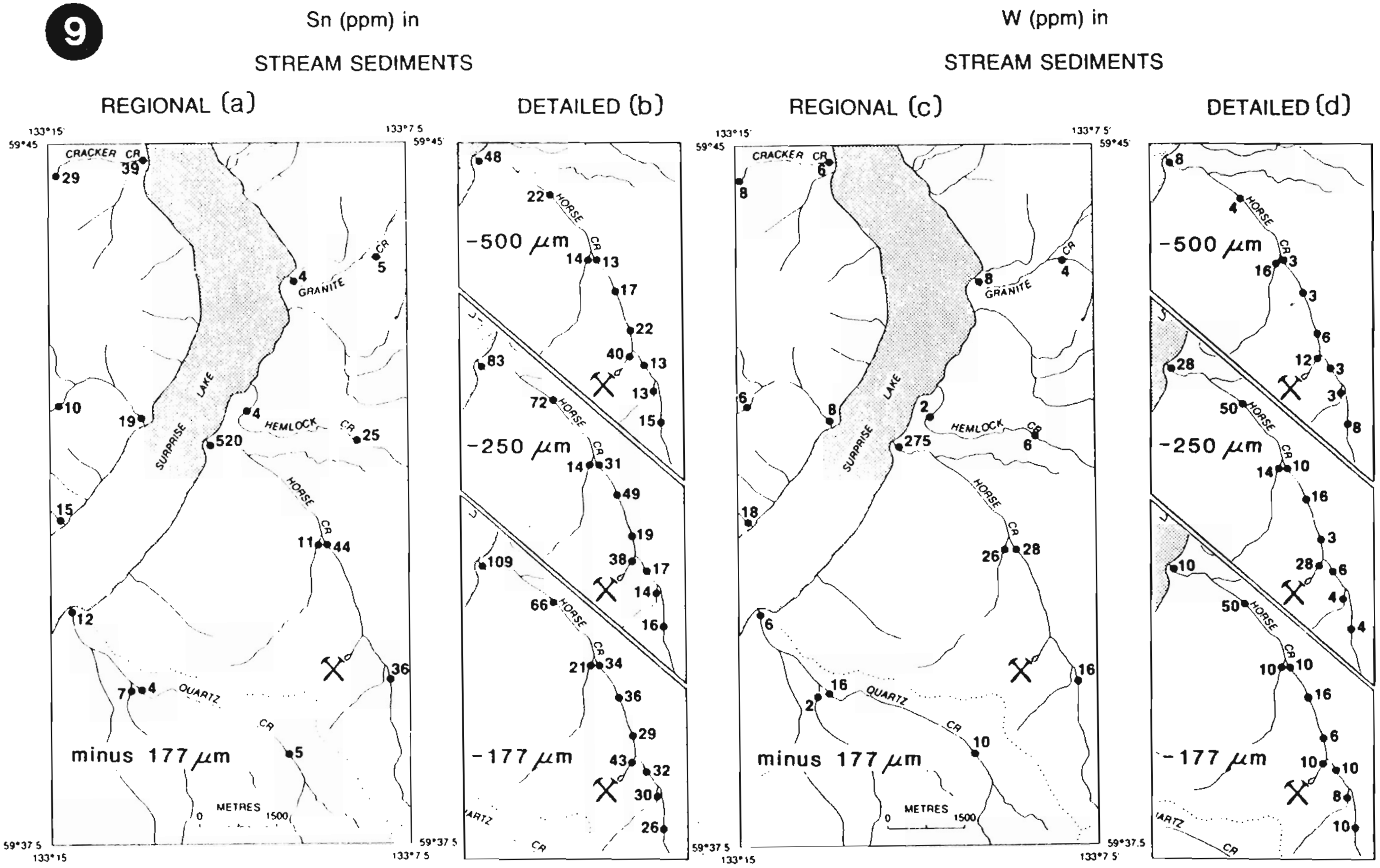


Fig. 9 a) Concentration of tin in regional stream sediment samples, Horse Creek study area.

b) Concentration of tin in three size fractions of detailed stream sediment samples, Horse Creek study area.

c) Concentration of tungsten in regional stream sediment samples, Horse Creek study area.

d) Concentration of tungsten in three size fractions of detailed stream sediment samples, Horse Creek study area.

detailed stream sediment sampling. This fluctuation in absolute contents is typical of mechanically dispersed mineral and element trains. Mineralogical examination of HMC showed the presence of cassiterite and wolframite grains.

2) Although not 'conventional', size fraction analysis may define the prospect area more specifically. Tin and tungsten levels reported for the coarser sized fractions for tributaries draining the mineralized zone have generally higher contents than samples on the main creek.

3) The areal distribution of anomalous HMC (Fig. 10) are coincident with results obtained for the various size fractions reported for the unpanned sediments. They show a greater contrast over sediments. The tin contents of the HMC sample located on the main Horse Creek drainage immediately below the tributary draining the mineralized zone contains tin contents two times, five times, and eleven times greater than the same size fractions of unpanned sediments. The tungsten contents in the minus 177 micron fraction of HMC range up to twenty-one times greater in the HMC.

4) Since all sample sites on a drainage are not suitable for HMC sampling, supplementary unpanned sediment samples helped to define and confirm anomalous results from HMC sampling. HMC sampling results can define specific prospecting areas within a catchment area.

5) The minus 2 mm plus 500 micron size fraction has the most elevated values for tin and tungsten at the HMC sample site closest to the headwaters of the Horse Creek drainage. This illustrates the mechanical sizing process at work by various factors within a high energy environment stream drainage system.

Weir Mountain

The Weir Mountain - Weir Creek area (Fig. 7, 8) was identified within the region NGR data as a Sn-F-Zn anomalous drainage with minor W anomalies on the periphery. Similar to the Horse Creek drainage, this area is totally underlain by leucocratic phases of the Surprise Lake batholith. The greatest enrichment of Sn on Weir Creek (120 ppm) is found at a confluence downstream from the Cariboo Creek (Fig. 8). Zinc anomalies are often greater than the 95th percentile of the data presented in Table 1, a perhaps surprising

10 HORSE CREEK STUDY AREA

HEAVY MINERAL CONCENTRATE FRACTIONS

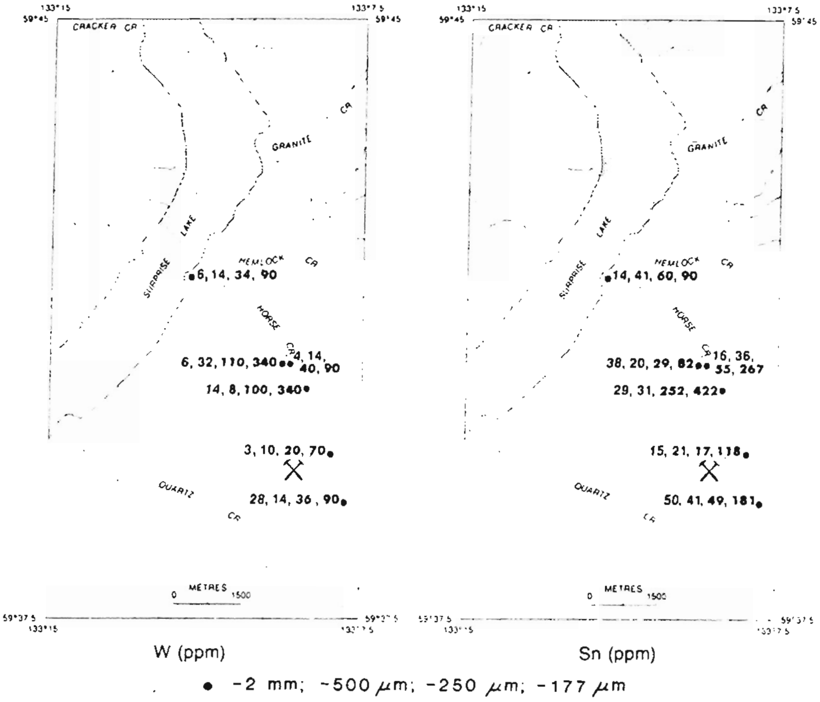


Fig. 10 Concentration of tin and tungsten in four size fractions of detailed heavy mineral panned concentrates, Horse Creek study area. The values at each site are posted in order of their grain size from coarse to fine.

11 Sn (ppm) IN HEAVY MINERAL CONCENTRATE FRACTIONS

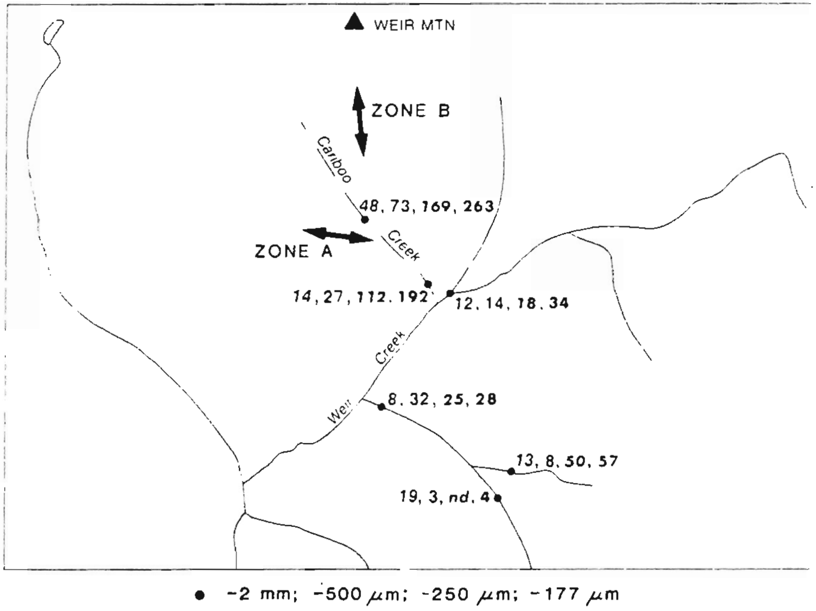


Fig. 11 Concentration of tin in four size fractions of detailed heavy mineral panned concentrates, Weir Mountain study area. The values at each site are posted in order of their grain size from coarse to fine. Insufficient material for analysis is represented by "ns". Mineralized zones are indicated.

result for drainages within a high-silica-fluorine granite (Fig. 8). During the follow-up survey, detailed sampling upstream from the enriched tin-zinc regional anomaly on Weir Creek was conducted using HMC panned material.

The contents of tin in four size fractions of HMC are reported in Figure 11 where Cariboo Creek is clearly shown to be the source of tin for the Weir Creek drainage system. Compared to the anomalous regional NGR unpanned stream sediment sample containing 120 ppm Sn and 285 ppm Zn, the zinc contents of the various size fractions of HMC showed very little enrichment ranging from 191-333 ppm. The most abundant HMC minerals identified from Cariboo Creek are magnetite, two different colours of cassiterite and gadolinite an yttrium-iron-beryllium silicate with specific gravity similar to cassiterite.

Mineralized zones A and B (Fig. 11) were discovered as a result of the detailed follow-up investigations. The minerals identified in HMC samples were important in the identification of previously unknown tin-bearing zones which consist of (a) quartz greisen veins and veinlets; (b) massive quartz-cassiterite-sericite-beryl greisen; (c) greisen sheeted veins ± fluorite and (d) kasolite and magnetite-sphalerite-galena-biotite replacement veins and pods with minor cassiterite. Classic quartz-wolframite, greisen-bordered, veins are peripheral to the Weir Mountain mineralized system.

The mineralization found to date on Weir Mountain explains the tin-zinc-fluorine and minor tungsten elemental associations found in the NGR regional stream sediment and water data (Fig. 7, 8) and the HMC response of the follow-up study.

The overall approach illustrated by the previous two samples demonstrates a successful geochemical exploration strategy which involved:

1) single element reconnaissance map interpretation of NGR data,
2) regional elemental association geochemical maps (3 elements) to better geochemically define areas of high exploration potential (the "specialized" Surprise Lake Batholith) and specific drainage system targets (Horse Creek and Weir Creek drainages),
3) complimentary stream sediment and HMC sampling utilizing various size fractions,
4) HMC mineral identification,

5) interpretation of results and successful ground investigations which led to the discovery of previously unknown mineralization (tin-tungsten-zinc granite hosted prospects).

Manto Deposits: Midway Deposits

Before leaving the region depicted in Figure 2, 4 and 6 we will re-examine the Zn-F-Sn patterns shown for NTS map areas 105B and 1040. This data was collected by the author and sampling crews in the summer of 1978 operating under NGR-URP survey methodology. Maps and results were released with a resultant 'staking rush' in the summer of 1979. The user should examine GSC Open File 733, 1981. It is a 1:2,000,000 colour compilation series of single element maps for the region.

The Zn anomaly pattern (Fig. 2) straddling the Yukon-British Columbia border in NTS map sheets 105B-1 and 1040-16 drew some immediate attention. Silver anomalies draining Pb-Zn-Ag veins and replacement bodies of the old Silvertip workings were staked on the day of the NGR data release. Barium results were only available for the Yukon data and they helped describe a pronounced coincident Pb, Zn, Ag anomalous pattern (GSC Open File 733, 1981) which stretched into British Columbia to the Silvertip deposit. This multi-element anomaly was actually plotting Upper Devonian-Lower Mississippian, Earn Group rocks hosting baritic 'sedex' model mineralization and stratigraphy not previously mapped as such in the area (Nelson and Bradford, 1987). In the early 1980's, follow-up geochemical surveys and prospecting by Cordilleran Engineering-Regional Resources of Vancouver made important new discoveries, the Midway, Discovery and Silver Creek Deposits. Early exploration was based on a "black-shale" sedex model. The development of a new ore deposit model was required because 1) strong sericitic alteration in noncarbonate lithologies is present, 2) felsic intrusive rocks are present, 3) irregular to replacement, Ag-bearing, massive sulphide mineralization was discovered, and 4) mineralization was hosted within karsted Middle Devonian McDame platformal carbonates. British Columbia now contains manto-silver-lead-zinc mineralization of Late Cretaceous-Eocene age. Ore minerals include galena, sphalerite, arsenopyrite, pyrite, marcasite, chalcopyrite, freibergite, pyrargyrite, geocromite and cassiterite, stannite, franckeite (Nelson and Bradford, 1987; Bradford and Godwin, 1988). Note the NGR regional Sn anomaly on Figure 4 in the extreme south east corner of map area 105B-01. The coincident F anomaly in Figure 6 is also important. The Midway is now an important, yet to be developed resource. (Total reserves in Silver Creek and Discovery areas: 1,185,000 tonnes averaging 410 gpt silver, 7% lead and 9.6% zinc - Canadian Mines Handbook 1990-91, page 380.) Considering the mineralogy, Manto deposits such as the Midway may be expected to reveal distinct and coincident multi-element anomalies in the NGR data. Sedex deposits may show stream sediment enrichments of Pb, Zn ± Ag but the strong Sb, As and Sn-F association and lack of Ba should define magmatic hydrothermal systems which give rise to this Midway manto-style deposit. It is interesting to note that 10 years after the release of the NGR data a Late Cretaceous age epigenetic manto deposit model for Midway has been developed (Bradford and Godwin, 1988). This model includes

1) the recognition of a 5 kilometre long, northwest-trending belt of hydrothermal sericite alteration associated with anomalous fluorine values.
2) mineralogical zoning which is reflected in lead-antimony sulphosalt contents and tin mineralogy (franckeite-stannite)
3) metal zonation Pb:Zn, Ag:Pb, Fe:Cu which is possibly related to distance from the source intrusion.
4) indications of buried felsic intrusions which core and generate large alteration haloes with fluorine, base-metal and lithophile element anomalies.

The exploration success at Midway certainly reinforces the fact that Mother Nature (hydromorphic and clastic dispersion processes) and NGR multi-media and multi-element stream data can define 'specialized' anomalous patterns (Ag, Pb, Zn, Sb, As, F and Sn) which eventually led to <u>new</u> resources and <u>new</u> ore-deposit models for the Cordillera!

The Ba anomaly in the Midway district is related to the Earn Group. It is excellent example of <u>diagnostic</u> stream sediment geochemical mapping of a geologic marker unit within specific stratigraphy. The Midway district Zn, Pb, Ag, Ba, Sn-F multi-element regional anomaly, however, is derived from numerous sources (geologic) and from different ore deposit types (sedex, exhalites, replacement lenses and veins related to Cassiar batholith, and manto bodies) of vastly different ages (Upper Devonian to Eocene). The users of stream drainage geochemical multi-media (water, sediments, HMC) and their resultant derived multi-element suites are cautioned against the dangerous assumption that the chemical and mechanically dispersed coincident or associated anomalous element suite is derived from a single source or deposit type. Geochemical follow-up surveys and prospecting are suggested before an ore-deposit model dependent exploration program is undertaken.

Granite Hosted Zinc - Logan Deposit

Returning to Figures 2 and 4 and map area 105B, note the zinc and tin coincident anomaly patterns associated with intrusive rocks north east of the body of Cassiar Batholith. Some of these anomalies showed silver enrichment. They also drew immediate attention and were staked soon after the NGR data release in 1979. Vigorous exploration by industry has now explained many but, it has been a difficult process of discovery. The Logan property deposits of zinc and silver with minor tin concentrations hosted within regional faults cutting Cretaceous granite are probably the most economically significant. This new type of deposit is interpreted by the author as being an exposed deeper portion of southern Bolivian Ag-Sn distinct ore bodies. Genetic models aside, it is an example of 'sphalerite is where you find it' even in mapped 'pink' granite. I am sure that prior to the NGR data release few explorationists would have planned programs to discover this resource. (Estimated geological reserves 13.6 million tons averaging 6.17% zinc and 0.77 opt silver - Canadian Mines Handbook 1990-91, page 172.) The Logan deposit pointedly suggests that NGR multi-element data should provide a framework for resource assessments especially in areas where few mineral occurrences are known.

Epithermal Bolivian Ag-Sn - Mount Mye Prospect

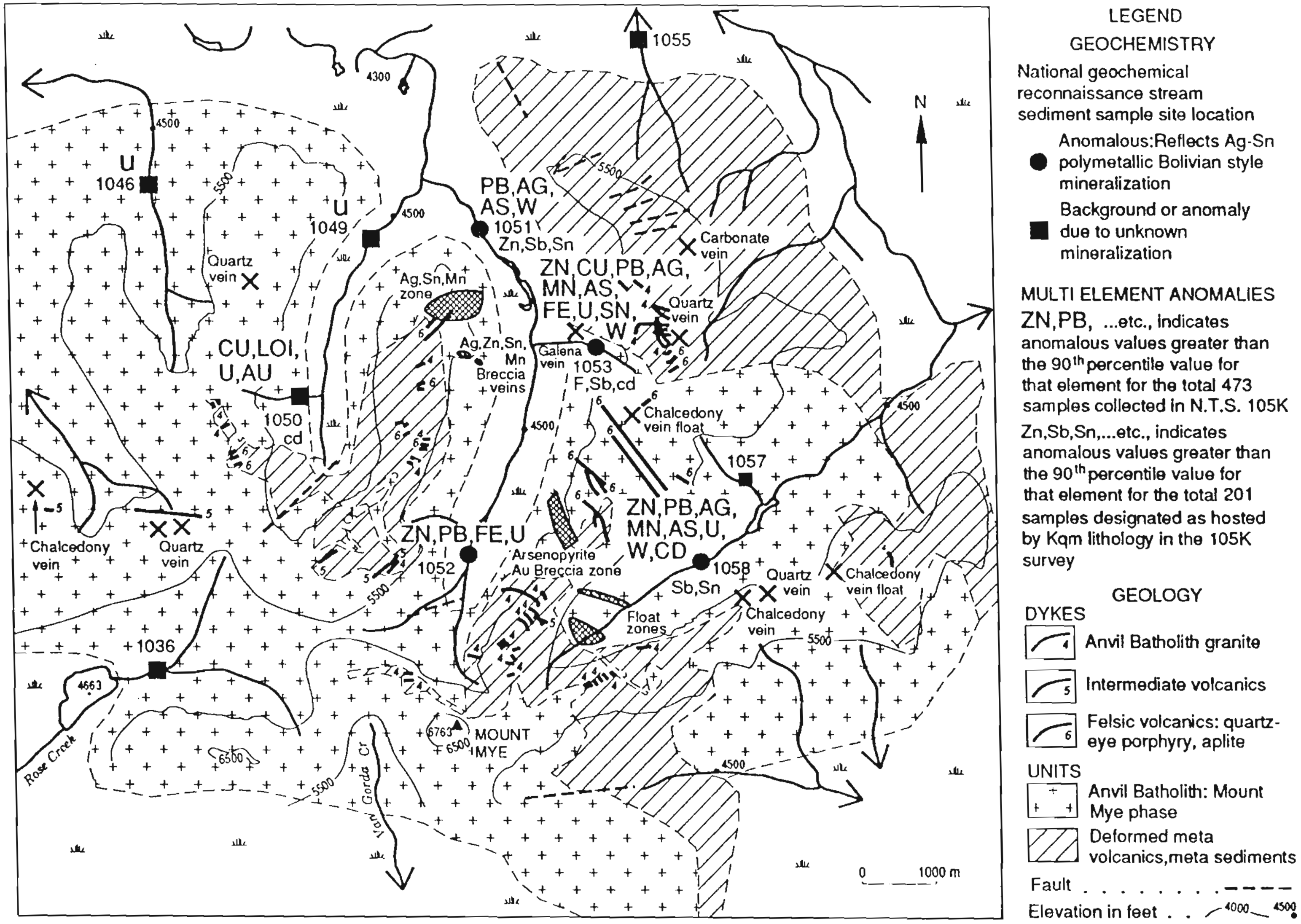
The Anvil-Faro district of central Yukon has recently been surveyed as part of the NGR sampling program (GSC Open File 1966, 2174). The region has a long history of exploration activity. Geochemical exploration methods were successfully applied during the 'discovery days' of this world class Pb-Zn-Ag district. Metasedimentary-hosted massive sulphide deposits were the target when most private industry geochemical stream sediment sampling was conducted over 25 years ago. Analysis generally only considered the elements Zn, Pb and Ag. Geochemical anomalies were identified but the search for source mineralization was directed within the context of a massive sulphide ore deposit model, hosted within Paleozoic rocks. The 1986 Mount Mye-Cody Ridge discovery of granite-hosted, polymetallic-precious metal veins and breccia bodies within the Anvil Plutonic Suite and the distinct NGR multi-element stream sediment anomalies related to this mineralization may require a reassessment of 'historic' anomalies and ore deposit models in NTS 105K, J.

Discussion of the regional geological setting (Gordey, 1988), mineralization and mineralogy will provide the framework required to interpret the NGR coincident anomalies of the elements Zn, Pb, Ag, As, Sn, Sb, Mn, Fe, Cd and U.

The Mount Mye-Cody Ridge polymetallic-precious metal vein and fracture filled breccia bodies lie within the Omineca Crystalline Belt of Central Yukon. They are located east of the town of Faro and north of the topographic high Mount Mye. The mineralization is hosted in the Mount Mye phase, biotite-muscovite granite, of the mid-Cretaceous Anvil Batholith of the Anvil Plutonic Suite. This batholith cores an uplift of polydeformed and metamorphosed Paleozoic volcanic and sedimentary rock of the North American miogeocline. Post-tectonic high level intrusion is evidenced by crosscutting relationships and by low-pressure metamorphic grades in the surrounding predominantly schist and phyllite units. Locally, roof pendents are present. Doming within the Anvil Arch and extensional normal faulting related to intrusion maybe important in the fracture control of the hydrothermal mineralizing system.

A mid-Cretaceous volcanic center is present in the district. Cogenetic South Fork Volcanics form spatially related collapse calderas (at least 8) and are equivalent to some Anvil Plutonic Suite phases (Gordey, 1988). Regional and local stress relationships due to pyroclastic eruption, magma chamber filling and venting, caldera collapse and coeval intrusive adjustment are not well known. However, volcanic center development would be expected to affect faulting and fracturing of surrounding country rocks and previously cooled portions of the Anvil Plutonic Suite. Mount Mye mineralization may be a consequence of district hydrothermal fluid development and localized fluid movement into structural conduits and related mineralized zones as a consequence of South Fork volcanic center development.

The Cody Ridge granite-hosted mineralization is totally different from the Anvil District-Faro metasedimentary hosted, base metal, massive sulphide, Pb-Zn-Ag deposits. In the district, previous exploration was generally focused within the Paleozoic rock in the search for massive sulphides. Doron Exploration reported the discovery of the Cody Ridge mineralization in 1986. Over 100 ounces per ton silver was measured in black manganese



12

MOUNT MYE STUDY AREA: GEOLOGY AND STREAM SEDIMENT GEOCHEMISTRY stained, quartz-rhodochrosite, ruby silver-bearing material. In 1987, 0.22 ounce per ton gold in quartz-sericite-arsenopyrite altered granitic material was also reported from a new zone. Our early investigation of the 1986 vein samples revealed the Ag-Sn association which led to our comparison of it with Southern Bolivian Ag-Sn ore types. Further lithogeochemical, microprobe and SEM studies on twenty-two samples collected from the property in 1988 have confirmed this comparison.

Our study has found pyrite, non-silver bearing galena, Fe-rich sphalerite, arsenopyrite, stannite, high-temperature needle-shaped cassiterite, canfieldite, diaphorite, pyragyrite, miagyrite, acanthite, Ag-bearing tetrahedrite, native silver, semseyite and covelline. Microprobe and SEM processing assisted by image analysis were both necessary in identifying and documenting this complex mineral assemblage.

We envisage mineralization events which caused multiple, repeated brecciation of early quartz veins within sericite, quartz, ±pyrite veinlet to stockwork alteration zones. This could be part of a silicifying-adularia event. Continued fluid introduction favoured fractures and ore shoots formed where brecciation was developed. Micro-brecciation of ore and gangue minerals continued with banded-colloidal-crystalline silica as quartz, ±chalcedony and carbonate as rhodochrosite being intermittently deposited in the veins, fractures and around breccia fragments. Complex ore fluids introduced Ag, Sn, Zn, Pb, Sb, Fe, As, Cu, Mn, Si and Ca during brecciation and vein development. This complex elemental assemblage and the resultant mineral assemblage found at Mount Mye-Cody Ridge is typical of Southern Bolivian Ag-Sn deposits.

Figure 12 shows the geology and NGR sample locations for the Mount Mye study area. The data interpretation involved N.T.S. map area 105K west half only (GSC Open File 1961) (Friske and Hornbrook, 1989).

A total of 473 sample sites were collected in the survey area and 201 of these samples were designated as being hosted by Anvil Batholith lithology, Kqm, (Cretaceous quartz monzonite). The data release provides the user with statistics based on percentile values for the total population of sites and also for sub-populations based on specific underlying lithologic units. (ie Kqm)

In the Mount Mye study area, the numerous uranium anomalies are interpreted as indicating the Mount Mye two-mica granite phase of the batholith. Manganese anomalies stained, quartz-rhodochrosite, ruby silver-bearing material. In 1987, 0.22 ounce per ton gold in quartz-sericite-arsenopyrite altered granitic material was also reported from a new zone. Our early investigation of the 1986 vein samples revealed the Ag-Sn association which led to our comparison of it with Southern Bolivian Ag-Sn ore types. Further lithogeochemical, microprobe and SEM studies on twenty-two samples collected from the property in 1988 have confirmed this comparison.

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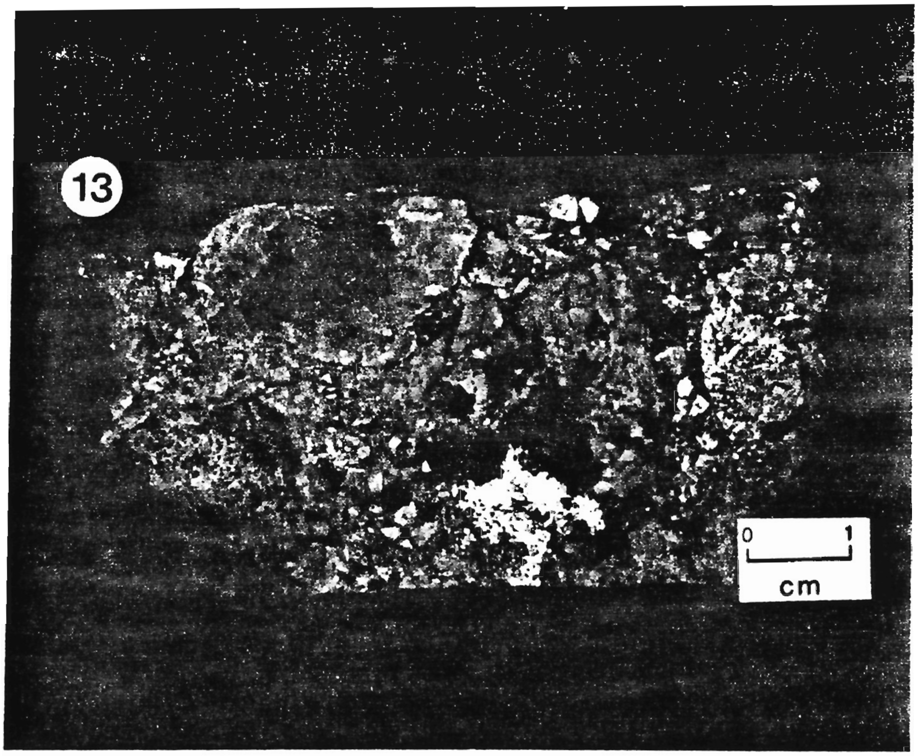
Fig 13: Mount Mye - Cody Ridge Yukon epithermal breccia sample from Anvil Batholith. Grey coloured gangue minerals include banded-coloidal-crystalline silica (quartz±chalcedony) and carbonate (rhodochrosite). Dark minerals in the breccia include sphalerite, arsenopyrite, galena, stannite, cassiterite, acanthite, pyragyrite, canfieldite, diaphorite, miargyrite, tetrahedrite, semseyite and covelline. This complex mineral assemblage is typical of Southern Bolivian Ag-Sn deposits.



are a product of rhodochrosite disintegration of the epithermal textured, breccia, veins and bodies (Fig. 13). Manganese is often considered as an unwanted scavenger of heavy metals. Some users of geochemical sediment data would automatically dismiss anomalies with high manganese contents as being 'false' anomalies. This is a dangerous practice when searching for precious metal deposits since manganese enrichment in carbonate alteration assemblages are often an important indication of hydrothermal (epithermal and mesothermal) processes. Black manganese-stained talus boulders led to the discovery of the Cody Ridge mineralization. The complex sulphide and sulpho salt mineral assemblage found inside these boulders is pristine and unoxidized. It must be assumed that the sediment anomalies are in part due to clastic dispersion. However, one should remember that generally stream waters issuing from granitoid rocks are relatively more acidic than water draining other lithologies. Therefore, multi-element hydromorphic dispersion could also play a role in the formation of stream sediment anomalies in the Mount Mye drainages. In any event, the anomalous samples would appear to be quite specific in relation to the known mineralized zones since other local drainages from the batholith contain background concentrations of most elements (Fig. 12).

In the stream sediments, anomalous concentrations of Fe and Cd are related to sphalerite mineralization in the breccias. Ag, Sb, As, Cu and Pb are assumed to be derived from the complex mineral sulpho salt assemblage. Sn anomalies are thought to be in response to rare stannite and fine grained, needle-shaped, cassiterite. However, canfieldite is a more abundant form of tin mineralization.

The Mount Mye study has demonstrated that even in well established mineral districts multi-element anomalies in the NGR data base can reflect new mineralization. This may be an indication that new ore deposit models must be considered. During evaluation (GSC Open Files 1966, 2174) (Friske and Hornbrook, 1989; Friske et al., 1990a,b) of stream sediment, anomalies associated with the Anvil Plutonic Suite and cogenetic South Fork Volcanic center should be considered by the user within the context of the Mount Mye-Cody Ridge mineralization. (Southern Bolivan Ag-Sn base metal ore types.)

DETAILED STREAM DRAINAGE STUDIES

Zinc and Pb may separate during hydromorphic dispersion in the secondary environment (Goodfellow, 1989; Jonasson et al., 1989). Under alkaline conditions Zn may be mobile, later to be precipitated as Zn, calcite, smithsonite and hemimorphite. This secondary zinc mineralization may also contain zones of Ni, Cd, Mo, Co and Fe enrichments. Pb, however, forms the insoluble secondary carbonate mineral cerussite which often coats and protects corroded galena grains. Hydromorphic dispersion of Pb is extremely limited when calcareous or carbonate rocks are present. If physical erosion occurs by streams cutting secondary Zn and Pb mineralization, mechanical transport of stable Zn-Pb minerals may create extended clastic dispersion trains in stream sediments. However, under alkaline conditions the mass wasting and chemical dispersion of Zn ± Cd, Ni is more common than Pb dispersion in stream waters and sediments.

Zn in stream sediment spatial distribution patterns related to stratiform sediment-hosted Pb-Zn deposits of the Selwyn Basin, Yukon, are more pronounced and intense than those of Pb. In fact, Pb anomalies can be subdued when associated with Early Silurian deposits hosted by calcareous shale and chert of the Road River Group (Howards Pass and Anniv deposits). The black clastic and chert stratigraphy of the Devonian-Mississippian Earn Group often contains significant pyrite and lower carbonate contents in contrast to Road River Group rocks. Oxidation of sulphides (mostly pyrite) commonly create acidic stream water conditions under which both Pb and Zn will be transported hydromorphically for some distance. Coincident Pb and Zn stream anomalies are therefore present in streams draining the Tom and Nor deposits. In the Nahanni map area, Selwyn Basin, Yukon, a detailed discussion of the geochemical responses to mineralization and lithology may be found in Goodfellow, 1989 and Jonasson et al., 1989.

Ketchika District

The NGR program was considering conducting surveys in NTS map areas 94E, F, K and L. The area is known as the Gataga-Kechika district of British Columbia which includes the southern extension of the Paleozoic Selwyn Basin, Yukon. In 1979 and 1980, in cooperation with the geological mapping program of D.G. MacIntyre (MacIntyre, 1981, 1983) and private industry explorationists, the author conducted detailed multi-element, multi-media geochemical orientation surveys in the Kechika trough. By using stream sediment geochemical surveys, private industry had already been successful in identifying numerous potential targets for stratiform sulphide deposits. In fact, while conducting helicopter-supported reconnaissance stream sampling programs zones of baritic mineralization were recognized at what are now known as the Mount Alcock and Cirque deposits.

Stratiform barite-iron-zinc-lead ± silver mineralization occurs in Middle-Late Devonian siliciclastic rocks, the Earn Group. These 'black clastics' which when weathered colour silver-grey are also known as the Gunsteel Formation. Stratiform barite horizons ± sulphides occur at 3-5 intervals within the highly deformed Earn Group stratigraphy often over semicontinuous strike lengths of 50 kilometres. Complex folding and thrust faulting has repeated horizons of typically massive to laminated to nodular-bebby barite and siliceous cherty argillite along strike.

Of particular importance to geochemical dispersion characteristics within the district is the fact that the stratigraphy, ranging in age from Hadrynain to early Mississippian, is composed of numerous calcareous to carbonate (limestone-dolomite) units. Because of tectnostratigraphic relationships including thrust faulting, chevron folding and ramping, elevations range from 1100 metres to over 2500 metres. Ridges and valleys, either of which may be dominated by carbonate units, are prominent. Water chemistry is highly alkaline, and where acidic, it is quickly buffered by carbonate units. The treeline reaches up to 1500 metres while outcrop is found in river and creek beds and at the higher ridge elevations.

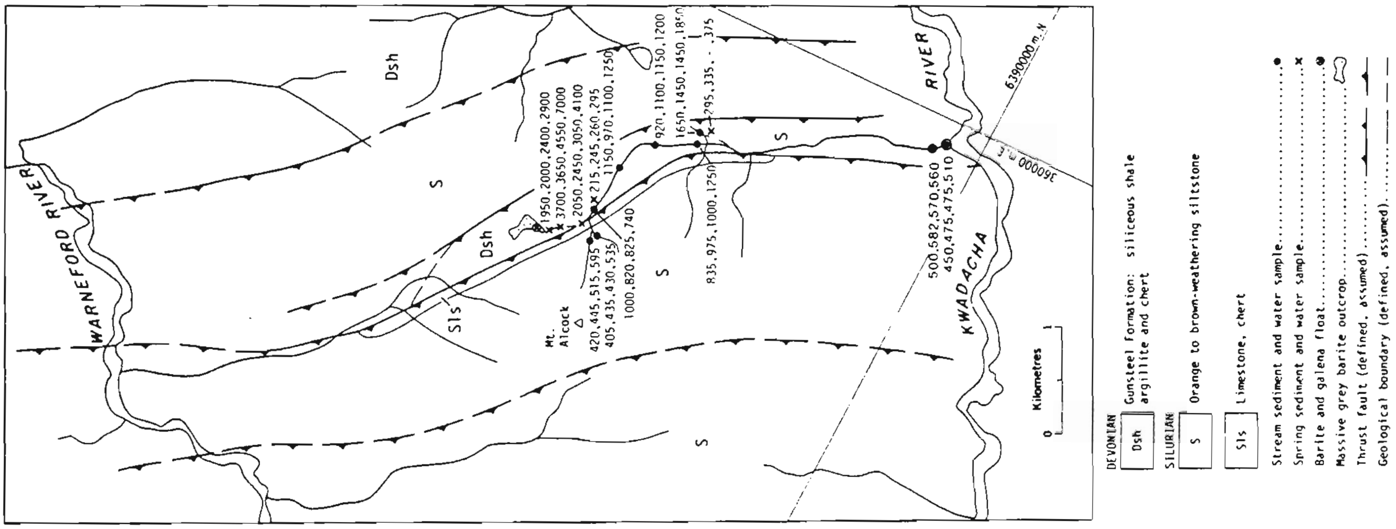
Mount Alcock Study

The Mount Alcock deposit is currently under active exploration. An example of geochemical dispersion of the elements Zn, Pb and Hg is given in Figure 14 for the outcropping barite and galena exposures. The stream draining the prospect enters the Kwadacha River at a well developed break in slope. It then rises steeply for about 4 kilometres where at its headwaters springs issue from Gunsteel Formation mineralized baritic horizons(s) while other tributaries drain Road River Formation (dolomitic siltstone).

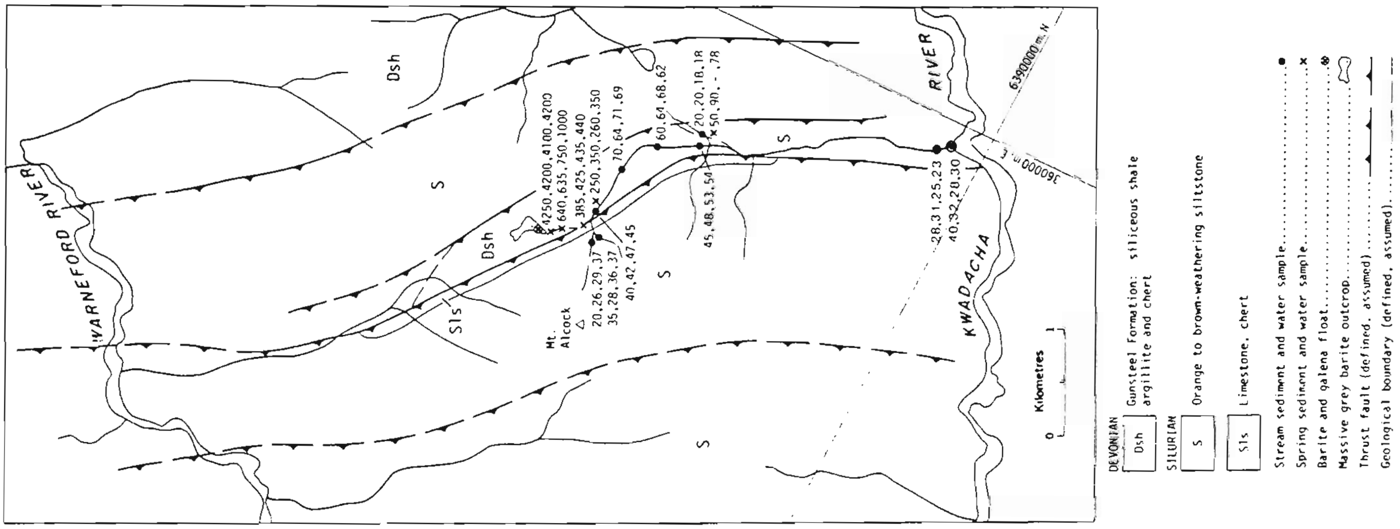
Spring sediment, water and stream sediment, and water samples were collected from sites on the main creek and its tributaries. One heavy mineral panned concentrate was

MOUNT ALCOCK STUDY AREA

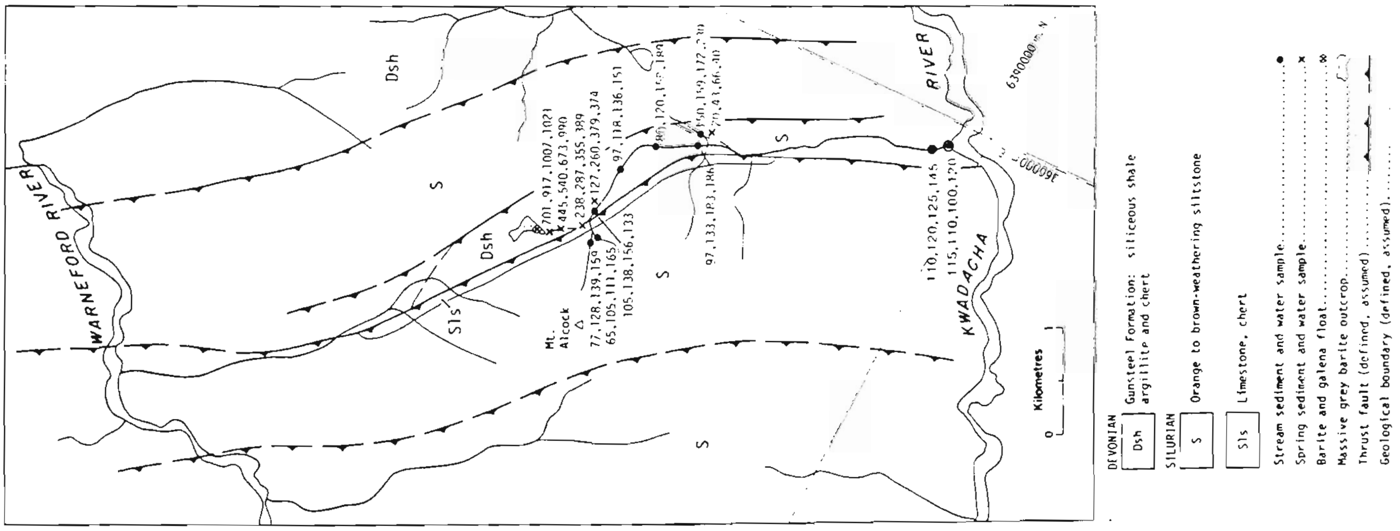
SIZE FRACTIONS: −10+35,−35+60,−60+80,−80 mesh



Zinc (ppm)



Lead (ppm)



⑭ **Mercury (ppb)**

collected at the only suitable sample site below the break in slope at its confluence.

Sample preparation of the sediments included size fraction separation of material into minus 10 + 35 mesh, minus 35 + 60 mesh, minus 60 + 80 and minus 80 mesh (ATSM) sub samples. Each fraction was then ball-milled to minus 200 mesh material before analysis. Analytical results for Zn, Pb and Hg are reported for the fractions given in the order above in Figure 14. The pH of spring and stream waters ranges from 7.1 to 8.5 respectively. The spring water contained Zn contents of 1400 ppb. Pb contents was measured at 8 ppb.

Zn and Pb hydromorphic dispersion in downstream waters is quickly limited. Zn in stream sediment concentrations are highly anomalous in all fractions of main creek samples. Spring sediments near the source show the greatest enrichment. Pb concentrations quickly become depleted from the headwaters to the mouth of the creek. Hg concentrations may be considered as a direct geochemical measurement of ore sulphides. Concentrations levels measured within the Alcock drainage certainly confirm this assumption. Both Pb and Hg concentration in stream sediments mark the Alcock drainage as being anomalous. A regional reconnaissance sample site if chosen at the mouth of the creek would return contents greater than the 90th percentile of the NGR data as shown in Table 1.

Ba contents are considered to be a direct measurement of mechanically dispersed barite. Ba reflects the presence of mineralization and is a diagnostic marker of Gunsteel stratigraphy. Little differences in relative levels of Ba concentration were observed between the size fractions. Absolute Ba contents range from about 2000 ppm at the mouth of the creek to over 2 percent at springs issuing from mineralization at the headwaters. Similarly, silver concentrations range from 0.4 ppm to 2.8 ppm from the mouth of the creek to springs at the headwaters. Pb, Ba and Ag contents from spring sediments (?) are probably the result of sampling mineralized talus material.

The HMC sample showed little advantage if any in enrichment of concentration levels over the stream sediment sample taken at the same site. This would perhaps indicate a predominant clastic component in the stream sediment sample.

Elf Creek Study

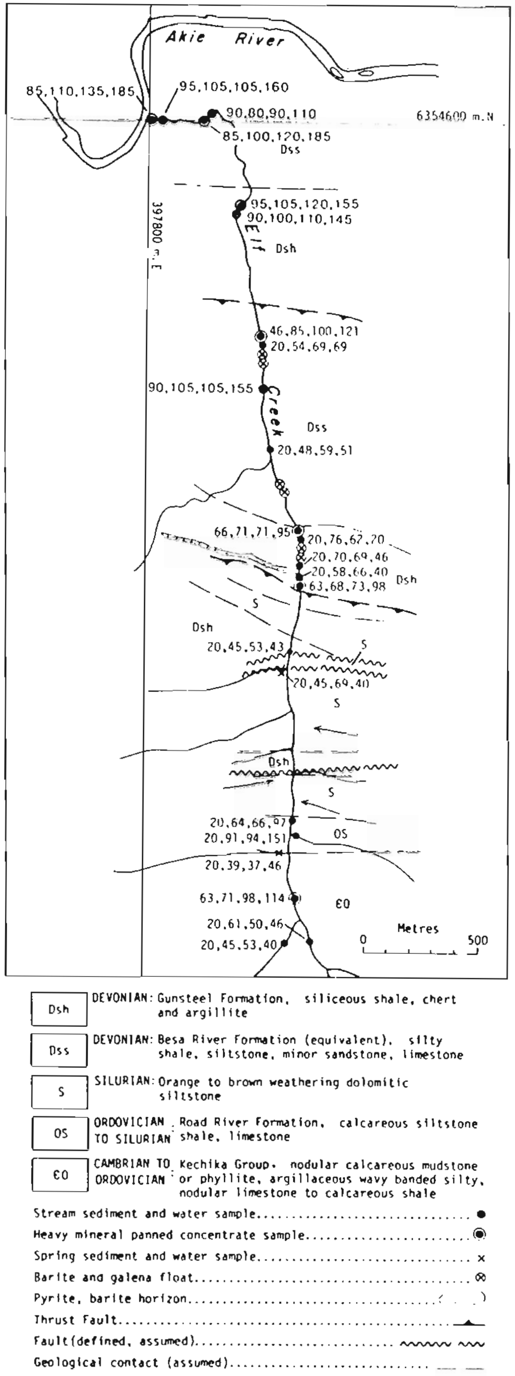
The Elf Creek drainage (Fig. 15) is similar in length to Mount Alcock Creek. It has a much greater velocity, with more steps in elevation. This provided more suitable HMC

ELF CREEK STUDY AREA

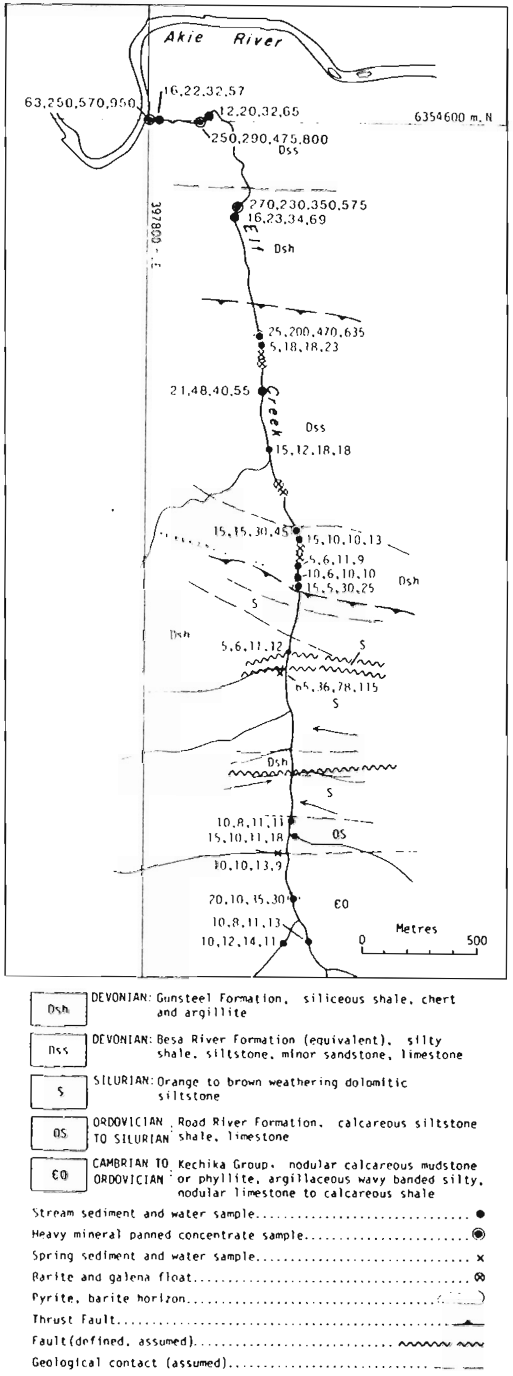
SIZE FRACTIONS: −10+35,−35+60,−60+80,−80 mesh

15

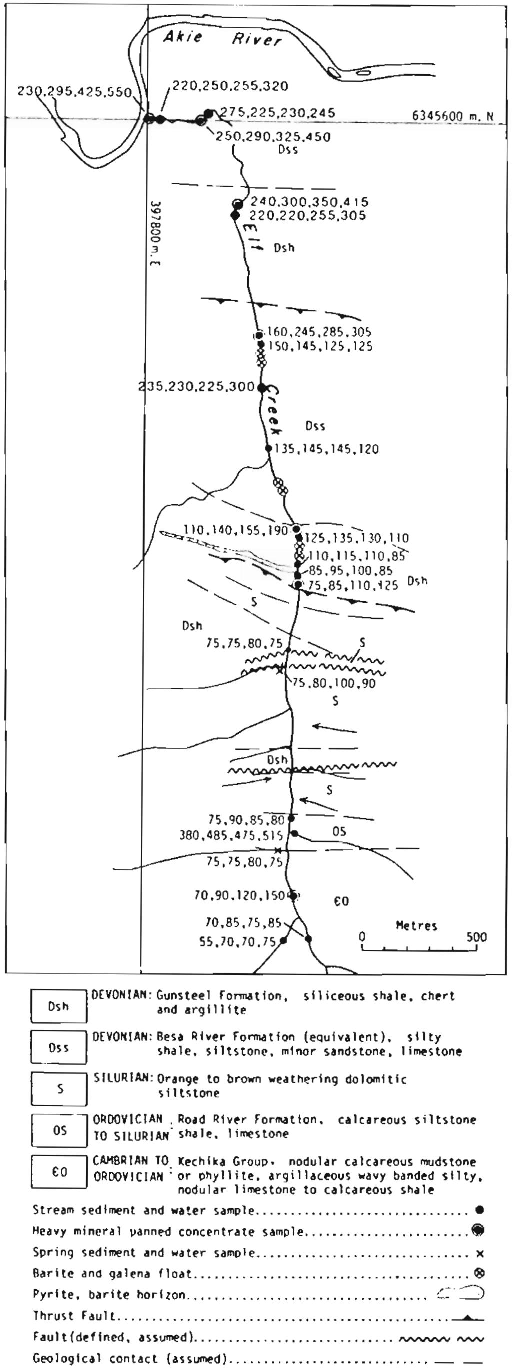
Mercury (ppb)



Lead (ppm)



Zinc (ppm)



dumping sites for 'mechanical' dispersion measurements. It crosses and down cuts the four principal and distinct tectnostratigraphic packages of the Ketchika-Gataga district. It dramatically depicts a common situation found in the district. Calcareous and limestone units are at higher elevations in the headwater portions of the drainage while the potentially mineralized chert, argillite and shale units are at lower elevations. The drainage basin is tree covered and it was discovered to be anomalous by stream sediment regional sampling. Huge impressive blocks of barite-galena float are found in the active stream bed (Fig. 15).

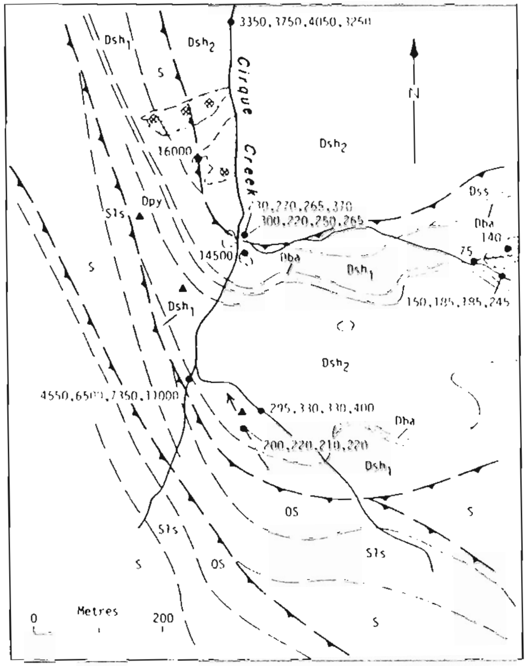
The pH of stream water collected from Elf Creek is 8.5. Zn contents are very subdued at a maximum of 7 ppb. These highly alkaline conditions due to the intense carbonate buffering capacity throughout the drainage system has severely limited hydromorphic dispersion. Therefore, stream sediment concentrations of all elements must be predominantly in response to mechanically dispersed mineral trains. Sample preparation and size fraction analysis is as described for Alcock Creek.

As reported in Figure 15 concentrations of Zn, Pb and Hg are enriched only in the lower reaches of the drainage and specifically in the minus 177 micron (-80 mesh) size fraction. Note that stream sediment samples taken in proximity to the mineralized float are quite subdued. The anomalous concentrations only appear at the final break in slope near the mouth of Elf Creek. The velocity of this drainage made the sampling of conventional stream sediments difficult. Fines are 'washed' to lower elevations where accumulation occurs. HMC sampling also shows the greatest anomaly contrast at the confluence. However, because of the concentration factors inherent in HMC prospecting methods, panning immediately below the mineralized float also gave strong indications of the presence of mechanically moved mineral grains in the bed load material. Barium concentrations reach percentage levels at the confluence due to the presence of barite grains. Compared to stream sediment samples taken throughout Elf Creek HMC samples provide superior anomaly contrasts.

Cirque Deposit Study

The Cirque deposit is currently being explored by underground development. It represents the most economically significant stratiform ore body discovered in the Ketchika trough. As the name suggests, the drainage (Fig. 16, 17, 18) headwaters back into a cirque

⑯ Zinc (ppm)



Dsh2	Argillite and shale
Dpy	Pyritic horizon, laminated pyrite in shale
Dba	Baritic horizon, black siliceous argillite or shale with nodular or blebby barite interbeds
Dsh1	Banded siliceous argillite and shale
Dss	Silty shale
S	Siltstone
S1s	Limestone, chert and shale
OS	Black shale

Stream sediment and stream water sample location .... 1001 ●

Heavy mineral panned concentrate ....

Gossan or seep precipitate and water sample location .... 3001 ●

Diamond drill hole location .... ▲

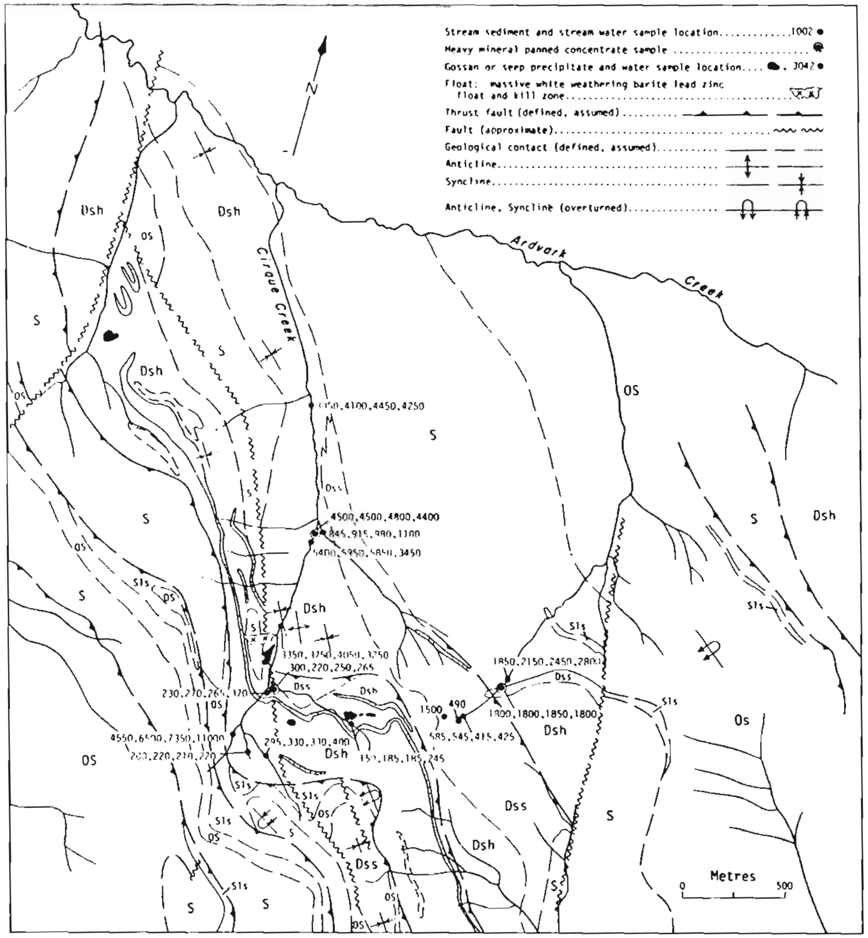
Mineralized barite Pb-Zn float .... ⊗

Gossan ....

Kill zone ....

Thrust fault ....

SIZE FRACTIONS: −10+35,−35+60,−60+80,−80 mesh



UPPER DEVONIAN

Dsh	Gunsteel Formation: bluish grey-weathering siliceous argillite or chert with carbonaceous black shale interbeds; rusty weathering pyritic carbonaceous black shale; weakly siliceous carbonaceous slate and argillite
	Black siliceous argillite or shale with nodular or blebby barite interbeds, local thickening into a massive barite horizon in mineralized zones
Dss	Besa River Formation: laminated silty shale with thin, poorly sorted siltstone sandstone, conglomerate, and limestone interbeds

SILURIAN

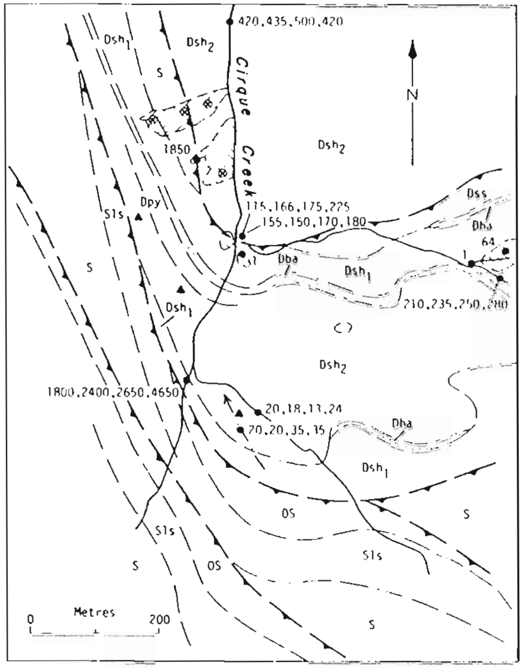
S	Nonda Formation(?): orange to brown weathering bioturbated dolomitic siltstone
S1s	Minor orange weathering limestone interbeds

LATE ORDOVICIAN TO EARLY SILURIAN

OS	Road River Formation: Buff to black weathering graptolitic shale and laminated calcareous siltstone and shale with limestone interbeds, local black chert interbedded with black carbonaceous shale

CIRQUE DEPOSIT STUDY AREA

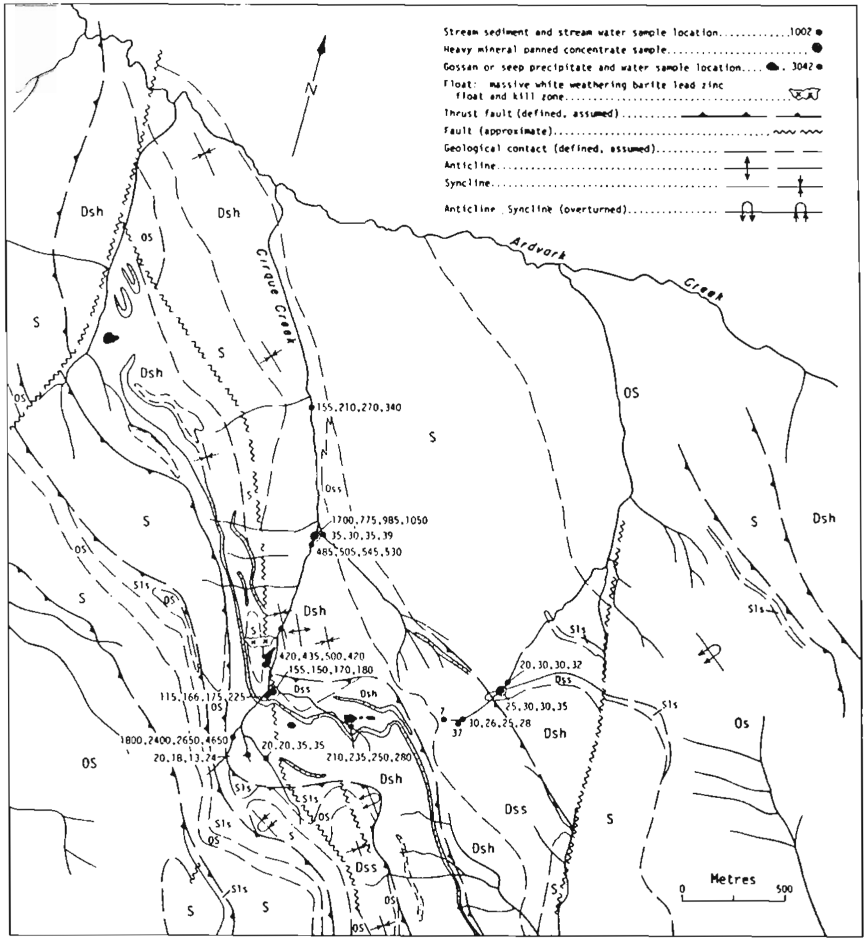
⑰ Lead (ppm)



Dsh₂	Argillite and shale
Dpy	Pyritic horizon, laminated pyrite in shale
Dba	Baritic horizon, black silicrous argillite or shale with nodular or blebby barite interbeds
Dsh₁	Banded siliceous argillite and shale
Dss	Silty shale
S	Siltstone
Sls	Limestone, chert and shale
OS	Black shale

Stream sediment and stream water sample location..............................1001 ●
Heavy mineral panned concentrate..............................
Gossan or seep precipitate and water sample location..............................3001 ●
Diamond drill hole location.............................. ▲
Mineralized barite Pb-Zn float.............................. ⊗
Gossan..............................
Kill zone..............................
Thrust fault..............................

SIZE FRACTIONS: −10+35,−35+60,−60+80,−80 mesh



UPPER DEVONIAN

Dsh	Gunsteel Formation: bluish grey-weathering siliceous argillite or chert with carbonaceous black shale interbeds; rusty weathering pyritic carbonaceous black shale; weakly siliceous carbonaceous slate and argillite
	Black siliceous argillite or shale with nodular or blebby barite interbeds, local thickening into a massive barite horizon in mineralized zones
Dss	Besa River Formation: laminated silty shale with thin, poorly sorted siltstone sandstone, conglomerate, and limestone interbeds

SILURIAN

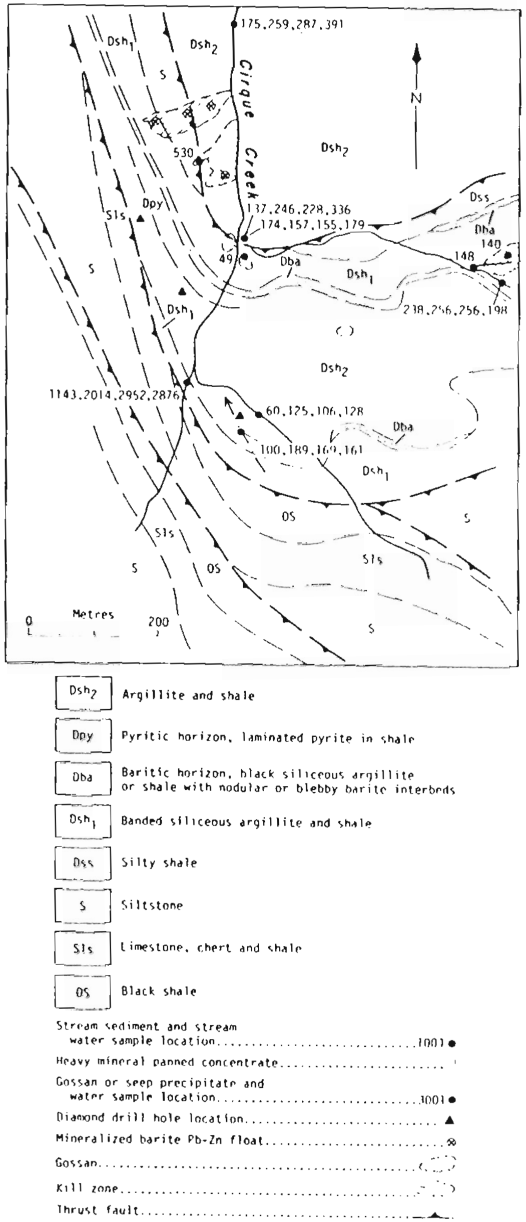
S	Nonda Formation(?): orange to brown weathering bioturbated dolomitic siltstone
Sls	Minor orange weathering limestone interbeds

LATE ORDOVICIAN TO EARLY SILURIAN

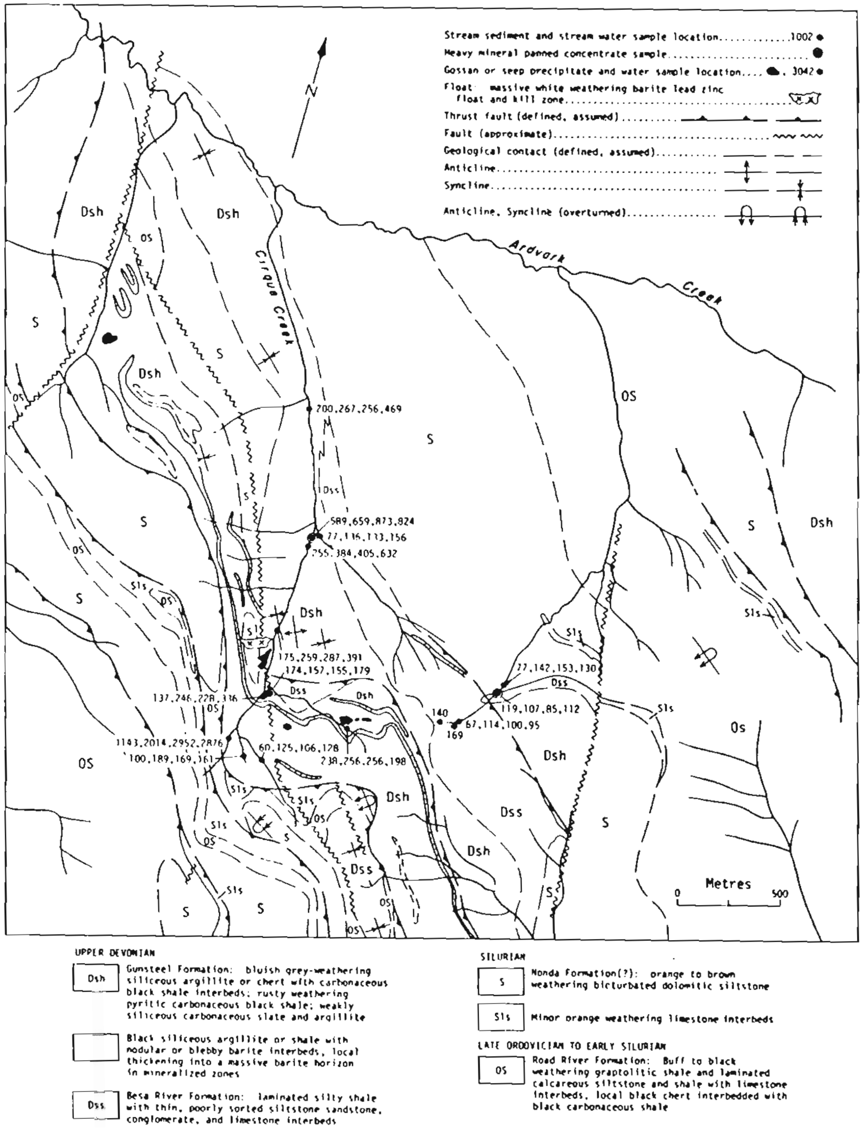
OS	Road River Formation: Buff to black weathering graptolitic shale and laminated calcareous siltstone and shale with limestone interbeds, local black chert interbedded with black carbonaceous shale

CIRQUE DEPOSIT STUDY AREA

⑱ Mercury (ppb)



SIZE FRACTIONS: −10+35,−35+60,−60+80,−80 mesh



CIRQUE DEPOSIT STUDY AREA

with above treeline exposures of pyritic, baritic mineralization and outcropping Ketchika trough tectonostratigraphic units.

Unlike Mount Alcock and Elf Creek, acidic water conditions are well developed at the headwaters of the Cirque Creek drainage system. Gossan derived seepage waters have pH levels of 3.2 and contain 7480 ppb Zn with anomalous Cd (29 ppb) and SO_4^{-2} (74 ppm) concentrations. Pb levels are subdued at 7 ppb. Stream tributary waters fed from springs issuing from Devonian pyritic shale, argillite and mineralized horizons contain 1927 ppb Zn at a pH level of 3.7. However, upon meeting upstream water derived from Silurian limestone units (ph 8.3), acidic waters are quickly buffered to pH levels of 8.0. Consequently, hydromorphically transported Zn in main Cirque Creek is subdued to 13 ppb levels in downstream alkaline stream waters. Pb concentrations were not detected in tributary or main creek water. It would appear that hydromorphic dispersion of Zn and Pb occurs at Cirque to a limited extent. Pb is chemically immobile except in the secondary environment of actively oxidizing sulphides. Zn is more mobile under acidic stream water conditions. However in Cirque Creek, its anomalous spatial distribution away from mineralized zones is also restricted even under alkaline conditions. Therefore, we must examine and evaluate stream sediment and HMC sampling results in the context of sulphide and/or their oxidation products being dispersed by clastic processes.

Stream sediments and HMC material were processed in the same manner as the other two 'case history' examples. In the main creek bedload material Zn, Pb and Hg anomalies are well developed in all size fractions of both media (Fig. 16, 17, 18). The main streams and tributaries at Cirque, are sourced from alpine meadow and exposed bedrock on the floor of the cirque. The relatively flat topography of the floor means that water velocities are slow and drainage channels are narrow. Clastic dispersion from source is minimal. As such element concentration levels and associations in bedload material bear the direct lithologic signature of the underlying rock unit(s). This is obvious for samples collected from headwater lithologies.

Baritic-mineralized rock slide material contributes bedload material to main Cirque Creek. Stream sediment and HMC samples downstream from the slide express this contribution but they are also diluted by unmineralized material from other lithologies. Compared to the most anomalous 'in place' sediment sample collected from a mineralized horizon at the headwaters these samples contain much less metal. Barium contents in the drainage may range between 1-5% with Ag concentrations as high as 11 ppm. The very high Hg, Ag and Ba concentrations are a direct reflection of clastically transported ore sulphides (silver-rich galena) and barite. Zn-Cd ± Hg concentrations in the drainage system reflect sphalerite compositions. Anomalous Zn concentrations may also be indicative of gossan and spring secondary zinc (precipitate-mineralization) being transported clastically in the bedload. The stream geochemistry around the Cirque deposit generally suggests that dispersion by clastic processes is predominant, therefore, Zn, Pb and Hg anomalies are not separated spatially in the secondary environment. Due to a lack of steep drainage gradients in the cirque 'bowl' at the headwaters, clastic dispersion of ore elements in not far from source.

The results from geochemical orientation surveys conducted in the Ketchka trough extension of Selwyn Basin show:

1) Spring and stream water geochemistry is controlled by mineralization and calcareous lithologies and thus chemical dispersion in solution may be restricted or show a separation of Zn and Pb anomalies in the secondary environment;
2) The ability of HMC and/or stream sediment sampling to define anomalies is dependent on optimizing sample site locations which will best reflect 'dumping zones' for clastically dispersed primary or secondary mineralization;
3) The identification of barite in HMC panned samples will give direct <u>in field evidence</u> of the presence of massive, laminated or blebby nodular baritic horizons. HMC can therefore direct detailed exploration for mineralized stratigraphy, namely, Lower Earn Group siliciclastics.
4) Elements such as Cd and Hg can be used to categorize zinc anomalies being derived from mineralization but coincident Zn-Pb ± Ag can not always be expected to be present.
5) Due to the predominance of clastic dispersion absolute concentrations of ore and pathfinder elements must not be used to compare anomalies between drainages. Care must be used when evaluating tributaries in specific drainages since highly variable results are noted between sample sites.
6) Detailed geochemical sampling using multi-elements and multi-media (water,

sediments, HMC and soils-talus fines) are considered to be an effective exploration method for first pass mineral resource evaluation of a drainage area in the Ketchika-Gataga districts of British Columbia.

HEAVY MINERAL CONCENTRATE STUDIES

Atlin Placer Gold District

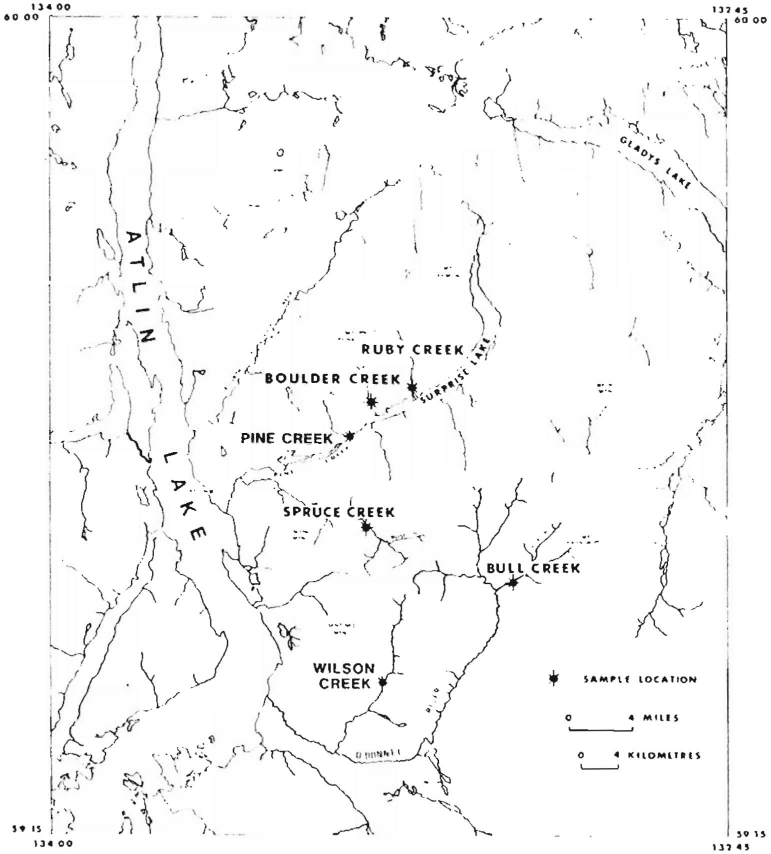
Most HMC geochemical surveys sample what is thought to be 'virgin' bedload material. A 'non-conventional' study of concentrate samples from placer operations on four gold-bearing creeks east of Atlin, British Columbia was completed by Mackinnon, 1986. Further studies of lode-gold deposits and other placer creeks in the district have been undertaken by the author (Ballantyne and Mackinnon, 1986) (Fig. 19).

The main objective of the study was to determine the type and abundance of minerals in placer concentrates. The economic significance of specific minerals which may be indicative of source mineral associations and deposits was also a focus. Morphology and composition of placer gold grains and lode gold from prospects in the Atlin area were compared.

Systematic preparation and examination procedures included point counting, determination of size distribution and relative abundance of minerals, mineral identification by binocular microscope, x-ray diffraction analysis (XRD), scanning electron microscope (SEM) and electron microprobe.

In the Mackinnon study, an amazing 93 different minerals or compounds were observed in the four placer concentrate samples (Table 4). This reflects the diversity of mineralized sources and bedrock lithologies in the area. Gold, cassiterite, chromite, scheelite and wolframite are the principal economic minerals found in placer concentrates. Their relative abundance varies widely among the creeks studied (Fig. 19). Some mineral species displayed a wide range in forms, habits, composition and colour (ie gold-electrum and cassiterite). Numerous grains were polymineralic and/or had iron and manganese coatings. It is clear from this study that much can be learned from the detailed examination of placer 'heavies' (Table 4).

Let us examine some of the economically significant points of interest developed from the Mackinnon study and our ongoing investigations at the G.S.C.



LOCATION MAP

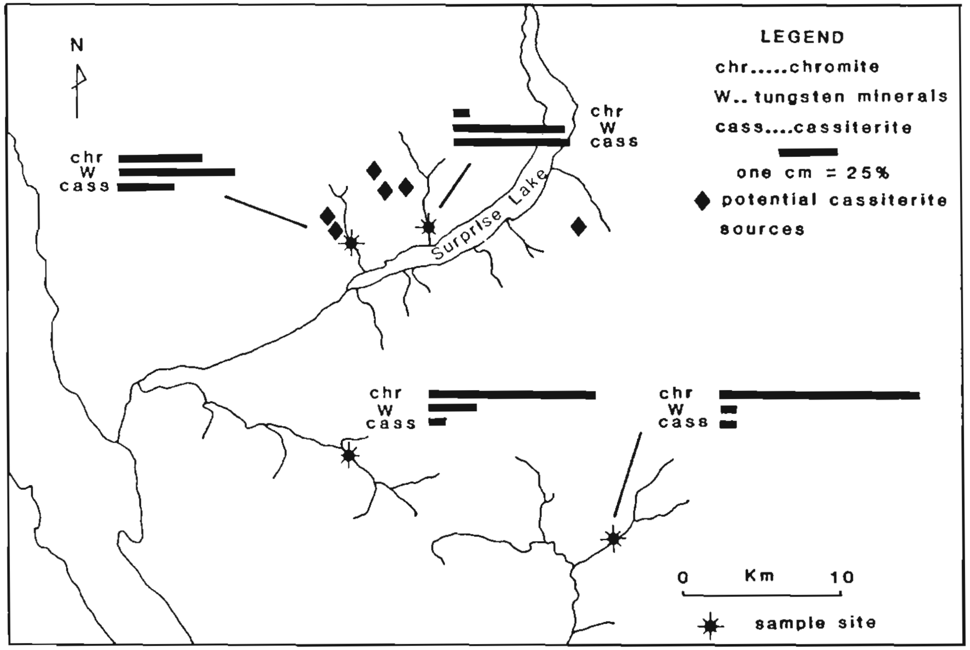


Figure 19 : Relative abundance of cassiterite, tungsten and chromite in each placer concentrate sample (total), Atlin, British Columbia. Some known potential bedrock cassiterite sources are shown (after Mackinnon, 1986).

Chromite abundance is directly related to the presence of Cache Creek ophiolite hostrocks in the drainage. Gold mineralization is related to listwanite alteration of these rocks.

NATIVE ELEMENTS OR ALLOYS	SIMPLIFIED FORMULA
Native gold	Au
Electrum	Au, Ag - (Ag > 20%)
Native zinc	Zn
Platinum Group Minerals (PGM)	Os, Ir, Ru alloys
TIN MINERALS	
• Cassiterite	SnO_2
CHROMIUM, TITANIUM, IRON AND SPINEL MINERALS	
• Chromite	$FeCr_2O_4$
Anatase	TiO_2
• Rutile	TiO_2
• Ilmenite	$FeTiO_3$
Leucoxene	-
• Magnetite	Fe_3O_4
Hematite	Fe_2O_3
• Goethite	$FeO \cdot OH$
Limonite	$FeO \cdot OHnH_2O$
Gahnite	$ZnAl_2O_4$
• Spinel Group	$MgAl_2O_4$
RARE EARTH, MOLYBDENUM, URANIUM, THORIUM, NIOBIUM, FLUORINE, AND/OR PHOSPHATE BEARING MINERALS	
Monzonite	(Ce, La, Y, Th) PO_4
Thorite	$ThSiO_4$
Unidentified	Nb, W, Fe, Mn/Ti, Se/
Metamict	Nb, Y/Th, U/Ca, Fe, W, Ti
Amorphous	Th, Ca
Apatite	$Ca_5(PO_4)_3(F, Cl, OH)$
Xenotime?	YPO_4
Molybdenite	MoS_2
Powellite	$CaMoO_4$
Fluorite	CaF_2
SILICATE MINERALS	
• Feldspar group	
• Garnet group	
Kyanite	Al_2SiO_5
• Olivine group	$(Mg, Fe)_2SiO_4$
• Quartz	SiO_2
• Serpentine group	$Mg_3Si_2O_5(OH)_4$
Pumpellyite	$Ca_2MgAl_2(SiO_4)(Si_2O_7)(OH)_2 \cdot H_2O$
• Zircon	$ZrSiO_4$
Epidote group	
Mica group	
• Amphibole group	
• Pyroxene group	

BISMUTH AND ARSENIC BEARING MINERALS	SIMPLIFIED FORMULA
Bismuth	Bi
Beyerite	$(Ca, Pb)Bi_2(CO_3)_2O_2$
Bismutite	$Bi_2(CO_3)O_2$
Unidentified	Bi, S
Arsenopyrite	FeAsS
Rammelsbergite	$NiAs_2$
Beudantite	$PbFe_3(AsO_4)(SO_4)(OH)_6$
TUNGSTEN MINERALS	
• Wolframite	$(Fe, Mn)WO_4$
• Scheelite	$CaWO_4$
LEAD, ZINC AND SULPHIDE MINERALS	
Galena	PbS
Beudantite	$PbFe_3(AsO_4)(SO_4)(OH)_6$
Beyerite	$(Ca, Pb)Bi_2(CO_3)_2O_2$
Litharge	PbO
Massicot	PbO
Plumboracrite	$Pb_{10}(CO_3)_6O(OH)_6$
Unidentified	Pb/Cr, Ti, Fe/
Sphalerite	(Zn, Fe) S
Gahnite	$ZnAl_2O_4$
Native zinc	Zn
Unidentified	Zn, Fe/ Zn, Si/ Zn, I/
Chalcopyrite	$CuFeS_2$
Pyrite	FeS_2
Pyrrhotite	$Fe_{1-x}S$
Molybdenite	MoS_2
Cinnabar	HgS
Arsenopyrite	FeAsS
Marcasite?	FeS_2
IODINE BEARING MINERALS	
Iodargyrite	AgI
Marshite	CuI
Unidentified	Zn, I
CARBONATE MINERALS	
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Others?	

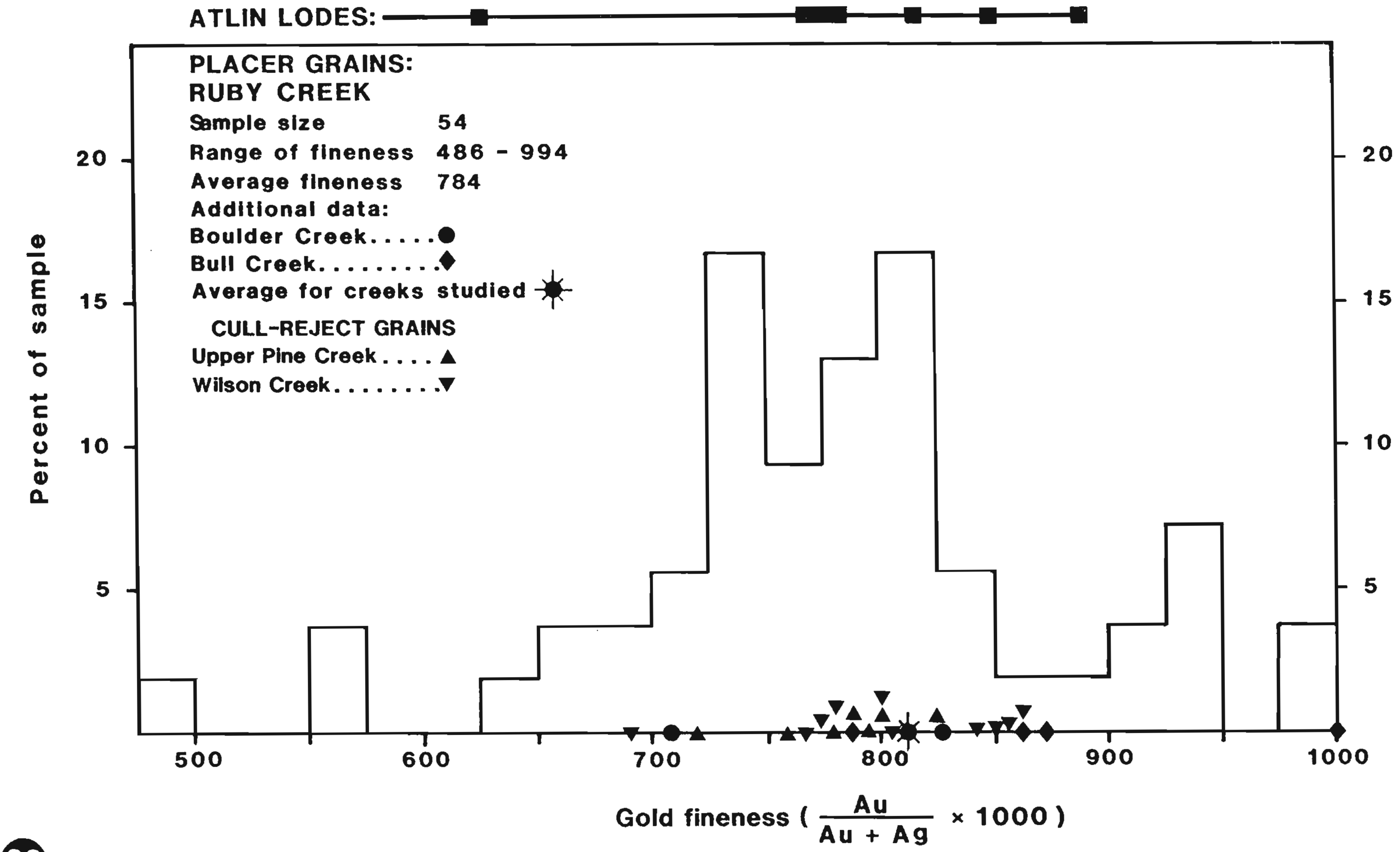
Table 4 : Minerals and compounds identified from Ruby Creek, Boulder Creek, Spruce Creek and Bull Creek placer concentrates, Atlin, British Columbia. * indicates minerals present in quantites greater than 1% (after Mackinnon, 1986).
Spectrum of this suite clearly defines the presence of granite-related mineralization, gold-bearing system(s) and lithologic units such as ultramafics and 'specialized' granitoids.

By using placer HMC material the researcher has a far greater ability to collect 'heavies' which will display a broad spectrum of sizes and mineral species than if personal collection was attempted. The concept of identifying 'blind or buried' mineral deposits within a placer district is an important criteria. Mineral populations with a relatively greater abundance were found to vary drastically between creeks. Therefore, economically significant differences can be determined but numerous creeks must be sampled. Mineral grains with small populations or 'odd' single complex grains can be very diagnostic of specific styles of alteration or genetic types of mineralization. The great concentration factors inherent in placer mining and recovery methods optimizes our ability to collect and identify these types of grains. The greatest concentration of heavies of different species was found to occur in the finer size fractions. The 150-106 micron size fraction was considered to be the best for detailed mineralogical study at Atlin, B.C.

Some explorationists utilize gold grain morphology and composition characteristics to evaluate distance from and types of gold source. Our studies of both lode and placer gold indicate that these criteria are at best misleading and often subjective.

Most placer gold grains examined were either Au-Ag or Au-Ag-Hg alloys. Copper or other base metals in minor or trace amounts are absent. Over 75% of the placer grains were found to be inhomogeneous in Au-Ag composition due to borders or rims of high fineness (F=1000xAu/Au+Ag) (see Fig. 27). Rims may develop during oxidation of the primary deposit by absorption, in situ gold precipitation or by 'refining' processes involving silver leaching either in situ or during transport. In any event, the gold colour of the rims bears little relationship to the electrum colour and composition of the core portions of the placer gold grains. Mercury concentrations in excess of one weight percent in up to 15% of the placer gold grains was also measured. Since mercury was not detected in gold grains from known gold lodes in the district it is assumed that mercury concentrations are contributed by the trace amounts of cinnabar found in the Atlin HMC samples.

Figure 36 shows a gold fineness histogram for placer gold grains from Ruby Creek, and some other Atlin creeks. This diagram is based on core compositions of the grains and Hg rich samples have not been plotted. The average compositions of gold grains extracted from all of the known Motherlode California-style, quartz-carbonate, gold-bearing veins in the Atlin placer district is also given. Gold-silver compositions are highly variable both in the



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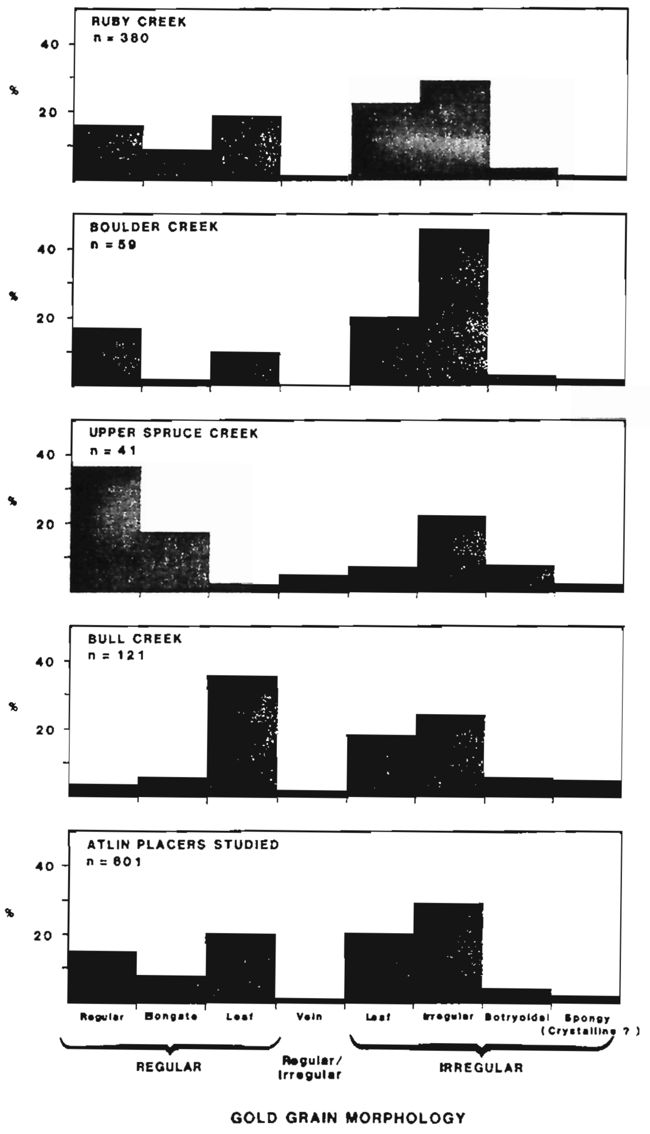
VEIN AND PLACER GOLD COMPOSITION, ATLIN, B.C.

Fig. 36b: Abundance of the various placer gold grain morphologies in the four placer concentrates examined, Atlin, British Columbia (after Mackinnon, 1986).
Note that of the 601 grains studied the 'vein' grains (culls or rejects) represent a very small proportion of the total recovered grains. It is these important grains which yield the most significant exploration data (see Fig 28, 30-35).



veins and in the placer gold grain cores. A quartz vein gave gold composition fineness of 627 and 838 from the same hand sample. The gold grains had quite different associated sulphide minerals indicating that different fluids were responsible for the different gold compositions. The listwainite associated, ribbon-banded, mesothermal, gold-bearing veins of the Atlin district are responsible for the highly variable placer gold grain Au-Ag compositions. However, when all shapes and size fractions of placer gold grains and their specific core compositions are examined in detail, one would be hard pressed to suggest that specific sources can be located by fineness measurements! (Fig. 36)

Let us now examine some of the shapes of free gold and gold closely associated with sulphide minerals taken from quartz lode prospects in the Atlin district. Figure 20 shows flake gold on pyrite; figure 21 is scalely, flat-leaf gold; figure 22 is spongy irregular to filigree gold intergrown with gersdorffite and pyrite; figure 23 is wire gold; and figure 26 shows well developed crystalline gold. All of these examples are taken from mesothermal veins. Of course these variable primary gold shapes can be flattened during tectonic adjustments such as faulting and shearing. Figures 24 and 25 are examples of 'epithermal' gold shapes preserved from a quartz-carbonate, brecciated vein, Caribou Ridge, Yukon. Note the quartz grain, crystal, 'casts' left as open spaces as this gold 'welded' the vuggy, open space epithermal texture together. All of these examples of primary gold textures were preserved by dissolving hand samples of quartz vein material with cold hydrofluoric acid.

Placer grains showing wire, crystalline and filigree or spongy gold textures are often suggested by some workers as evidence for 'new' gold formation processes. Flattened and leaf gold is often ascribed to long-travelled, 'pounded' gold which has undergone clastic transport. Our detailed study of primary gold textures clearly suggests that great caution must be used when applying subjective shape factors to placer gold grain distance of transport criteria. In Atlin, all of the variable shapes of primary gold are inherited by the placer grains found in the creeks. Many grains are bearly modified at all! (see fig 29).

In our attempt to examine and classify the various placer gold grain morphologies in the four Atlin Creek samples we found a significant number of grains which we termed 'vein' gold (Fig. 36b). These grains contained mineral or rock fragment 'gauge' which was assumed to have been derived from the primary in situ source. Placer miners are also quite aware of 'vein' gold and they 'reject' it as 'culls' when separating grains and nuggets for jewellery gold.

For exploration purposes these 'culls' are the most important placer gold to be recovered.

Most 'conventional' placer gold studies have focused on 'pure' gold and its composition. Figures 28, 30-35 illustrate 'vein' placer gold 'culls' from Pine and Wilson Creeks, Atlin, B.C. Most of us have seen golf-ball sized gold and quartz vein samples collected from placer operations. However, it is the less than one mm grains of 'vein' placer gold that are the most informative as to the true source. With the aid of the SEM and microprobe the explorationist can quickly assess primary gold compositions (fineness), shapes and sizes, sulphide associations (pyrite), alteration minerals or gauge (Fe carbonate), and often the host rock type. A close examination of Figures 27, 28 and 30-35 may suggest that gold and electrum are present in quartz, Fe-Mn carbonate veinlets, rarely associated with iron pyrite, and that chromium mica and tremolite (talc) may indicate carbonatized ultramafic hosts. The very presence of significant 'vein' placer gold may also suggest that the placer miner is digging up buried primary source material either in place or close to source!

Base metal sulphide inclusions are rare in Atlin placer gold and sulphide minerals recovered from placer operations are not significant in abundance compared to other heavy minerals. Galena, hessite, tetradymite, bismuthinite, gersdorffite-rammelsbergite, chalcopyrite, pyrrhotite and millerite are found rarely in the gold-bearing quartz veins. Examination of Table 4 of the identified placer bismuth, arsenic and lead bearing minerals gives a strong indication of primary mineral heritage. For exploration purposes, it is important to document 'vein' placer gold mineral assemblages and associations and to document the rare (small population) mineral grains as well. Note that many of these 'rare' grains are secondary minerals, the products of oxidization in the secondary environment. The influence of granite hosted and skarn mineralization related to the 'specialized' Surprise Lake batholith is also well characterized in the placer HMC suite (Table 4) (Fig. 19).

Although an 'unconventional' HMC study, I believe that this Atlin research has demonstrated the utility to exploration in the systematic documentation of heavy mineral suites collected from active placer mining operations. The ability to map rock units, alteration and ore deposit types which are perhaps buried under the 'overburden' in placer drainages should not be overlooked.

Figures 20-26: Gold morphologies and sulphide associations of native gold-electrum extracted from quartz lodes and veins by cold hydrofluoric acid digestion.

Figure 27: Cut and polished mount of the interior of a gold-electrum 'vein' or 'cull' grain recovered from placer operations, Atlin, B.C.

All figures are SEM images. Note micron to millimetre scale bar in the middle-top of each figure.

Figure 20: Late primary gold on pyrite. Note the variable sizes and shapes of gold particles that will be liberated when this mineralization is weathered and as pyrite is oxidized. Note the flake and flat gold shapes.

Figure 21: Primary flat-leaf gold, some scaley protrusions. This gold filled fracture is in quartz.

Figure 22: Primary spongy, irregular to filigree gold intergrown with gersdorffite and pyrite. This gold,if it undergoes weathering of sulphides, would result in a delicate spongy-like texture.

Figure 23: Primary wire gold with delicate hairlike protrusions.

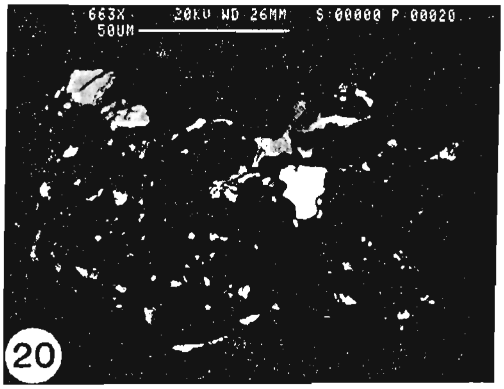
Note : Figure 20-23 and 26 are all examples of mesothermal listwainite-hosted gold from quartz-carbonate, low sulphide, veins, Atlin, B.C.

Figure 24: Primary epithermal gold from quartz-carbonate breccia veins, Caribou Ridge, Yukon. Spectacular visible gold in quartz is present in hand and core samples.

Figure 25: Primary gold as above; close-up view shows quartz grain casts now black spaces surrounded by gold. This late gold could have filled void spaces in the epithermal vein.

Figure 26: Primary delicate gold crystal shapes liberated from quartz bearing drill core, Yellowjacket property, Atlin, B.C. (mesothermal Motherlode California type of deposit).

Figure 27: High fineness gold rim with delicate protrusions and electrum core - placer 'culled' grain. Gold refining (ie silver leaching) only on some portions of the grain. Gold refining of rims is thought to occur in weathered profile and in soils. Primary gold grains from surface prospects show no rim formation in the Atlin gold camp.



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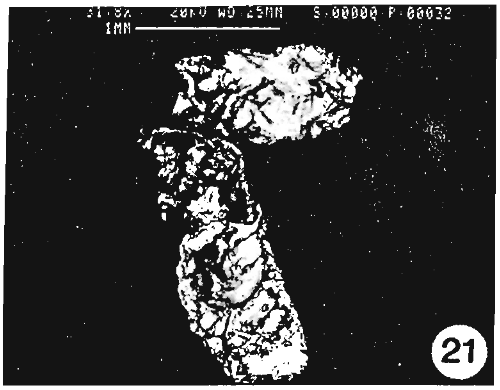

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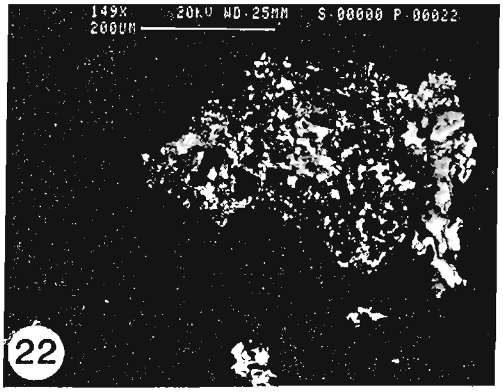

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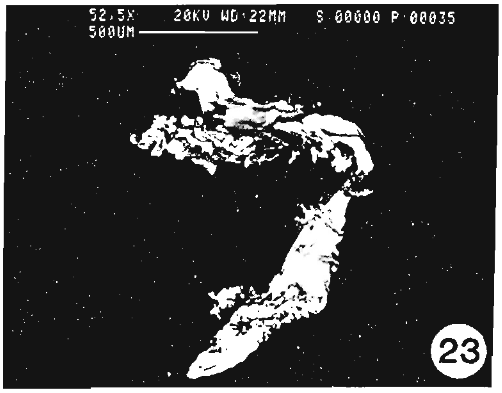

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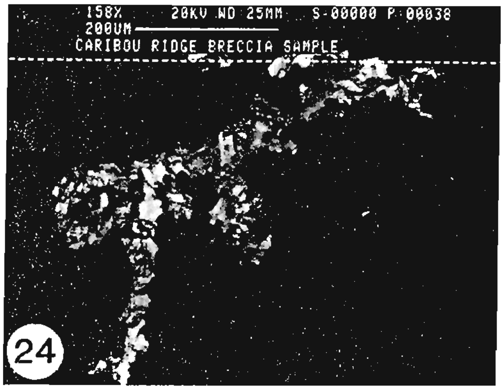

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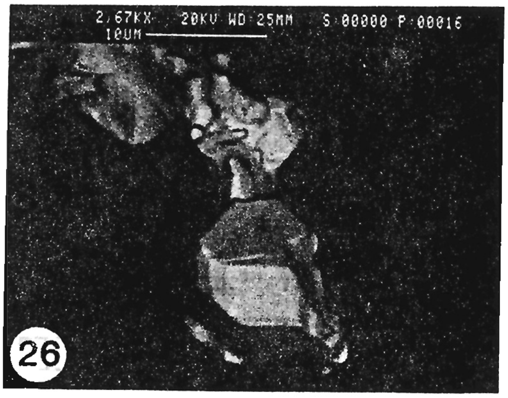

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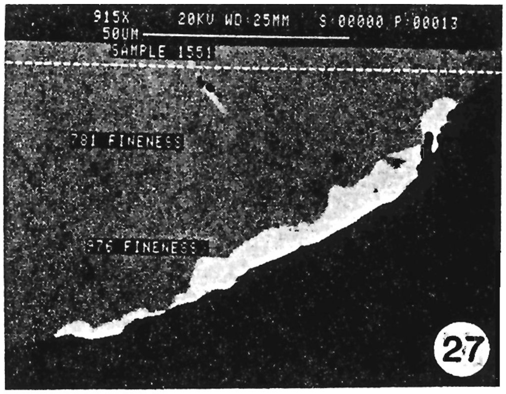

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Figures: 28-35 are SEM images of placer grains recovered from Wilson and Pine Creeks, Atlin B.C. Figures 28, 30-35 are known as 'culls' or 'rejects' by placer miners. They are important to the explorationist and can be classed placer 'vein' gold. Note the scale bar in the middle top of each image. Also note that gold composition varies from gold (Au), to electrum (Au:Ag), between grains.

Figure 28: Placer 'vein' gold grain-mineral gangue composition shows that gold is associated with quartz and chromium-mica.

Figure 29: Placer grain shows electrum composition and very irregular shape, similar to the primary gold in Fig. 22.

Figure 30: Placer grain shows gold is entirely hosted by quartz and the iron-manganese carbonate gangue is adjacent to the gold-quartz veinlet.

Figure 31: Typical mixture and shape of placer 'vein' grain of electrum quartz and Si:Al:Mg gangue.

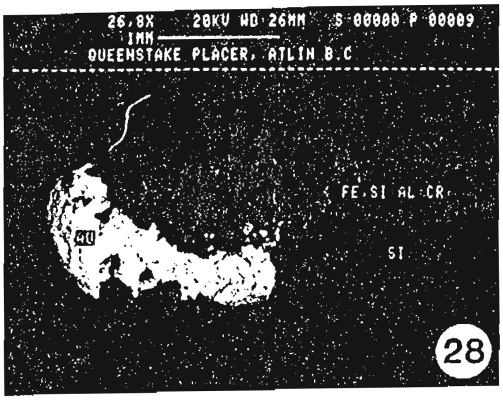
Figure 32: Close-up of iron carbonate and quartz gangue with electrum from a placer 'cull'.

Figure 33: Close-up of gold cross cutting fractures and following grain boundaries of tremolite gangue. (Identified composition by microprobe) If gold is liberated from this placer grain of tremolite, the weathered gold morphology would appear as wires.

Figure 34: Close-up cross section of interior of a placer 'cull' showing quartz and gold 'casts'. Compare with Fig. 25.

Figure 35: Placer grain close-up of rare pyrite and associated gold and Si:Mg:Fe gangue.

Note: The 'vein' placer gold depicted in these images has diagnostically defined the shapes and sizes of gold-electrum, and the vein and gangue mineralogy of the primary gold mineralization known in the Atlin camp.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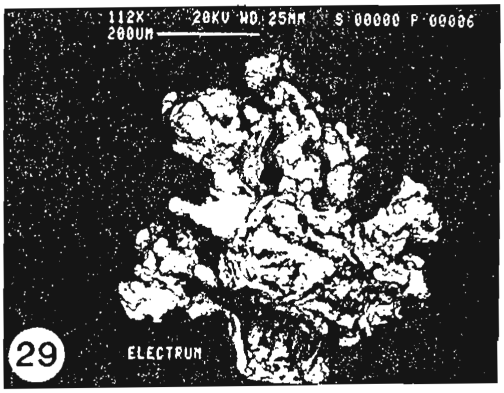
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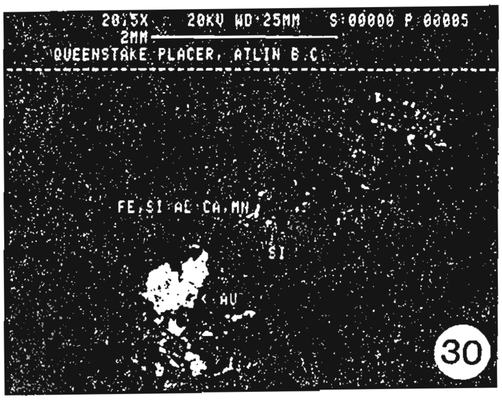
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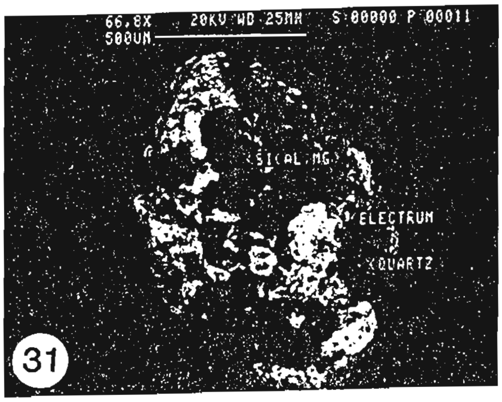
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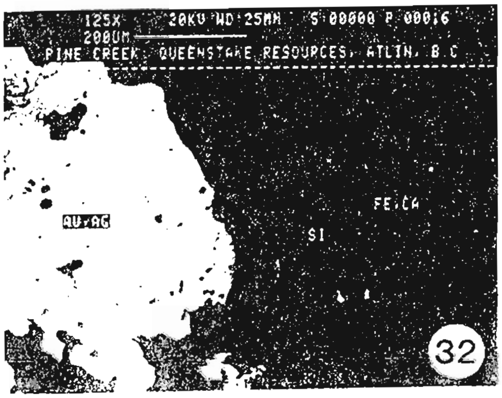
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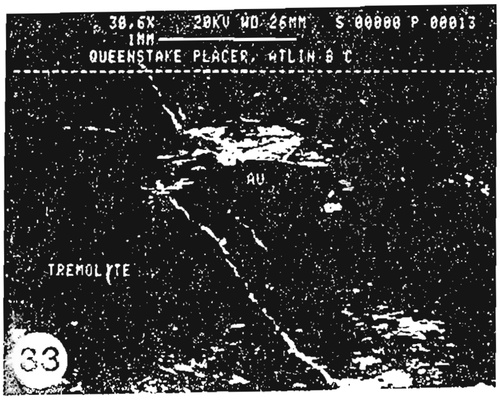
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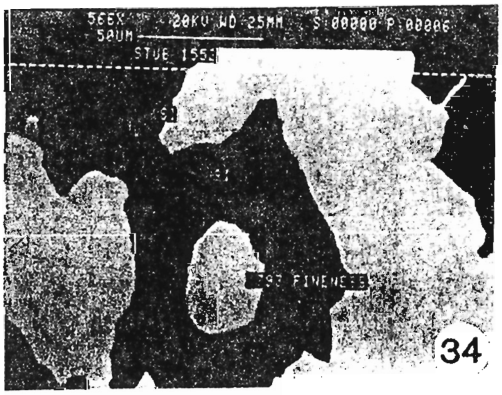
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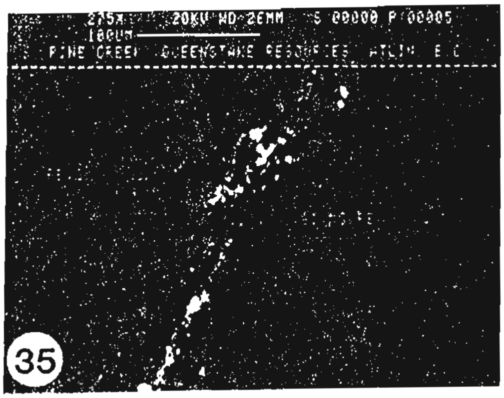
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HYDROGEOCHEMICAL STUDIES

Gold in Cordilleran Waters

Hydrogeochemical prospecting techniques are not commonly used in Canada. This geochemical exploration method must consider the wide range of climatic, physiographic and lithotectonic terrains found in the Canadian Cordillera. Currently, gold hydrogeochemistry is being tested as an exploration strategy.

This ongoing investigation aims to:

1) examine the link between known lode, precious metal, deposits and their associated placer gold deposits by measuring present day gold in water concentrations from drainages within placer gold districts.

2) determine the nature of gold distribution in natural waters associated with a number of known precious metal deposits of various genetic classifications.

3) assess the reliability of gold hydrogeochemical sampling by monitoring stream water anomalies for seasonal variability and from year to year.

4) test sampling techniques and the chosen analytical method.

5) compare the gold hydrogeochemical response to conventional stream silt and heavy mineral panning techniques and outcrop gold concentration levels.

6) establish a preliminary data base for gold concentrations in stream, spring, seepage, lake and mine water with varying pH units. The diversity of occurrence of gold (composition mineralogy, gangue-sulphide or carbonate), size and shape of gold grains, host rock and alteration, structural setting etc. will be assessed in terms of this data.

Analytical Procedures - Gold in Natural Waters

The recommended procedure is a modification of the method described by McHugh (1984). All determinations have been conducted in the G.S.C. analytical chemistry laboratories by the same analyst, Judy Vaive. This quality research and development is fully acknowledged. A more detailed discussion of gold hydrogeochemical analytical methods and assessment of the results are provided in Hall, Vaive and Ballantyne (1986).

Method

1) Water samples were filtered through 0.45 micron millepore HAWP filter paper and were returned to their original collection bottle.

2) The samples were acidified with 10ml of 5%(V/V) bromine-hydrochloric acid solution and allowed to stand for at least two days to desorb any gold which may have been lost to the container walls.

3) The sample was then transferred to a 1L beaker and then evaporated to dryness ~10 hours.

4) 7ml of 0.5%(V/V) Br_2-HBr solution was added and warmed.

5) 7ml of H_2O was added and the gold was extracted into MIBK.

6) Fe was removed by backwashing the MIBK with 0.1M HBr.

7) The MIBK portion was analyzed for gold by graphite furnace atomic absorption spectrometry (GFASS).

Practical detection limits range from 0.1 to 1 ppt depending on the original volume of water collected.

STUDY RESULTS (Figure 37)

Placer Waters

A limited number of stream waters have been collected from placer gold districts where pH's range from 7.2-8.2 units.

Unglaciated Area

In the 60 mile district of the Yukon, Miller Creek contained 0.6 ppt gold and Bedrock Creek 0.7 ppt gold.

In the Klondike district, gold concentrations in stream water from famous Hunker Creek measured 2.1 ppt, Tinhorn Gulch 1.0 ppt, Germaine Creek 0.6 ppt while Last Chance Creek and Gold Bottom Creek contained less than 0.5 ppt.

Gold in solution maybe tracing haloes surrounding:

1) preserved fossil hot-spring epithermal systems such as those found at Miller and Germaine Creeks and Tinhorn Gulch,

2) white channel gravel auriferous zones,

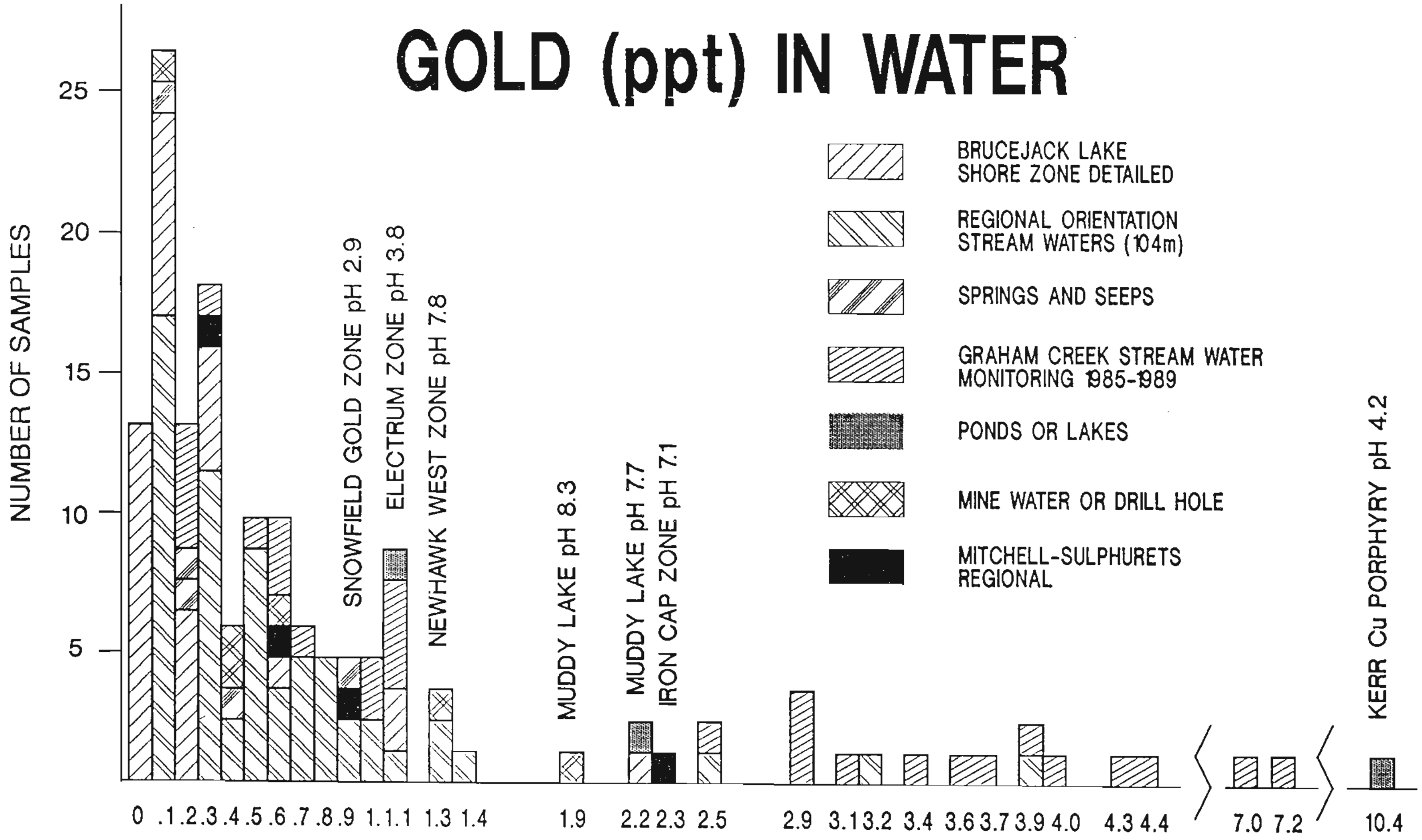

FIGURE 37 Note: most water contains little or not detectible gold contents. Anomalous gold concentrations (greater than 0.5ppt) are found 1) over a wide range of pH; 2) in all water types; 3) to be related to a spectrum of precious metal deposit types.

3) preserved supergene gold in latertitic weathering profiles,

4) mesothermal quartz-carbonate-gold veins.

Glaciated Area

In the Atlin placer district British Columbia, glaciation has exposed Motherlode District California quartz-gold veins hosted extensively carbonatized ophiolitic Cache Creek group rocks. On Monarch Mountain a small pond is situated directly below an exposed minor sulphide-bearing, quartz-carbonate, visible gold-bearing vein. The pond water was found to contain 1.1 ppt gold at pH 7.5.

Mine and Lake Waters

A limited number of mine waters have been collected from newly developed precious metals deposits in British Columbia. Underground waters issuing from cracks, faults and diamond drill holes at the Muddy Lake-Golden Bear and Brucejack Lake West Zone deposits have similar chemical features. $CaCO_3$ content is high ranging from 271-383 ppm with a pH range of 7.8 to 8.3. One sample each from the West Zone and Muddy Lake contained 1.3 and 1.9 ppt respectively. Three other samples from the West Zone had gold concentrations ranging from 0.4-0.6 ppb.

At the Kerr copper-gold porphyry deposit a low electrical conductivity (17.6 Uno) and pH pond (4.2) situated directly below the B-Zone mineralization contained 10.4 ppt gold. Sulphurets Lake, which receives water from the Kerr and Brucejack Lake mineralization contains 8.1 ppt gold. A lake water sample taken from the dock at Muddy Lake contained 2.2 ppt gold at pH 7.7. Mess Lake contained 0.8 ppt gold at pH 8.1.

DETAILED HYDROGEOCHEMICAL SURVEYS

Mitchell Sulphurets District

In a two day period during August 1987, water samples from creeks and ponds were collected north-west of Brucejack Lake and east of the Brucejack lineament. This survey was conducted prior to development of the Goldwedge gold deposit and before extensive surface exploration of the Shore and Gossan mineralized zones. The West Zone has been developed underground into a significant Ag-Au deposit. This detailed survey (34 samples) included ponds of pure snow melt water, small lakes and moderately flowing creeks, all of which drained glaciated outcrop exposures of altered and unaltered rocks.

The most anomalous sample contained 2.2 ppt gold in water and helped outline a new bedrock gold discovery. This claim group study can be compared to the regional sampling near the Iron Cap, Electrum and Snowfield gold zones (Fig. 37).

Multi-element trace element measurements and Au in water determinations are a practical exploration and environmental assessment expense EARLY in the development of a precious-metal property.

Regional 1:50000 Scale Survey
Stream Waters NTS 104M, Bennett Lake, B.C.

The BCGSB and GSC cooperative regional orientation stream water sampling survey area lies to the west of Graham Creek in NTS 104M 09, 10. Sixty samples collected in the 1988 field season showed a variable pH in the range of 5.8-7.6. with an average of 6.86. Gold values ranged from the detection limit of 0.1-3.9 ppt. Approximately 15 percent of the samples contained gold concentrations greater than 1 ppt. Mineral occurrences east of Mount Lawson and portions of the Llewellyn Fault Zone gave positive gold hydrogeochemical responses. Correlation of the water and stream sediment data is in progress. Analytical determinations for the 1989 stream water samples show similar pH levels and gold contents reaching 4.4 ppt. The full data set of 1988 and 1989 will be produced as an Open File Release.

Detailed Monitoring Study - NTS 104M
Graham Creek Gold in Stream Water

Stream water samples were collected in July 1985 from the Graham Creek drainage as part of an evaluation of field and laboratory methods in determining gold in natural waters (Hall, Vaive and Ballantyne, 1986). A resampling and monitoring of gold contents has continued since the original anomalous values of 1.1 and 2.5 ppt were determined. On July 18, 1987 ten stream water samples were collected. Very anomalous gold concentrations ranging from 2.9-7.0 ppt over the pH range 7.3-7.8 were determined. Anomalous arsenic concentrations of up to 6.9 ppb were also discovered. Seven stream water samples collected

Figure 38 : Outcropping epithermal hot spring samples, Graham Creek drainage (NTS 104M).

Samples have no precious metal enrichments but Sb, Ba and As concentrations are highly anomalous. Multi-generation chalcedony breccia samples are from a low sulphur, quartz-adularia, epithermal system. Sulphides and Sb-Pb sulphosalts (less than 50 microns in size) were extracted from the samples by cold hydrofluoric acid digestion. The consistently anomalous gold hydrogeochemistry in the Graham Creek alkaline drainage may be reflecting this low sulphur precious metal hot spring system.

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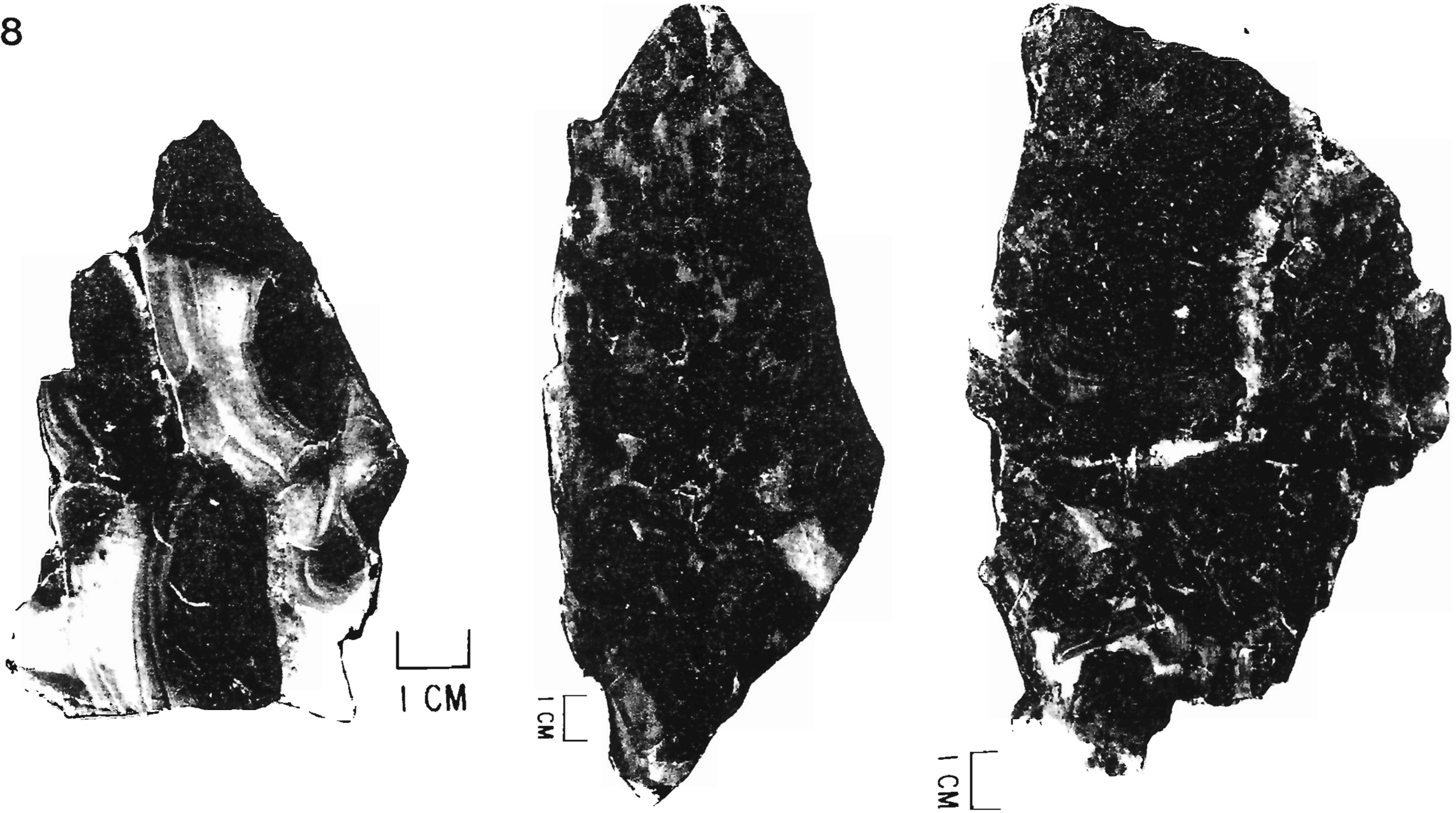

July 16, 1988 had a range of pH of 7.3-8.0 and gold concentrations ranging from less than the detection limit of 0.5 ppt to 1.1 ppt. August 1, 1988 samples (9) had pH values ranging from 7.0-8.0 and gold contents ranging from less than 0.5 ppt to 7.2 ppt. Of seven samples collected on June 30, 1989 only two contained anomalous gold contents of 0.5 ppt and 0.6 ppt with a detection limit of 0.1 ppt.

During the hydrogeochemical investigations of the Graham Creek drainage heavy mineral panned concentrates, stream silts and rock samples were also collected. Gold grains from a limited area of past placer mining were examined. They were found to be electrum in composition as well as containing iron oxide crusts and/or rock or vein gangue of variable composition. Evidence of potential gold mineralization within the drainage include outcropping examples of epithermal hot spring activity (Fig. 38) and quartz carbonate vein formation. The multi-generation chalcedony breccia samples are anomalous in Sb, Ba, and As concentrations. Complex Sb-Pb sulphosalts, barite, pyrite, melonite, molybdenite and galena have been extracted from these rocks. The sulphides are less than 50 microns in size. In the stream bed itself, outcrops of altered rhyolite were found. Quartz-carbonate veinlets and disseminated vein arsenopyrite mineralization consistently yield one ounce silver assays. Conventional minus 177 micron stream silt samples yield maximum gold contents of 10 ppb, however, lead and arsenic anomalies are more widespread within the drainage system. These findings and the consistent anomalous gold hydrogeochemical results suggest the presence of precious metal mineralization within the drainage.

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Without the excellent support of the GSC mineralogy and chemistry laboratories and staff, my ability to appreciate and decipher geochemical anomalies would have been reduced to a "number crunching" exercise.

A. Pantelyev and D. MacIntyre, project geologists with B.C.'s Geological Survey Branch, provided logistical support during cooperative programs and willingly taught me their concepts of B.C.'s ore deposit models.

In recent years, the British Columbia Geological Survey Branch has developed an Applied Geochemistry Subsection. Paul Matysek and staff have enthusiastically promoted NGR surveys and the effective use of stream geochemistry in B.C.

Most importantly, I wish to thank and acknowledge the experience and trust of the placer miners, prospectors, exploration geologists and mining companies who have provided logistical support over the years, access to data and properties and who demanded answers to their geochemical problems. As researchers, we are indebted to this curiosity and to Mother Nature since it is the continuing objective of modern exploration geochemistry to develop and test methods and models applicable to the variety of geological and surficial environments of the Canadian cordillera.

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PAPER #7

BIOGEOCHEMISTRY IN MINERAL EXPLORATION

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Abstract

In many parts of Canada abundant vegetation conceals the rocks and their mineral wealth. Trees and shrubs absorb metals in the substrate (rocks, soils, sediments and waters) and, depending upon the plant species, distribute these metals in various proportions among different tissues. In general, heavy metals tend to concentrate in the extremities of the trees - tops, twig ends, and outer bark (especially of conifers).

In order to conduct a successful exploration program for minerals using biogeochemical methods, it is first necessary to be familiar with the few *common* trees and shrubs of the northern forests, and to be aware of certain natural variations of metals that occur. These variations include seasonal and annual changes in chemistry. Six basic rules are given which will assist in conducting a successful survey.

Procedures for preparing and analyzing samples involve drying, separating tissue types (e.g. needles from twigs), and either macerating and briquetting, or ashing, prior to instrumental neutron activation analysis (and/or ICP-AES). Prior washing of samples is not necessary unless they come from a dusty area.

Examples are given which demonstrate the relationship between gold enrichments in vegetation and the presence of concealed gold mineralization.

Résumé

Dans de nombreuses régions du Canada, une végétation abondante cache les roches et leur richesse minérale. Les arbres et les arbustes absorbent les métaux du substrat (roches, sols, sédiments et eaux) et, compte tenu de l'espèce de la plante, ces métaux sont distribués en diverses proportions dans les différents tissus. En général, les métaux lourds ont tendance à se concentrer dans les extrémités des arbres: les faîtes, les extrémités des branches et l'écorce extérieure (surtout dans le cas des conifères).

Pour réaliser un programme d'exploration minérale par des méthodes biogéochimiques, il faut d'abord identifier les quelques arbres et arbustes les plus courants qui poussent dans les forêts nordiques et être au fait de certaines variations naturelles des métaux, notamment les variations chimiques saisonnières et annuelles. Six règles de base sont données pour réussir un levé.

Les procédés de préparation et d'analyse des échantillons consistent, entre autres, à sécher les types de tissus (par exemple, les aiguilles des branches), les séparer et, soit les macérer ou former des briquettes, soit les réduire en cendres, avant de les analyser par activation neutronique (ou par la méthode au plasma à couplage inductif: ICP-AES). Le lavage préalable des échantillons n'est pas nécessaire à moins qu'ils ne proviennent d'une zone poussiéreuse.

Des exemples montrant le lien entre les enrichissements aurifères dans la végétation et la présence d'une minéralisation aurifère masquée sont présentés.

INTRODUCTION

From a geochemical standpoint, trees and shrubs can be considered as the above surface extension of the geological substrate. The chemical elements of which they are composed are drawn from the soils, sediments, rocks and groundwaters. Commonly, if there is an enrichment of metals in the ground (such as a mineral deposit), there will be an enrichment of these metals in the vegetation. However, each plant species has its particular requirements and tolerances to metals, and therefore the trick in exploration is to know which plant (and, in fact, which part of a plant) to collect in order to best detect concealed mineralization.

A large tree has an extensive root system that is continually extracting elements from many cubic metres of soil and/or bedrock and the contained groundwaters. A tree requires some elements for its very existence. Other elements that are not required may be drawn up into the tree and sequestered out of harms way: in the same way that the human body tends to push toxic elements such as lead and arsenic to the hair and fingernails, the tree pushes non-essential elements to its extremities - outer bark, twigs, and tree tops.

Sampling procedures are mostly very simple, but a number of precautions need to be taken. The basic rule to be remembered when conducting a survey is 'be consistent'- just as you would in any geochemical survey. In broad terms - take the same plant organ and amount of growth, all from the same species, and as much as possible collect from trees of similar appearance and state of health. Unless dead tissue (such as bark scales) is to be sampled, seasonal changes in plant chemistry must be considered.

It is important to remember that the biogeochemical method of exploration is just another tool that an explorationist has at his or her disposal, and it should be used in conjunction with all other available geological, geochemical and geophysical information. It is not a panacea, and in some environments it is not the best tool to use. However, we now have sufficient knowledge of its application and usefulness that the thoughtful explorationist should consider using biogeochemistry as part of a mineral exploration program. It should no longer be considered a 'when all else fails' technique - vegetation chemistry frequently can provide information on the substrate that can not be obtained by other means.

FIELD ACCESSORIES

The only additions to the usual field equipment of the geologist are: a) a pair of anvil-type pruning snips, preferably Teflon-coated (no brass); b) fairly large sample bags - about 20 x 30cm - made either of heavy duty coarse brown paper if conditions are dry (e.g. 16 lb hardware bags), or cloth if conditions are wet; c) a roll of masking tape or stapler to close the bags; and d) a very large back pack, because the volume of material collected soon becomes quite large (but not heavy). Bark sampling requires a hunting knife, and a hatchet is valuable for some surveys (e.g. thick bark, such as that of Douglas-fir).

BIOGEOCHEMICAL SAMPLE MEDIA - PLANTS YOU SHOULD KNOW

It commonly occurs that when you first get out into the forest to conduct a biogeochemical survey there seems to be a bewildering array of sample media: various different trees and shrubs in different stages of growth and states of health. The first problem is to identify the common plant species, then to ascertain which species are sufficiently well distributed thoughout the survey area to permit the collection of samples at most (if not all) of the desired sample sites. Fortunately, in the vast area of Canada covered with boreal (or 'northern') forests, there are only a few common tree species which are likely to occur in sufficient abundance to be of use for a biogeochemical survey. In the temperate forests of British Columbia there are rather more species, requiring a bit more effort to be made in tree identification. In the boreal forests the most common conifers are spruce, pine, fir, and tamarack; the most common deciduous trees are birch and aspen; and the most common shrubs are alder, willow and Labrador tea. Learn to recognize these nine types of tree and shrub, and you are well on your way to conducting a consistent and successful biogeochemical sampling program. In the southern forests there is greater diversity of flora, but many elements of the northern forests are commonly interspersed. In fact these additional trees of the southern forests are mostly deciduous (e.g. maple, beech, elm, oak) and in general they are less biogeochemically informative than the nine trees and shrubs noted above.

It is necessary to take the plant identification one step further. The trees and shrubs named so far are all 'genus' names; for some genera a few species must be differentiated. Table 1 lists the main genera and species to be aware of, and a few tips to assist in their identification. This is by no means a full diagnostic description of each species - it is intended as a practical guide to help the non-botanist to distinguish among common plants that may be of use. For more details refer to widely available and inexpensive texts such as Hosie[1], Petrides[2], and Brockman[3]. It is strongly advisable to carry one of these books in a back-pack - a few minutes spent comparing a tree in the forest with the charts and descriptions in the text book helps greatly in identification of species.

In the temperate forests of British Columbia there are several 'biogeoclimatic' zones containing different floral assemblages and species not found in the boreal forest. In general, as in the boreal forest, the conifers are the most useful, especially lodgepole pine, pacific silver fir, hemlock (western and mountain), Englemann spruce, Douglas-fir, and red cedar. In different climatic settings there occur other species of pine, spruce, fir, larch, yew and cedar[1]. Of the many deciduous species that may occur, alder, birch, maple, willow and poplar are the most common[1]. The choice of sample medium depends very much on which part of the province you are in, and at what elevation. Before embarking on a survey in B.C. it would be worth spending $15 on a map entitled 'Biogeoclimatic Zones of British Columbia, 1988', published by the B.C. Ministry of Forests, Parliament Buildings, Victoria, B.C., V8W 3E7. This attractive map gives you a very good idea of what species you might expect at any locality.

Trees		
Common Name	**Botanical Name**	**Some Diagnostic Features**
Black spruce	*Picea mariana*	Needles <1 cm long, 4-sided, rigid, not prickly; small hairs on twigs. Scaly outer bark, olive-brown.
White spruce	*Picea glauca*	Needles <2 cm long, 4-sided, rigid, prickly; hairless twigs. Greyish-white bark with poorly developed or tough scales (on mature trees).
Red spruce	*Picea rubra*	Needles <1.5 cm long; Similar features to black spruce, but reddish bark. Restricted to Maritimes.
Jack pine	*Pinus banksiana*	Needles 3-4 cm long, in pairs. Scaly outer bark looks similar to black spruce. Common on poor, sandy, well-drained soils or felsic rocks.
Balsam fir	*Abies balsamea*	Needles flat, 2-4 cm long, notched at ends. Flat, circular scars on twigs when needles removed. Smooth bark with resin blisters.
Tamarack	*Larix laricina*	Soft flat needles (deciduous) in brush-like clusters. Scaly outer bark. Poorly-drained areas.
Paper birch	*Betula papyrifera*	White, peeling, multi-layered bark.
Trembling aspen	*Populus tremuloides*	Off-white, solid bark with black patches.
Shrubs		
Speckled alder	*Alnus rugosa*	Multi-branched shrub (2 - 5 m) with speckled, dark bark; toothed leaves. Occurs in wet areas.
Mountain alder	*Alnus crispa*	Multi-branched shrub (2 - 3 m) with smooth dark bark. Finely serrated leaf margins. Dry to damp areas.
Pussy willow	*Salix discolor*	Elliptical leaves, several slender reddish branches.
Labrador tea	*Ledum groenlandicum*	Low shrub with elongate evergreen leaves that have dense rusty hairs underneath. Common in damp to wet areas.

Table 1: *Common trees and shrubs of the boreal forests, and notes on some of their diagnostic features.*

SAMPLE COLLECTION

The Inhomogeneity of Trees

There are commonly substantial differences in the chemistry of different species, and also of different tissue types from the same tree (e.g. the chemistry of leaves is different from that of twigs). As an example Fig. 1 shows gold concentrations (ppb in ash) in a jack pine from near the old Rottenstone Ni/Cu/PGM/Au mine in northern Saskatchewan. Note on the upper right side of this figure that by far the highest gold concentration occurred in a sample of outer bark (140 ppb).

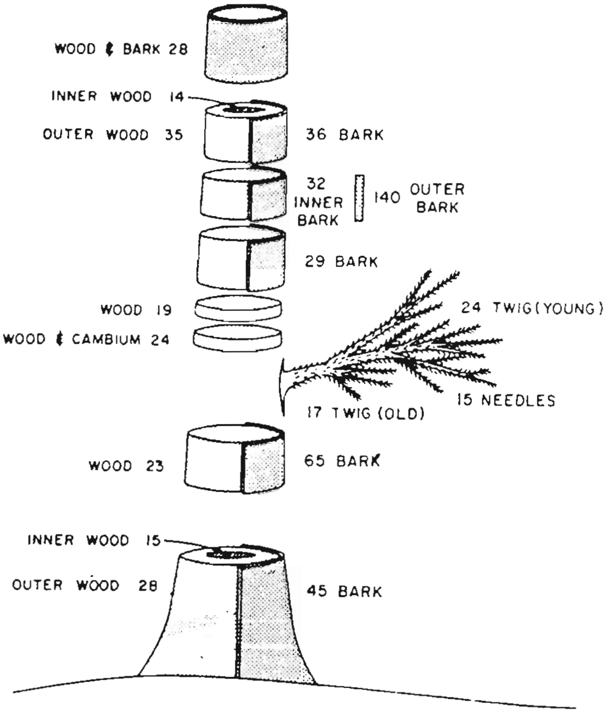

Fig. 1: *Gold content (ppb) of ashed components of a single jack pine from the vicinity of the Rottenstone Ni-Cu-Pt-Pd-Au mine, Saskatchewan*

Table 2 compares the chemistry of inner and outer bark from two red spruce trees from Nova Scotia - most elements are more highly concentrated in the outer than in the inner bark, so care must be taken to scrape only the outer bark. This is easily accomplished by using a blunt knife to remove the outer dry scales, leaving the 'live' inner bark intact.

	TREE A		TREE B	
	Inner	Outer	Inner	Outer
Au ppb	<5	**51**	9	**126**
As ppm	2	**56**	93	**300**
Sb ppm	0.1	**10**	0.7	**3.5**
Cr ppm	1	**41**	7	**18**
Fe ppm	500	**16000**	2200	**16000**
La ppm	0.5	**16**	3	**18**
Ba ppm	3600	**1500**	5100	**2500**
Zn ppm	3300	**1600**	9200	**3900**
Ca %	30	**18**	32	**28**

Table 2: *Red spruce (Nova Scotia) - the chemistry of inner and outer bark*

If twigs are the desired sample medium (such as balsam fir or shrub alder which have no scaly outer bark) the needles or leaves should be removed prior to analysis, since the foliage a) commonly contains lower levels of heavy and base metals than the twigs, and b) undergoes more rapid changes in chemistry than the twigs, both due to leaf growth and washing of salts from leaf surfaces during showers.

Therefore, for any survey ensure that you always collect the same type of plant tissue from the same species of tree, unless you have prior knowledge that no significant chemical differences occur between two or more species.

Most heavy metals, especially the precious metals, concentrate in the extremities of plants - the outer bark, the twig ends, and the tops of trees. Some metals collect in the roots, but these are impractical to collect, and few geologists can be persuaded to uproot trees in order to obtain samples! An effective biogeochemical survey needs to be simple and practical, so that an assistant can be trained to provide a consistent sample with minimal supervision.

A further complication is that the chemistry of a twig varies along its length. Most heavy and toxic metals occur toward the tips, probably because the ratio of twig bark (containing most of the metals) to twig wood is higher as the twig diameter decreases. Figure 2 shows the uranium content of dry black spruce twigs from near Saskatchewan's Athabasca uranium deposits. In this environment 10 years growth is 25 - 30 cm in length, with a maximum twig diameter of about 5 mm. The figure shows that the uranium content is much higher in the 2 - 6 year-old growth than in the older growth. It is evident that if you were to collect 3 years growth at one site and 10 years growth from another a comparison of the analytical data received would give very misleading results.

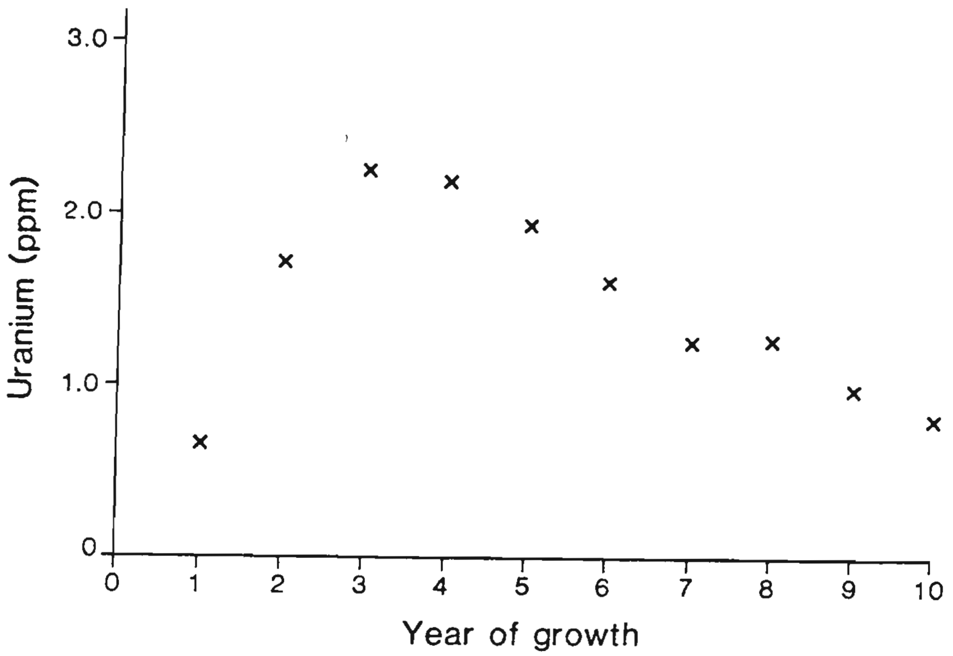

Fig. 2: *Variation in uranium concentration of dry black spruce twig growth.*

Table 3 is another example of chemical variation along a twig/branch - in this case it is western hemlock from close to gold mineralization at the Carolin Mine in British Columbia. The differences in Au, As, and Cr distributions are particularly striking, with each being most concentrated toward the twig ends. Note, too, that not all elements follow the same trend: Ca is more enriched in the thick part of the branch, whereas Sr and Zn are homogeneously distributed.

	Thick **(> 10 mm dia.)**	**Medium** **(5 - 10 mm dia.)**	**Thin** **(<5 mm dia.)**
Au (ppb)	530	650	1590
As (ppm)	22	31	82
Cr (ppm)	32	26	84
Co (ppm)	11	12	21
Ca (%)	29	24	14
Fe (%)	0.8	1.1	2.3
Na (%)	0.4	0.4	1.1
La (ppm)	2	3	6
Br (ppm)	19	18	18
Cs (ppm)	2	2	2
Sr (ppm)	430	480	450
Zn (ppm)	1500	1400	1900

Table 3: *Element distribution along branches of western hemlock (Carolin Mine, B.C.)*

Seasonal Variations in Chemistry

Outer bark may be collected at any time of the year, because it is dead material and so its chemistry changes very little with time. However, living tree parts commonly exhibit seasonal changes in chemistry, and therefore if twigs or leaves are the selected sample medium, then they should be collected in as short a time frame as possible (2 - 3 weeks). Table 4 demonstrates this point - several alder shrubs were sampled at different times of the year and analyzed for gold. Clearly the greatest anomaly contrast was obtained in the early spring (April, 1985) and no significant contrast was discernible in late summer.

Site	Alder Twigs Gold (ppb) in ash				Alder Leaves Gold (ppb) in ash		
	1984			1985	1984		
	Early June	Early August	Mid September	Mid April	June	August	September
1	32	7	23	250			
2	53	6	17	47			
3	58	9	20	130	43	6	19
4	34	6	15	166	48	7	15
5	29	8	10	37	27	18	11
6	35	7	11	34	21	6	12
7	23	6	13	57	25	7	13
8	25	8	13	41	21	13	13
9	25	11	20	27	21	11	16
10	8	20	14	20	6	<5	11
11	29	20	23	75	11	8	22
12	35	10	22	58	8	7	8
13	23	8	14	51	6	6	9
14	12	17	18	33	10	8	8
15	24	10	11	53	14	7	18
16	25	11	12	42	5	10	13
17	14	11	9	66	13	<5	13
18	21	10	38	48	8	7	14
Mean[1]	28 (0.56)	10 (0.2)	17 (0.34)	69 (1.38)	18 (0.9)	8 (0.4)	14 (0.7)

[1] Values in parentheses have been recalculated to dry weight basis.
Ash yield of dry twigs is about 2 percent; Ash yeield of dry leaves is 5 - 6 percent.

Table 4: *Seasonal changes in the gold content of ashed alder twigs and leaves*

Practical Considerations

Detailed knowledge of element distributions in the plant kingdom is needed for studies related to specific metals, and there are obviously many potential complications. However, in an exploration survey most of these complications can be avoided by just being consistent with your procedures: i.e. collect twigs of similar diameter and length. It is advisable to collect about the same number of years of growth - which can be determined by counting the growth nodes along the twig, or by counting the number of growth rings in a cut cross section (a standard geological hand lens is suitable for this). Usually if twigs of similar length and diameter are obtained, they will be of similar age, and so this is not a real problem. Exceptions occur where there are significant changes in environmental conditions, such as traverses that move from dry to boggy areas, or if there is a major change in lithology. Under such conditions a best compromise has to be taken - for example if you are collecting about 10 years of twig growth and you come to a tree with scrawny growth it might be better to collect 12 years growth. By collecting 10 years you are already integrating annual changes in chemistry throughout the growth period - by taking two more years of growth you will not affect the period of integration by much, yet you will be obtaining twigs of similar diameter and therefore similar twig bark to twig 'wood' ratios.

In bark surveys it is, once again, important to be consistent. For gold or PGE surveys collect either the outer bark, or if this is impractical, take the entire bark profile. The inner bark is the preferred medium for Ag, Ba, Rb and Zn, because that is where the higher concentrations occur (e.g. Table 2).

The procedures, the precautions, and the reasons for them can be summarized in just six key points that are outlined in Table 5.

	Basic Rules	Reasons
1.	Collect same species.	Every species has a different chemical composition, and trace element requirements and tolerances.
2.	Collect same plant organ.	Each plant organ has different capacity to store trace elements.
3.	Collect same amount (i.e. age) of growth, from same area of tree (e.g. chest height), preferably from all sides.	There are chemical variations along a twig (see Table 4). Heterogeneity in bark scales can be minimized by scraping from around the tree.
4.	Try to collect samples from plants of similar age and appearance.	This is the basic inter-site consistency that is required for any geochemical sample medium.
5.	If living tissue is the selected medium, collect at same time of year (i.e. conduct survey in 2-3 week period).	There are significant seasonal changes in plant chemistry.
	[Dead tissue (e.g. outer bark) can be collected at any time	No appreciable seasonal change]
6.	Do not return to a previously sampled tree and expect to obtain exactly the same analyses.	This is unrealistic in view of the heterogeneity of element distributions and seasonal variations in composition (and to a leser extent annual variations). Be satisfied if an anomaly is the same order of magnitude.

Table 5: *Basic rules to be applied at each sampling station when conducting a biogeochemical survey.*

There is not always the species of tree present at the site from which you would like a sample (perhaps a traverse goes from dry to wet terrain, resulting in the presence of different species). In this situation it is possible to establish relative element concentrations in different species by collecting samples of both species from the same location at several sites in the transition zone between vegetation zones. This permits normalization of the data from the different species and establishment of broad (but less precise) patterns of metal concentrations. Bear in mind that this technique does not always provide the desired results because of the different tolerances and abilities of species to absorb metals.

SAMPLE SPACING - WITH EXAMPLES

A common question is 'what is the best sample interval?'. There is no single answer, of course, because it depends on the objectives and scale of the survey (detailed or reconnaissance), and the type of mineralization being sought (e.g. if gold is the target is the geological environment expected to yield narrow quartz-hosted gold veins or broadly disseminated deposits of gold with arsenopyrite?). It is true that trees may extract metals from many cubic metres of soil, bedrock and the waters that flow through the substrate, therefore biogeochemical sample spacing can be more widely spaced than that of soils. It is probable that sample spacing of 200 m will be sufficient to detect many metal deposits, especially if the multi-element approach is used. For example quartz-hosted gold deposits may have a halo of As and Sb, associated with K metasomatism or Na depletion. Multi-element data should be used to look for patterns of enrichment or depletion that might be related to mineralization.

Sample intervals of 200 m were selected, also, for a study in British Columbia that involved snipping tree tops from a helicopter[4]. Douglas-fir tops were collected in the vicinity of poorly exposed Au mineralization associated with pyritic stockworks in propylitized basalts and tuffs (QR deposit). This sample spacing was adequate to clearly outline down-ice and down-slope movement of gold from the main deposit.

Locally, more detailed sampling may be warranted, for example to try and locate Au-rich parts of vein systems or shear zones. In 1985 the Rod Zone in the La Ronge Belt of northern Saskatchewan was known to have quartz-hosted gold. Quartz veining was thought to extend beneath thin cover of glacial material covered by moist to wet spruce forest. Spruce bark samples were collected from 20 sites at 50 m intervals along the suspected trend of the quartz vein. Background levels of gold in ashed spruce bark are, in this area, <5 ppb Au. In contrast, at the trench the bark ash yielded 230 ppb Au, and levels greater than 100 ppb were recorded in bark from four additional sites. Subsequent drilling of these sites yielded gold in each hole (Table 6 - drill-hole data couresy of G. Burrill)[5]. The area is now the site of the Jolu gold mine.

Gold (ppb) in Ashed Spruce Bark	Overburden Thickness	Drill Results
230	1 m	Near main trench.
120	1 m	Erratic mineralization: 1 m of 0.85 oz/ton (25 ppm) Au at depth of 50 m.
690	2.5 m	Subcropping mineralization - 0.11 oz (3 ppm) Au over 60 cm.
450	1 m	Subcropping mineralization - 0.3 to 0.7 oz/ton (10 - 22 ppm) Au over 4 m.
200	3 m	Mineralization, locally over 1 oz/ton (30 ppm), at shallow depth.

Table 6: *Relationship Between Gold Concentrations in the Outer Bark of Black Spruce, and Results of Subsequent Drilling Program (Rod Zone [now the Jolu Mine]), Saskatchewan.*

Reconnaissance scale sampling can be of value, too. As part of a large survey of a 5000 sq km area of eastern Nova Scotia, spruce bark was collected at a density of 1 site per 50 sq km. Analyses of Au, As, Sb and Se all successfully outlined the main gold camps[6]. A more detailed survey using balsam fir twigs at 1 per 8 sq km proved adequate to outline all known gold camps, and identified others with similar anomalies warranting investigation[7]. More recently a company collected over 5000 sagebrush samples along more than 1600 km ofrange front in Nevada and identifed 25 multi-site gold anomalies. After eliminating several of known origin and sites leased to other companies, several of unknown origin remained. Subsequently, property encompassing four of the anomalies was acquired and drilled. Gold was found in two[8].

SAMPLE PREPARATION

Washing

If samples have come from a dusty area they should be washed prior to further treatment. Rinsing in a stream or lake, or under a tap is usually sufficient. More thorough washing can be accomplished, if thought necessary, by adding a little detergent. Usually, samples need not be washed prior to analysis - remember that the dust on the samples is in most cases just silica. It is unlikely to be highly concentrated in, for example, gold to give you a spurious anomaly. Table 7 shows data from washed and unwashed portions of the same sample. In this test the washing was extremely rigorous in that the washed portions were placed in deionized water in an ultrasonic bath for one hour. The only element to show an appreciable and consistent difference was potassium.

	Sagebrush Twig		Sagebrush Leaf		Lodgepole Pine Bark	
	Unwashed	Washed	Unwashed	Washed	Unwashed	Washed
Au (ppb)	270	294	279	267	293	298
As (ppm)	100	95	50	64	150	160
Ba (ppm)	330	300	140	150	590	590
Co (ppm)	4	4	2	2	11	10
Fe (ppm)	6300	5500	2500	2800	17600	17200
K (%)	26.3	24.3	17.4	13.2	3.2	1.5
Mo (ppm)	11	10	9	11	2	3
Sb (ppm)	1.7	1.5	0.7	1.1	4.2	4.3
Zn (ppm)	570	550	530	610	1300	1400

Table 7: *Effects of thorough washing in distilled water (1 hour in ultrasonic bath) on the chemical composition of different plant tissues.*

Drying

Samples should be spread out to dry, if possible on the day of collection. If samples in paper bags are left in a back-pack or box, moisture released from the vegetation will soon cause the disintegration of the bags. If they are stored in plastic bags they will soon grow a mould and begin to rot, making sample handling very unpleasant. Furthermore, redistribution of chemical elements among tissue types may occur. Moulds can grow, too, on cloth bags. The samples do not need to be removed from the bags in which they were collected, provided the bags are moderately porous so that the air can get to the samples to dry them out. If plastic bags are used, samples must be removed on the day of collection.

It takes several weeks for samples to dry fully in a warm, dry atmosphere. Faster methods are to dry them in an oven for 24 hours at just over 100°C, or place them in a microwave oven for 10 to 40 minutes, depending upon how wet they are. Be careful, however, not to dry them too much in a microwave, and to make sure that no metal object (such as a staple) is put in with the bags - they will catch fire!

Separation

Once the moisture has been removed, it is a simple process (for most species) to remove the foliage from the twigs by pummelling the bag, then rubbing your hands through the sample to remove the brittle leaves. Remember to remove any rings and wash your hands thoroughly before doing this! This separation procedure is always advisable, because the chemistry of the different tissue types is not the same, and the density of foliage may vary from one sample to the next (therefore the ratio of twig to foliage will vary, so will the chemistry giving false anomalies).

Bark, of course, needs no further separation, since any separation of inner from outer bark will have been performed in the field - it is much easier to do this separation when the samples are moist. Drying just bakes the layers together.

The dried and separated material is then ready for either:
a) maceration and direct analysis; or
b) ashing to preconcentrate the metals prior to analysis.

a) Maceration

If a decision has been made to analyze the dry tissue, the material should next be homogenized by macerating (chopping) it in an appropriate blender or mill. The most commonly used apparatus is a 'Wylie Mill' which contains steel blades that rapidly reduce the material to small fragments that are then forced through a sieve to provide 'sawdust' powder of moderately uniform size. The material can then be pressed into pellets for trace element analysis by instrumental neutron activation (INAA) or major element analysis by XRF. The pellets for INAA are obtained by pressing 8 g or 30 g aliquots of material at 35 tons in an XRF press (this service and the maceration are provided by most commercial laboratories). Wet chemical analysis can be performed on the dry powder, but most procedures are tedious and detection limits are commonly inadequate.

b) Ashing

Preconcentration of the vegetation by ashing (available from commercial labs.) brings the levels of many metals to concentrations that are easily detectable by ICP-ES, atomic absorption, or even simple colorimetry. Maceration is not usually necessary, since 50 - 100 g of material can be placed in an aluminium tray and, after bringing the temperature slowly up to 470°C, it can be ashed for 12 -24 hours until all charcoal has disappeared. It is important that the material should just *smoulder*; if it acutally ignites some elements will volatilize.

The ash is then ready for analysis by whatever chemical method that is available and appropriate. Tests performed on the analysis of ashed and unashed tissues of the same sample indicate that a few elements (e.g. Br) volatilize during this controlled ashing procedure. With other elements there may be loss of a small portion, but data indicate that loss is a fairly consistent percentage. Figure 3 shows that for Zn there is no loss. Detailed chemical studies conducted at the GSC indicate that ashing of common plants of the boreal forests does not volatilize gold. A word of caution: a few species (not commonly used in biogeochemical surveys), especially those belonging to the rose family, contain cyanogenic glycocides. These combine with gold causing volatilization long before the usual ashing temperature is reached. Therefore, the ash yields little or no gold. Conversely, palladium forms a very stable monoxide during ashing to 470°C, requiring that the temperature be raised to 870°C to fully break this bond prior to analysis. By ashing at a lower temperature only a portion of the Pd is released upon acid digestion.

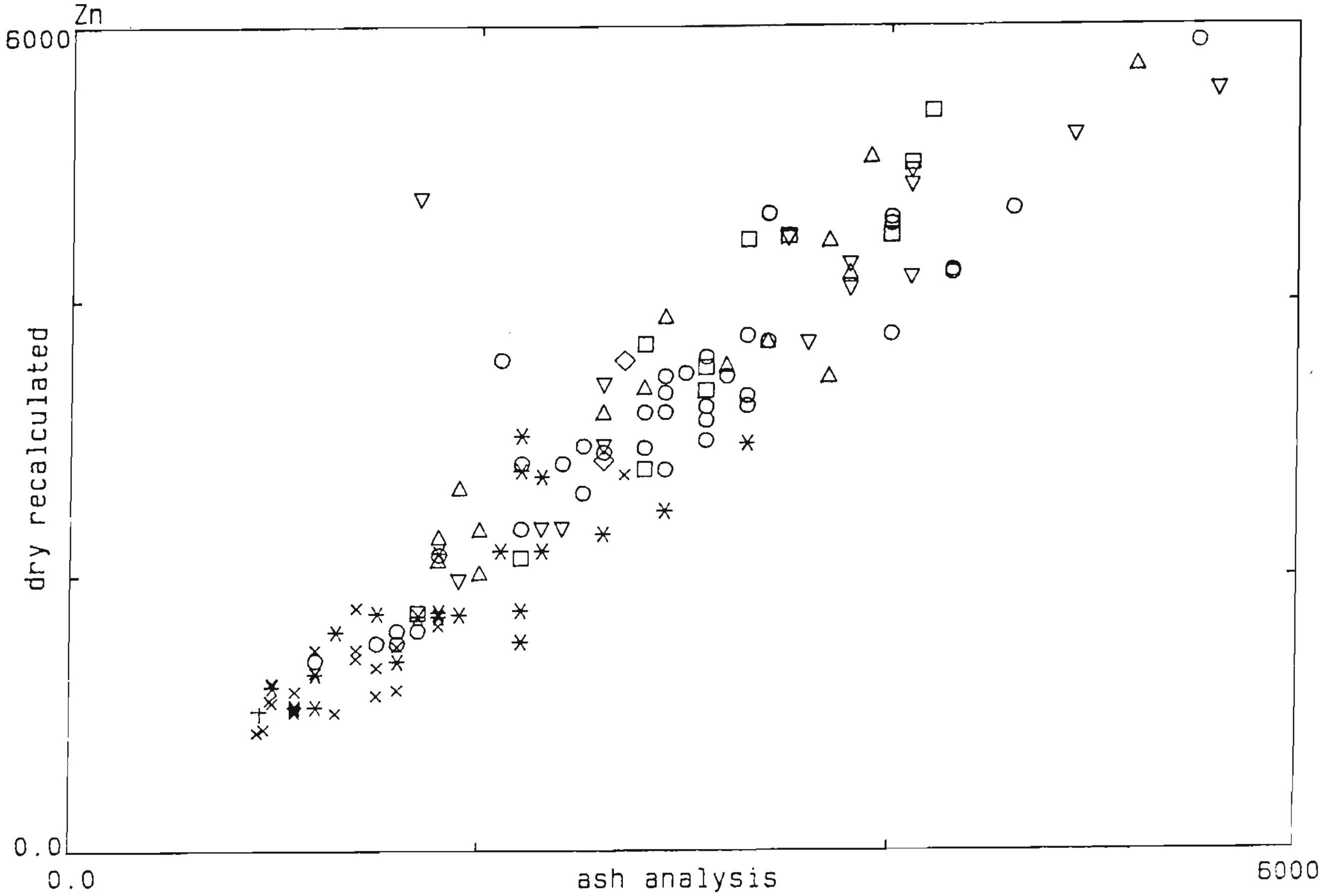

Fig. 3: *Comparison of the Zn content of ashed plant tissue with that in dry tissue (normalized to ash weight basis). Symbol shapes represent different tissue types.*

ANALYSIS

This subject is dealt with in another part of the workshop, and so only a few comments need to be made here. The analysis of *dry* plant material is best performed by briquetting the material followed by direct instrumental neutron activation analysis (INAA). Different sizes of briquettes can be made, but the larger the better in order to obtain the best representivity of the material and the best analytical precision. The largest size commercially available requires a 30 g sample. Element concentrations in dry material are low, but because interferences are far fewer than for complex silicates, the precision and accuracy of the data are remarkably good.

The analysis of *ash* may be simply performed by INAA, ICP-ES, or AAS. For any of these methods a minimum of 0.5 g of ash is recommended in order to obtain good precision. The ashing process does, of course, highly concentrate the original material so that element concentrations are typically much higher than in soils or rocks, and for many elements levels are appreciably above detection levels so that data may be quoted with a high degree of confidence in their precision. Since INAA is a non-destructive technique of high accuracy, it is recommended that for most exploration programs this method be employed first. After a period of radioactive decay of isotopes the samples can then be analyzed by wet chemical methods to obtain data for those elements not readily determined by INAA (e.g. Cu, Pb, low levels of Ni, Ag, Cd, V).

As with any geochemical technique it is *absolutely essential* that duplicate samples and appropriate standards are inserted by the client at random among a batch of samples in order that an accurate assessment of precision and accuracy can be made.

Table 8 is a broad guide to the element concentrations to be expected in ashed tissues of some commonly used sample media of boreal forests.

Element	Detection Limits	Common Concentrations in Ash		
		Alder Twig	Outer Bark Scales	
			Spruce	Jack Pine
Ag	5 ppm	<5		
As	0.5 ppm	<.5 - 1	2 - 4	4 - 8
Au	5 ppb	10 - 20	5 - 15	10 - 20
Ba	150 ppm	1000 - 3000	3000 - 5000	500 - 1000
Br[2]	0.5 ppm	20 - 40	30 - 60	10 - 50
Ca	0.5%	15 - 25	25 - 35	15 - 30
Co	1 ppm	5 - 20	5 - 10	5 - 10
Cr	2 ppm	<2 - 5	10 - 20	10 - 30
Cs	0.5 ppm	1 - 3	1 - 3	2 - 4
Fe	0.02%	0.1 - 0.2	0.2 - 1.5	0.5 - 2
Hf	1 ppm	<1	<1	1 - 2
Mo	1 ppm	1 - 5	<2	<2
Na	100 ppm	Highly variable		
Ni	200 ppm	<200		
Rb	20 ppm	100 - 500	50 - 100	50 - 150
Sb	0.2 ppm	<2	.5 - 1.5	1 - 4
Sc	0.1 ppm	0.1 - 0.3	1 - 3	2 - 4
Se	3 ppm	<3		
Sr	500 ppm	500 - 2000	500 - 1500	<500 - 1000
Ta	1 ppm	<1		
Th	0.5 ppm	<.5	1 - 2	1 - 3
U	0.5 ppm	<.5	0.5 - 1	0.5 - 2
W	1 ppm	<1		
Zn	20 ppm	500 - 1500	1000 - 2000	1000 - 2000
La	0.5 ppm	1 - 3	4 - 8	4 - 12
Ce	3 ppm	<3	6 - 12	10 - 20
Nd	5 ppm	<5	<5	5 - 10
Sm	0.1 ppm	0.1	0.5 - 1.5	1 - 2
Eu	0.5 ppm	<0.5	<0.5	0.5 - 1
Yb	0.2 ppm	<0.2	0.2 - 0.6	0.3 - 1
Lu	0.05 ppm	<0.05	0.05 - 0.1	0.05 - 0.15
Ash	%	1.5 - 2.5	2 - 3	1 - 2

Table 8: *Typical element concentrations in ashed vegetation from the Precambrian Shield. Detection limits are those that were commercially available by INAA in the mid-1980s; limits have been appreciably lowered for Ag, Ba, Ca, Na, Ni, Rb, Sr, Th, U, and most of the rare earths. Other elements now available with this analytical package include Ir (2ppb) and Hg (1 ppm), and K (0.05%).*

COMMENT

For reasons that we do not yet fully understand some mineral deposits yield only weak biogeochemical anomalies. In other areas biogeochemical anomalies have been found for which their source has not been found. However, the examples given above and a host of others in the literature demonstrate the potential value of biogeochemical methods in assisting exploration. The literature on biogeochemical exporation is extensive and growing rapidly as more success stories occur. Appended are selected references to which the interested reader may refer for greater detail.

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** *This paper lists over 200 references to papers published between 1977 and 1987.*

PAPER #8

ANALYTICAL METHODS USED IN EXPLORATION GEOCHEMISTRY

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Abstract

This paper reviews analytical methods of widespread use in production oriented laboratories for the determination of elements, primarily metallic, in support of exploration geochemistry studies. The sample media under discussion are rocks, soils and sediments, and, to a lesser extent, vegetation and waters. Assay methods used in the analysis of ores and concentrates fall outside the objectives of this review, as do colorimetric techniques still employed in developing countries and in remote locations.

The two predominant techniques, certainly in North American laboratories, are inductively coupled plasma atomic emission spectrometry (ICP-AES) and instrumental neutron activation analysis (INAA). "Analytical packages" have developed based upon not only elements of interest in exploration but on mutual compatibility in procedural schemes (irradiation time, delay period, counting time, etc.) designed for analysis by INA and on the applicability of a particular sample decomposition procedure used in conjunction with ICP-AES. Acid attack by aqua regia ($HCl-HNO_3$) and $HF-HClO_4-HNO_3-HCl$ are commonly employed and, when total decomposition is required, fusion by lithium metaborate has become popular due to its simplicity and universality. The advantages and limitations of sample decomposition by acid attack and by fusion are discussed.

Applications of atomic absorption spectrometry (AAS) employing a flame (F-AAS), quartz tube (QT-AAS) or graphite furnace (GF-AAS) as the sample cell are reviewed. Although AAS suffers in productivity and linear dynamic range compared to ICP-AES, the low cost and ruggedness of F-AAS make it preferable when only a few elements are to be determined and the high sensitivity of GF-AAS ensure it a prominent place for the determination of low abundance elements such as the precious metals, Tl and Te.

The impact on geoanalysis of the youngest solution-based technique, ICP mass spectrometry (ICP-MS), is presented. The powerful detection capability of ICP-MS combined with its essentially simultaneous mode of measurement has led to its unrivalled position in the determination of the rare earth elements (REEs), Au and the platinum group elements (PGEs). Its application to date in the determination of isotope ratios rather than abundances is not covered in this paper.

The other solid-based technique besides INAA is X-ray fluorescence (XRF). The techniques complement each other well, XRF yielding outstanding precision in analysis for the major elements together with Rb, Sr, Y, Zr and Nb while the strength of INAA lies in the determination of traces such as Au, Ir, As, Sb, Mo, W, Hf, Ta, U and the REEs. The significant advantages of these techniques over ICP-AES, AAS and ICP-MS are: the elimination of the dissolution procedure and hence the errors which could be introduced there; and the preservation of the sample for future work. The ease with which each technique can be employed to detect elements at their crustal abundance levels is shown in a grading scheme in Periodic Tables for the five techniques discussed.

Résumé

Ce rapport passe en revue les méthodes d'analyse largement utilisées dans les laboratoires de production pour mesurer les concentrations d'éléments, principalement métalliques, en appui aux études géochimiques d'exploration. Les échantillons dont il est question sont des échantillons de roches, de sédiments et, dans une moindre mesure, de plantes et d'eau. On ne discutera pas des méthodes d'analyse des minerais et des concentrés des techniques colorimétriques encore utilisées dans les pays en développement et dans les régions éloignées.

Les deux principales techniques, utilisées dans les laboratoires nord-américains, sont la spectrométrie d'émission atomique par plasma à couplage inductif (ICP-AES) et l'analyse par activation neutronique (INAA). On a rassemblé nombres d'éléments en "groupes d'analyse" basés non seulement sur les éléments d'intérêt en exploration mais sur une compatibilité mutuelle des procédés (durée d'exposition aux rayonnements, période d'attente, durée du comptage, etc.) conçus pour une analyse par activation neutronique et sur la possibilité d'appliquer une méthode de décomposition d'échantillons particulière combinée à l'ICP-AES. On recourt couramment à l'attaque acide par eau régale ($HCl-HNO_3$) et $HF-HClO_4-HNO_3-HCl$ et, lorsqu'il faut obtenir une décomposition totale, on recourt à une fusion par le métaborate de lithium dont l'utilisation est devenue populaire en raison de sa simplicité et de son universalité. Nous présenterons les avantages et les restrictions associés à l'usage de la décomposition des échantillons par attaque à l'acide et par fusion.

Les applications de la spectrométrie par absorption atomique (AAS) utilisant une flamme (F-AAS), un tube de quartz (QT-AAS) ou un four de graphite (GF-AAS) pour exciter l'échantillon sont passées en revue. Même si la productivité et l'intervalle dynamique linéaire de la méthode AAS sont inférieurs à ceux de l'ICP-AES, il est préférable de recourir

à la méthode F-AAS, en raison de son faible coût et de sa robustesse, lorsque les éléments à déterminer sont peu nombreux. La grande sensibilité de la méthode GF-AAS lui assure une utilisation importante pour déterminer les éléments peu abondants comme les métaux précieux, le Tl et le Te.

On évalue l'impact de la technique d'analyse à base de solution la plus récente, c'est-à-dire la spectrométrie de masse par plasma à couplage inductif. Comme cette méthode possède une puissante capacité de détection combinée à un mode de mesure simultané, elle est sans égales pour déterminer les terres rares, l'or et les éléments du groupe du platine. Son application pour déterminer les rapports isotopiques plutôt que les abondances n'est pas traité dans ce document.

Outre l'INAA, l'autre technique utilisant un échantillon solide est l'analyse par fluorescence des rayons X (XRF). Ces deux techniques se complètent très bien l'une l'autre: la méthode XRF permet une précision remarquable dans l'analyse des éléments majeurs et du Rb, du Sr, de l'Y, du Zr et du Nb. En revanche, la méthode INAA permet de déterminer certains éléments traces comme tels que Au, Ir, As, Sb, Mo, W, Hf, Ta, U et les terres rares. Les principaux avantages de ces techniques par rapport aux techniques ICP-AES, AAS et ICP-MS sont : l'élimination du procédé de dissolution et de ce fait des erreurs qui pourraient être introduites; et la préservation de l'échantillon pour des travaux ultérieurs. La facilité avec laquelle chaque technique peut être utilisée pour détecter les éléments à leur niveau d'abondance dans la croûte est montrée dans un schéma de classement dans les tableaux périodiques des cinq techniques traitées.

INTRODUCTION

The growth of geochemical exploration since the 1960s has gone hand in hand with advances in analytical techniques. Laitinen was the first to relate Shakespeare's seven ages of man to a common set of seven phases through which every new analytical technique passes on its way to old age and senescence. In today's well equipped laboratory, I would suggest that colorimetry and DC arc emission spectrometry have passed through all these ages and consequently these topics will be omitted from discussion here. Flame atomic absorption spectrometry's (F-AAS) heyday is certainly over, though it does find specialised usage still, and graphite furnace (GF-) AAS has enjoyed a revival. Conventional X-ray fluoresence (XRF), it is thought by some, is approaching phase seven but in the author's view plays a unique position in geoanalysis. The era of the 1980s *goldrush* saw great expansion in the use of instrumental neutron activation analysis (INAA). Its competitor in terms of volume of data produced is probably inductively coupled plasma atomic emission spectrometry (ICP-AES), currently in its fifth phase (attainment of maturity, automation of operations and computer management). Younger by a phase is ICP mass spectrometry (ICP-MS) and though early developments took place in geoanalytical labs (1983 on) its presence in commercial labs is still restricted. These are the techniques of prevalence in modern labs and their individual merits are discussed in this article. Table 1 gives the reader an appreciation of the relative sensitivities of F-AAS, GF-AAS, ICP-AES and ICP-MS in the analysis of "pure" solutions and for rocks, assuming common dilution factors (e.g., 1 g of rock dissolved to 20 ml, DF=20). Clearly ICP-MS has the advantage of sensitivity combined with essentially simultaneous multi-element capability. Its capital cost, however, is about twice that

Table 1. *Comparison of detection limit performance of F-AAS, GF-AAS, ICP-AES and ICP-MS techniques. [From Potts, 1987].*

	Limit of determination						
	F-AAS		GF-AAS	ICP-AES		ICP-MS	
Element	Solution (µg/mL)	Whole rock (ppm)	Solution (µg/mL)	Solution (µg/mL)	Whole rock (ppm)	Solution (µg/mL)	Whole rock (ppm)
Al	0.06	12	0.00015	0.046	9	0.003	3
Sb	0.12	5	0.00012	0.64	20		
As	0.3	60	0.0015	0.106	15	0.060	60
Ba	0.06	10	0.0006	0.0026	1	0.002	2
Be	0.003	0.6	0.00003	0.00054	0.1		
Bi	0.12	5	0.00015	0.068	20	0.002	2
B	2.1	90	0.225	0.0096	2	0.004	4
Cd	0.003	0.8	0.000003	0.0050	5	0.002	2
Ca	0.003	0.3	0.00015	0.020	4		
C				0.35	70	0.1	
Ce				0.104	15	0.003	3
Cs	0.06	12	0.0003	83.0	16600	0.002	2
Cr	0.009	3	0.000075	0.014	3	0.002	2
Co	0.015	2	0.00012	0.012	2	0.002	2
Cu	0.009	1	0.00010	0.0108	5	0.002	2
Dy	0.15	30		0.054	15	0.002	2
Er	0.12	21	0.0045	0.036	15	0.004	4
Eu	0.09	18	0.0015	0.0054	2	0.004	4
Gd	6	1200	0.12	0.050	5	0.004	4
Ga	0.21	42	0.0003	0.092	16		
Ge	0.3	60	0.015	0.096	40	0.004	4
Au	0.03	6	0.0015	0.034	10	0.001	1
Hf	6.0	1200		0.030	6		
Ho	0.18	36	0.0105	0.0114	15	0.001	1
In	0.12	24	0.003	0.126	25	0.002	
Ir	1.5	300	0.0075	0.054	11	0.004	4
Fe	0.015	3	0.00015	0.0124	2.5	0.004	4
La	6.0	1200	0.0075	0.020	7	0.004	4
Pb	0.06	1	0.000010	0.084	20	0.002	2
Li	0.003	1	0.00015	0.045	3	0.008	8
Lu	0.9	180		0.002	0.4		
Mg	0.0006	0.12	0.000003	0.060	12	0.002	2
Mn	0.006	1.2	0.00001	0.0028	15	0.004	4
Hg	0.51	102	0.003	0.050	10	0.004	4
Mo	0.06	6	0.00045	0.0158	10	0.004	4
Nd	3.0	600		0.272	30	0.004	4
Ni	0.015	3	0.00075	0.030	6	0.004	4
Nb	6.0	90		0.072	10	0.002	2
Os	0.3	60	0.03	0.0007	0.14	0.002	2
Pd	0.045	9	0.015	0.088	18	0.001	1
P	120.0	24000	0.3	0.152	30	0.6	600
Pt	0.21	42	0.003	0.11	22	0.002	2
K	0.003	0.6	0.000045	2400			
Pr	15.0	3000		0.094	40	0.002	2
Re	2.4	480	0.15	0.012	2.4	0.004	4
Rh	0.015	3	0.0015	0.088	18	0.002	2
Rb	0.015	1		75	15000	0.002	2
Ru	0.9	180		0.060	12	0.008	8
Sm	3.0	600		0.086	15	0.004	4
Sc	0.15	10		0.0030	2	0.006	6
Se	0.6	120	0.0015	0.15	50	0.1	100
Si	0.045	90	0.003	0.024	5		

Table 1. (cont.)

	Limit of Determination						
	F-AAS		GF-AAS	ICP-AES		ICP-MS	
Element	Solution (µg/mL)	Whole rock (ppm)	Solution (µg/mL)	Solution (µg/mL)	Whole rock (ppm)	Solution (µg/mL)	Whole rock (ppm)
Ag	0.006	1	0.00003	0.014	5	0.002	2
Na	0.001	0.2	0.000045	0.058	12	0.004	4
Sr	0.015	1	0.00015	0.00084	2	0.002	2
Ta	4.5	900		0.056	10		
Te	0.15	30	0.00075	0.082	16	0.002	2
Tb	3.0	600		0.056	80	0.004	4
Tl	0.06	12	0.00015	0.080	16	0.002	2
Th				0.166	30	0.004	4
Tm	0.3	60		0.0104	2	0.001	1
Sn	0.3	20	0.0009	0.09	6	0.004	4
Ti	0.21	42	0.0045	0.0076	1.5	0.004	4
W	3.6	90		0.060	15	0.004	4
U	90.0	90	0.45	0.500	80	0.002	2
V	0.15	1	0.0015	0.150	4	0.004	4
Yb	0.12	24	0.00015	0.0036	1	0.002	2
Y	0.6	50	0.15	0.0070	2	0.002	2
Zn	0.003	0.8	0.00003	0.008	5	0.006	6
Zr	4.5	90		0.142	6	0.002	2

Ideal solution detection limit is an estimate of the six-sigma detection limit of single element solution. Resultant values have been arbitrarily increased by a factor of two to allow for non-ideal behavior when analysing real samples.

of ICP-AES and it is probably fair to say it does not yet equal the robustness of the latter. The extremely high sensitivity of GF-AAS is counterbalanced by its low productivity (1 or 2 elements simultaneously and long cycle time).

Of equal importance when defining the whole analytical method employed is the decomposition procedure used in the case of solution based techniques such as AAS, ICP-AES and ICP-MS. All too often, one reads or hears "*the sample was analysed by ICP*". This is a completely meaningless statement. An ICP is simply a source of energy used to volatilise, atomise and ionise an analyte. How was the analyte put into solution? A fusion, which one? An acid attack? Was it completely effective for the mineralogy in question? Was the measurement by AES, MS or, less frequently, atomic fluorescence spectrometry (AFS)? Decomposition procedures in common use are also described here. This time consuming step remains the weak link in geoanalytical methods amidst the plethora of sophisticated and automated instrumental techniques. There is a great deal of research being done in *direct solid analysis* based on techniques such as ICP-AES and AAS, originally designed to accept solutions. However, this work is in its infancy and has not reached much beyond phase three, successful demonstration of the idea. Chemists are also actively engaged in finding alternative robust sample introduction techniques in ICP-AES and -MS, to replace the inefficient nebuliser (98% loss of analyte solution in the spray chamber), but for the time being this remains the standard choice.

Suggested reading material is listed with each subject in its section and books and articles of a more general nature are listed at the end of the article. Quality control procedures, still not practised widely enough by geochemists, are discussed in R. G. Garrett's contribution. The emphasis in this article is on methods in use today for the analysis of geochemical exploration samples (rocks, sediments, soils mainly) and not on assay methods for ores and minerals.

DECOMPOSITION TECHNIQUES

After preparation of the sample to a fineness of at least 150 μm, preferably 75 μm (200 mesh sieving), the elements of interest must be brought into solution for analysis by techniques such as ICP-AES, ICP-AFS, ICP-MS, AAS and electrochemical methods. Decompositions are based largely on two modes of breaking up the crystal lattice : the use of acids and fusions. The terms "partial" or "total" are used somewhat liberably to describe the effectiveness of digestion. Phase-selective leaches are being revived currently in geochemical exploration and will be discussed later in this section. In choosing the most appropriate decomposition, the following criteria must be addressed: the chemical and mineralogical properties of the sample; the elements of interest; the constraints imposed by the analytical technique(s) to be employed (e.g., interferences, especially from major constituents); the precision and accuracy limits acceptable to meet the objectives of the program; the selection of a partial or total attack for the greatest degree of contrast; and cost.

Acid digestion

The two acid digestions in common use are aqua regia and HF-$HClO_4$-HNO_3-HCl, though many combinations can be employed for different objectives. The advantages enjoyed by acid as opposed to fusion decomposition include: extraneous salts are not added to the analyte solution; acids can be obtained at a high degree of purity; Si can be volatilised with HF, thus reducing salt content; and, procedures are adaptable to large scale production. Acids high in oxidising strength include HNO_3, $HClO_4$ and H_2SO_4, while those non-oxidising in their action are HCl, HF, HBr, H_3PO_4 and dilute $HClO_4$ and H_2SO_4.

HF is most effective in breaking up the Si-O bond to form SiF_4 which volatilises upon heating. Fluorides of As, B, Ti, Nb, Ta, Ge and Sb may be lost to varying extents upon heating. HCl, a strong acid, is effective in the dissolution of carbonates, phosphates, borates and sulphates (except barite) and has become an almost universal solvent suitable for most techniques (possible exception of ICP-MS due to the formation of Cl-molecular species). Its capacity to attack Fe and Mn oxides is superior to that of HNO_3 due to its reducing and complexing properties. Pyrite is only slightly soluble in HCl while pyrrhotite, sphalerite and marmatite dissolve completely. Hot, concentrated HNO_3 is used to decompose sulphides, selenides, tellurides, arsenides, sulphoarsenides and phosphates through oxidative degradation (S is oxidised to SO_4). HNO_3 dissolves the majority of metals occurring in nature, with the exception of Au and Pt. Iron sulphides and molybdenite dissolve easily. Practically all O-containing primary U minerals are decomposed with conc. HNO_3. The powerful oxidising and dehydrating properties of hot, conc. $HClO_4$ are effective in decomposing sulphides and organic matter. Its high boiling point makes it useful in driving off HF and more volatile acids. Although H_2SO_4 has similar properties, it has not found such widespread application probably due to the interference effects created by SO_4 in AAS (1960s and 70s when much R&D was carried out into decomposition methods) and to the low solubility of alkaline earth and Pb sulphates.

HF is customarily used with mineral acids to effect decomposition of oxides and sulphides as well as silicates. Fluoride is usually removed by evaporation with $HClO_4$ thereby preventing the precipitation of insoluble fluorides (e.g., Ca, REEs) later in the digestion. Teflon or Pt dishes are employed and the absence of HF in the analyte solution makes it suitable for passage through glass nebulisers, spray chambers and torches. HNO_3 is added to moderate the action of $HClO_4$ on organic material which could be explosive. There are many variations on the procedure but normally the mixed acids are evaporated to dryness and the residue dissolved in HCl (0.5-1 M) for analysis. Although this attack is often referred to as *total*, it does not dissolve the refractory minerals cassiterite, wolframite, chromite, spinel, beryl, zircon, tourmaline, magnetite and high concentrations of barite, amongst others. Ignoring this fact can lead to misinterpretation of data and subsequently to incorrect hypotheses, as exemplified in chondrite plots for the REEs (see ICP-MS section).

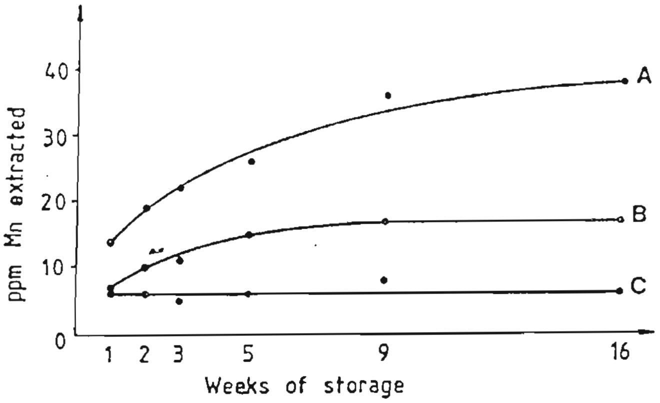
The less rigorous digestion - aqua regia - is employed more frequently than HF-$HClO_4$-HNO_3 in geochemical exploration when the elements of interest (e.g., Cu, Pb, Zn) are sorbed onto clay minerals or in other readily decomposed phases. Some labs also add HF to attack the silicates. The mixture of 3 parts HCl to 1 part HNO_3 (aqua regia) has a strong oxidising power due to the formation of nascent chlorine and nitrosyl chloride. [The Lefort digestion is the reverse mixture of these acids]. Hot aqua regia is an efficient solvent for numerous sulphides (e.g., those of As, Se, Te, Bi, Fe, Mo), arsenides, selenides, tellurides, sulphosalts, and native Au, Pt and Pd. The minerals belonging to the group of simple oxides and their hydrates (e.g., Fe-Mn) are completely decomposed with aqua regia. Natural U oxides, Ca phosphates and most sulphates (except barite) are solubilised, as are some silicates such as the zeolites. The oxidising strength of aqua regia can be enhanced by adding bromine. In Canadian labs,there has been a trend away from employing the $HClO_4$-HNO_3 attack, requiring special fume hoods, for the decomposition of organic- and sulphide-bearing material in favour of the simpler aqua regia procedure. Evaporation to dryness with conc. HCl converts salts to chlorides, ready for final solubilisation in dilute (0.5-1 M) mineral acid which is compatible with the analytical technique. Aqua regia digestion for As, Sb, Bi, Se and Te should not be taken to dryness to avoid loss of analytes via volatilisation. Strong oxidising acid mixtures are required to convert all forms of Hg to Hg^{2+}.

The effectiveness of extraction naturally depends upon the temperature, pressure and time of sample\acid contact. More complete decomposition is achieved by closed rather than open system digestion where increased temperature and pressure conditions prevail. Various types of vessels are available such as PTFE crucibles encased in metal ("bombs") and all Teflon vessels of different shapes. Polypropylene and polycarbonate bottles can be used up to 130°C while PTFE-lined vessels can withstand temperatures of 150-250°C. Pressure decomposition with mixed acids may attack certain refractory minerals (e.g., beryl, pyrite) not completely solubilised in open digestion. Unlike most of these vessels, screwcapped Teflon vials of 15 ml volume or greater are inexpensive enough to be applicable to large scale decomposition schemes. Closed system digestion is increasingly being used with the energy source being microwave radiation rather than heat. The advantages include more complete dissolution in much less time, lower volume of acids required and less exposure to toxic fumes. Adaptation to high production has been slow due to the manipulations involved but newer designs are addressing this issue.

Phase-selective leaches

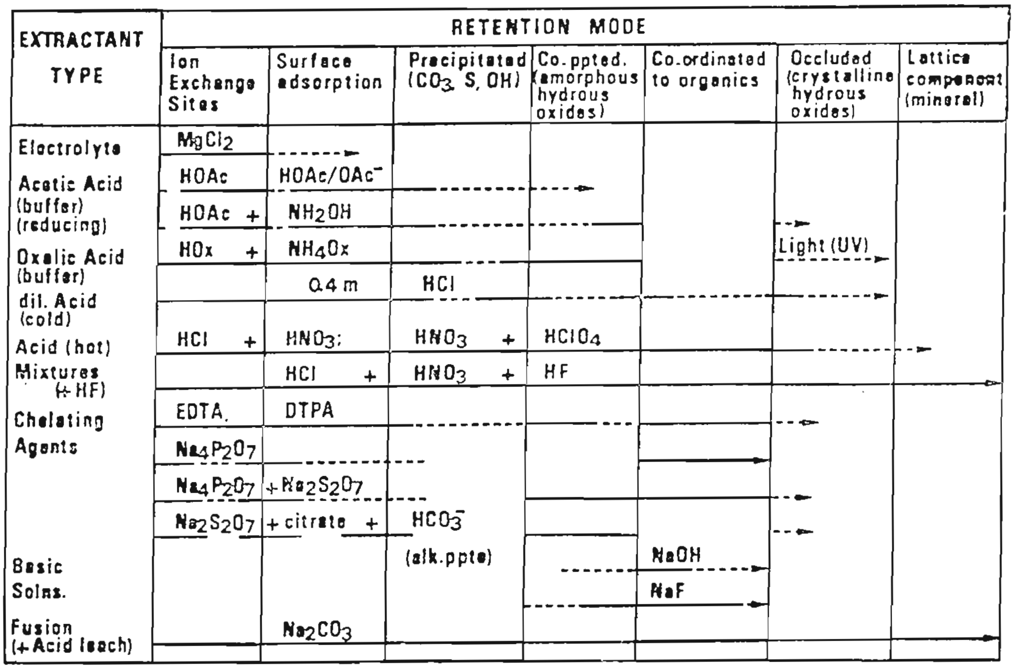
Wet chemical extractions provide a convenient means to determine the major accumulative phases for metals in sedimentary deposits and mechanisms of their diagenetic transformation. Mineralogical constituents considered important in controlling metal concentrations in sediments and soils are hydrous oxides of Fe and Mn, organic matter and clays. Fractionation is usually performed by a sequence of selective chemical extraction techniques which include the successive removal of these minerals and their associated metals. The concept of leaching is based on the idea that a particular chemical solvent is either phase or mechanistic specific (e.g., buffered acetic acid will attack and dissolve only carbonates, neutral magnesium chloride will only displace adsorbates). Reality is that the amounts extracted are *operationally defined* (e.g., time and temperature specified, number of extractions used) so that a clear distinction is not always possible. Sample storage and preparation clearly affects results; oven and even air drying can cause major equilibrium shifts, as shown in Figure 1 for Mn.

Figure 1: *Increase in Mn extractedby pH 4.8 from acetate with time, from loamy fine sand kept air dry (A), moist frozen (B), and moist at room temperature (C). [From Batley, 1989].*



A schematic representation of the different extractants in common use and their relevant phases is given in Figure 2. Probably the two most important phases in geochemical exploration are Fe and Mn hydrous oxides and organic fractions. The various reagents suitable for the former are outlined in Table 2; "soluble" organics can be extracted with alkaline solutions of NaOH or $Na_4P_2O_7$, or oxidised with reagents such as NaOCl or acidified H_2O_2. In designing a scheme, one must bear in mind the other phases which could be coextracted and incorporate the necessary steps for their separation. Examples of sequential schemes published in the literature since 1973 are shown in Table 3.

Figure 2: *Schematic representation of the ability of different extractants to release metals retained in different modes or associated with specific sediment fractions. Dashed lines indicate areas of uncertainty. [From Batley, 1989].*



Various schemes are used to separate the sulphide from silicate phase; the two most effective are probably $KClO_3$\HCl (with HNO_3 attack on the residue) and bromine\methanol. Such sequential procedures are time consuming and so have been employed relatively rarely in geochemical exploration but the wealth of information they provide is encouraging a rebirth of this approach in the 1990s.

Table 2: *Reagents used for extracting sediment Fe- and Mn-oxide fractions. [From Batley, 1989].*

Extractant	**Solution**	**Time**	**Conditions**
Hydroxylamine hydrochloride	0.1 *M* $NH_2OH{\cdot}HCl$, pH 2 /0.01 *M* HNO_3	30 min	Reciprocating
Oxalate buffer	0.2 *M* $(NH_4)_2C_2O_4$, pH 3 /0.2 *M* $H_2C_2O_4$	4 h	Reciprocating, dark
Ascorbic chloride/oxalate	Oxalate above + 0.1 *M* ascorbic acid	30 min	97°C, stir intermittently
Stannous acid/oxalate	Oxalate above + 0.1 g $SnCl_2$	30 min	97°C, stir intermittently
Hydroxylamine/sodium acetate	0.25 *M* $NH_2OH{\cdot}HCl$ + 1 *M* NaOAc, pH 5		
Hydroxylamine/citrate buffer	1.0 *M* $NH_2OH{\cdot}HCl$ + 0.175 *M* Na citrate, pH 5	10 min	Vortex mix
Hydroxylamine/acetic acid	1.0 *M* $NH_2OH{\cdot}HCl$ in 25% (v/v) HOAc	30 min	Reciprocating
Hydroxylamine/hydrochloric acid	0.25 *M* $NH_2OH{\cdot}HCl$ in 0.25 *M* HCl	30 min	50°C, stir intermittently
Dithionite/citrate buffer (DCB)	20 g citrate + 2 g dithionite per 100 ml	Overnight	Reciprocating

FUSIONS

The great efficiency of fusion compared to acid attack is due to the effect of the high temperature (500-1100°C). Heterogeneous reactions taking place in the melt are of two types: acid-base and oxidation-reduction. Alkaline flux reagents include Na and K carbonate (and bi-), Na and K hydroxide, and sodium tetraborate; acid fluxes include Na and K hydrosulphate, Na and K pyrosulphate, boron trioxide and hydrofluoride. Oxidative reagents comprise largely Na_2O_2, KNO_3 and $KClO_3$ while carbonaceous substances such as flour and starch are added to flux mixtures for a reducing action. The drawbacks of a fusion are: (1) the potential addition of contaminants due to the high flux:sample ratio (3:1 to 10:1); (2) the high salt concentration introduced and subsequent need for a higher dilution factor; and, (3) the difficulty in streamlining the operation for high throughput.

Although classical methods of silicate analysis relied heavily upon the Na_2CO_3 flux, borate fusion, particularly $LiBO_2$ rather than $Li_2B_4O_7$, now dominates in geoanalysis due to its widespread applicability and effectiveness at low flux:sample ratios (3:1 or greater). Flux and sample are simply mixed together in a graphite or Pt crucible, fused at 1000^oC for 30 min. with gentle swirling, allowed to cool and the melt dissolved in HNO_3 or HCl. This fusion is employed for major and minor element determination as well as for traces where a dilution factor of ca. 500 suffices. More work is needed in designing automated preconcentration schemes so that this efficient method of decomposition can cover a wide range of trace elements using various analytical techniques.

Boron is often determined after a Na_2CO_3-$NaNO_3$ fusion; other oxyanion forming elements such as Cr, V, Mo and W can be determined simultaneously. Potassium pyrosulphate is useful in decomposing some refractory oxides such as rutile and ilmenite as well as oxides of Nb and Ta whereas silicates are not effectively attacked. Ammonium iodide is considered to be specific to convert cassiterite-Sn to SnI_4, thus providing a method to classify Sn-binding ($LiBO_2$ fusion would represent total Sn). Fusion with Na_2O_2 is effective for the decomposition of sulphides, arsenides, REE phosphates, W, Nb and Ta minerals, vanadates, chromite and zircon.

A combination of acid attack and fusion, as a way of ensuring total dissolution of all minerals while retaining a low dilution factor of ca. 100, has been described by Thompson and Walsh (1989). The residue remaining after an HF-$HClO_4$-HNO_3 digestion is fused with a small amount of $LiBO_2$, dissolved in acid and the two extracts combined for analysis.

Decomposition methods for Au and the PGEs are discussed in a separate section.

Table 3: *Some sequential extraction schemes used between 1973 and 1986. [From Batley, 1989].*

	Exchangeable[a]	Specifically sorbed, carbonate bound	Easily reducible substrates	Easily extractable organics	Moderately reducible oxides	Oxidizable oxides and sulfides	Crystalline Fe-oxides	Residual minerals
A	$CaCl_2$	HOAc		$K_4P_2O_7$	NH_4Ox/HOx			HF
B	NH_4OAc	HOAc			$NH_2OH \cdot HCl/HOAc^{4b}$	$H_2O_2{}^3$	(DCB^4)	$HNO_3/HF/HClO_4$
C	$MgCl_2$			$NaOCl/DCB^3$			DCB^2	Fusion
D	NH_4OAc		$NH_2OH \cdot HCl$ pH 2			H_2O_2/NH_4OAc	DCB	HF/HNO_3
E	NH_4OAc		$NH_2OH \cdot HCl/NH_4OAc$			H_2O_2/NH_4OAc	$NH_2NH_2 \cdot HCl$	HF
F		HOAc	$NH_2OH \cdot HCl$ pH 2		$NH_2OH \cdot HCl/HOAc^4$	H_2O_2/NH_4OAc		$HF/HNO_3/HClO_4$
G			$NH_2OH \cdot HCl$ pH 2^2	$NaOCl^1$	NH_4Ox/HOx		DCB	$HClO_4/HNO_3$
H	$MgCl_2$	NaOAc pH 5			$NH_2OH \cdot HCl/HOAc$	H_2O_2/NH_4OAc		$HF/HClO_4$
I	NH_4OAc		$NH_2OH \cdot HCl$ pH 2			H_2O_2/NH_4OAc		$HF/HClO_4$
J	$NH_4OAc/MgOAc$		$NH_2OH \cdot HCl$ pH 2^3			H_2O_2/NH_4OAc^2		—
K	$NH_4OAc^1/CuOAc^2/NaOAc^4$			$Na_4P_2O_7{}^3$			HNO_3	—
L			$NH_2OH \cdot HCl$ pH 2^2	$NaOCl^1$	$NH_2OH \cdot HCl/HOAc$			HNO_3
M	$BaCl_2$	NaOAc pH 5^1			$NH_2OH \cdot HCl/HOAc^4$	H_2O_2/NH_4OAc^2		$HF/HClO_4/HNO_3$
N	$MgNO_3$		$NH_2OH \cdot HCl$ pH 2^3	$NaOCl^2$	NH_4Ox/HOx			$HF/HNO_3/HCl$
O	$MgCl_2$	NaOAc pH 5			$NH_2OH \cdot HCl/HOAc$	H_2O_2/NH_4OAc		$HF/HClO_4/HCl$
P	NH_4citrate		$NH_2OH \cdot HCl$ pH 2	$NaOCl/HCl$			$NH_2NH_2 \cdot HCl$	—
Q		NaOAc pH 5		$SDS/NaHCO_3$	$NH_2OH \cdot HCl$/ci-trate			HF/HNO_3
R	$MgCl_2$	NaOAc pH 5	$NH_2OH \cdot HCl$ pH 2		$NH_2OH \cdot HCl/HOAc^5$	H_2O_2/NH_4OAc		—
S	NH_4OAc	NaOAc pH 5	$NH_2OH \cdot HCl$ pH 2		NH_4Ox/HOx	H_2O_2/NH_4OAc		HNO_3
T	NH_4OAc	NaOAc pH 5	$NH_2OH \cdot HCl$ pH 2		$NH_2OH \cdot HCl/HOAc$	H_2O_2		$HNO_3/HCl/HF$
U	$MgCl_2$	$NH_2OH \cdot HCl/NaOAc$ pH 5		$Na_4P_2O_7$	$NH_2OH \cdot HCl/HOAc$	H_2O_2/NH_4OAc		—

[a] Some schemes extract the interstitial and water-soluble fraction before the exchangeable, which is not indicated here.

[b] Order of attack noted by superscript numbers, where it differs from left to right.

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ATOMIC ABSORPTION SPECTROMETRY (AAS)

AAS was rapidly adapted to geoanalytical applications in the early 1960s following the availability of commercial instrumentation and it remained the leading technique in the analysis of solutions until the advent of ICP-AES in the late 70s. The reason for its decline in favour of ICP-AES is due mainly to the fact that only one element at a time can be determined by AAS and hence it cannot compete in speed with multi-element techniques. Furthermore, the short linear dynamic range of AAS necessitates dilution for the more highly concentrated analytes which leads to reduced productivity and greater error. The principle advantages of AAS comprise its specificity, simplicity, low capital outlay, ruggedness and relative freedom from interferences. Today, probably the most important geological applications of AAS lie in the specialised areas where flame atomisation is replaced by graphite furnace or vapour generation\quartz tube modifications.

An AA spectrometer consists of: a light source (usually a hollow cathode lamp,HCL) which emits a sharp line of the analyte; a chopper to eliminate emitted light from the cell; an atomisation cell (flame, furnace, quartz tube); a monochromator to select the line of interest; a photomultiplier detector; and a read-out system (Figure 3). Thus, conventionally, a solution containing the element of interest is nebulised into an air-acetylene (2200°C) or nitrous oxide-acetylene (2900°C) flame which dissociates compounds into atoms and absorption of light at the resonant wavelength(s) emitted by the specific HCL takes place. The concentration of analyte is proportional to the absorbance measured and calibration is made against known standard solutions. Double-beam instruments (Figure 3) compensate for drift in lamp intensity; one manufacturer offers two monochromators for simultaneous detection of two analytes. Options range from a basic single beam unit to a fully automated micro-processor controlled instrument.

Interferences fall broadly into the following categories: spectral; chemical; ionisation; and viscosity effects. Spectral overlap, that is the inability to resolve adjacent absorption lines of two elements is rare; non-specific broad-band absorption by molecules such as CaOH is subtracted by correction procedures employing deuterium arc, Zeeman or Smith-Heiftje measurement. Background correction should be employed routinely for elements such as Pb, Ag, Ni and Co. Chemical interference occurs when the analyte is bound in a stable

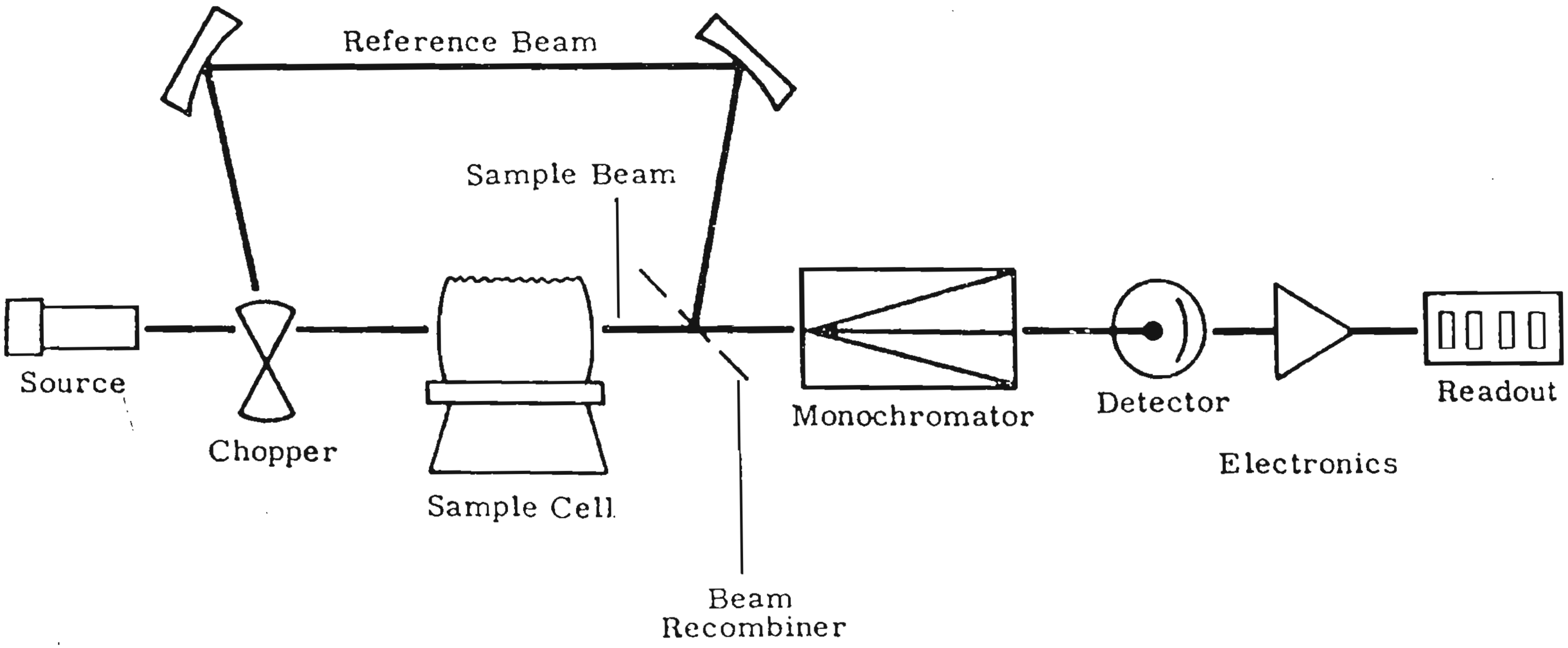


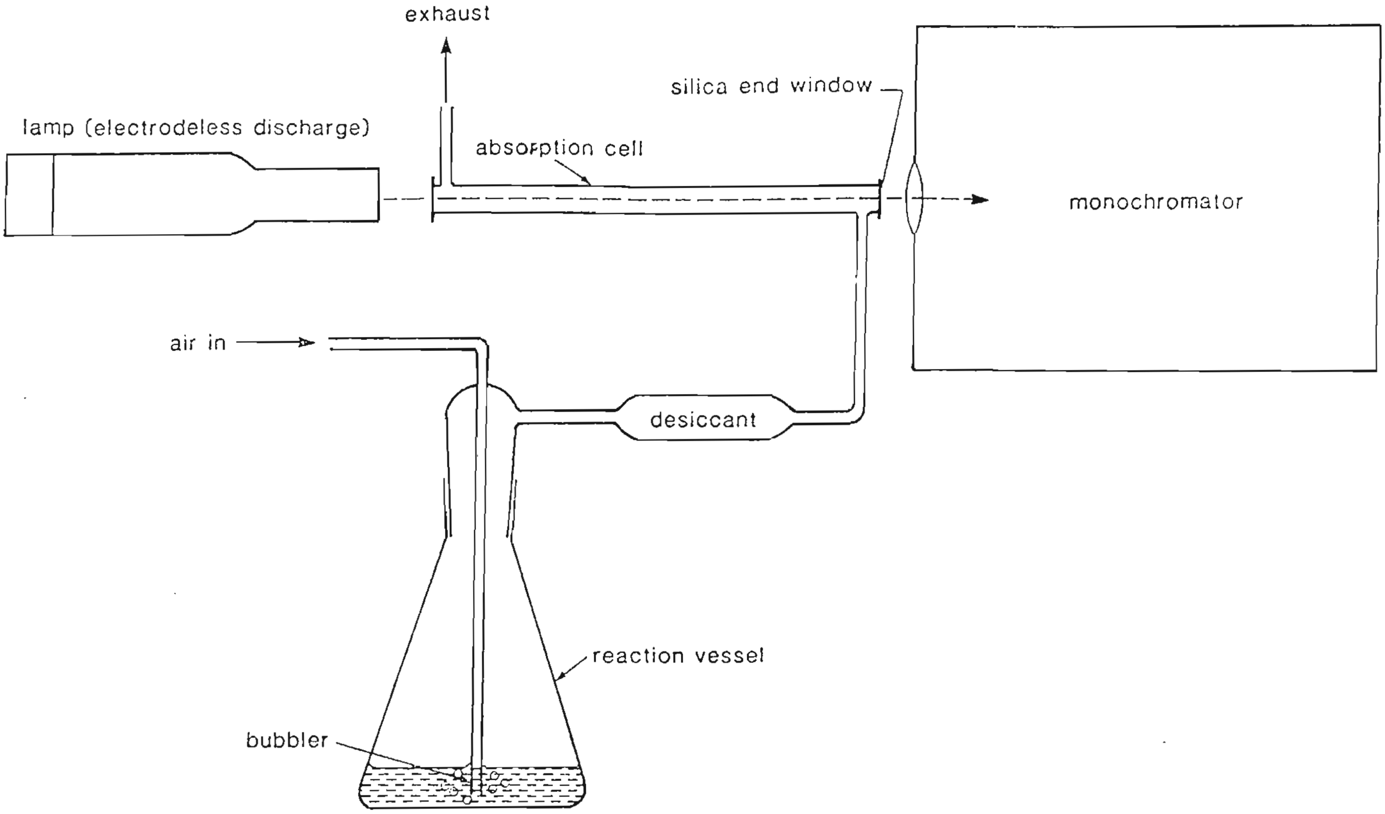
Figure 3: *Double beam AA spectrometer.*

compound in the flame rather than being present as a free atom. For example, Ca-O-P and Al-O-Mg bonding is relatively stable in an air-acetylene flame but is broken down in the hotter nitrous oxide-acetylene environment. Alternatively, a releasing agent such as La is added in solution which preferentially binds with O. Alkali and alkaline-earth elements suffer from ionisation effects (low ionisation potential, IP) where the population of ground state atoms is depleted by formation of their ions and hence the measured absorbance of resonance light is depressed. Addition of an excess of another alkali of low IP (e.g., Cs) creates a large population of free electrons in the flame, thus suppressing analyte ionisation. Differences in viscosity or surface tension properties and hence nebulisation efficiency can be overcome by matrix matching or the method of standard additions, but this interference is rare.

Elements which can normally be determined by flame AAS include the majors and minors Si, Ca, Mg, Na, K, Al, Fe, Ti, Mn and the traces Ba, Be, Co, Cr, Li, Ni, Pb, Rb, Sr, V and Zn. Other geochemically important trace elements require a preconcentration step such as that developed by Viets and colleagues at the USGS which is based on the extraction of metal iodides into MIBK-Aliquat 336 (a quaternary alkylammonium chloride). This procedure improves detection capability for such elements as Ag, Bi, Cd, Pb, Mo, Sb, As, Ga, In, Tl and Se and has been adopted for ICP-AES measurement by several commercial geoanalytical laboratories.

Cold-vapour (CV) AAS remains the analytical technique of choice for the determination of Hg (Figure 4). Hg ions, present in an acid leachate (H_2SO_4-HNO_3; HCl-HNO_3; or HNO_3-$HClO_4$) of the sample, are reduced to the metal (with sodium borohydride or stannous sulphate) which is then swept in vapour form with air and liberated H_2 into an absorption cell located in the optical axis of an AA spectrometer. Measurement of absorbance at 253.7 nm results in detection limits in the range of 5-15 ppb based on the decomposition of a 1 g sample. Interference via the formation of stable Hg compounds with precious metals, Se and Te is minimal due to the low natural abundance of these elements and to their incomplete digestion by common acid attacks. An alternative procedure eliminates the digestion stage by combustion of the sample at 1000^{0}C, capture of the evolved

Figure 4: *Apparatus for the CV-AAS determination of Hg. [From Potts, 1987].*

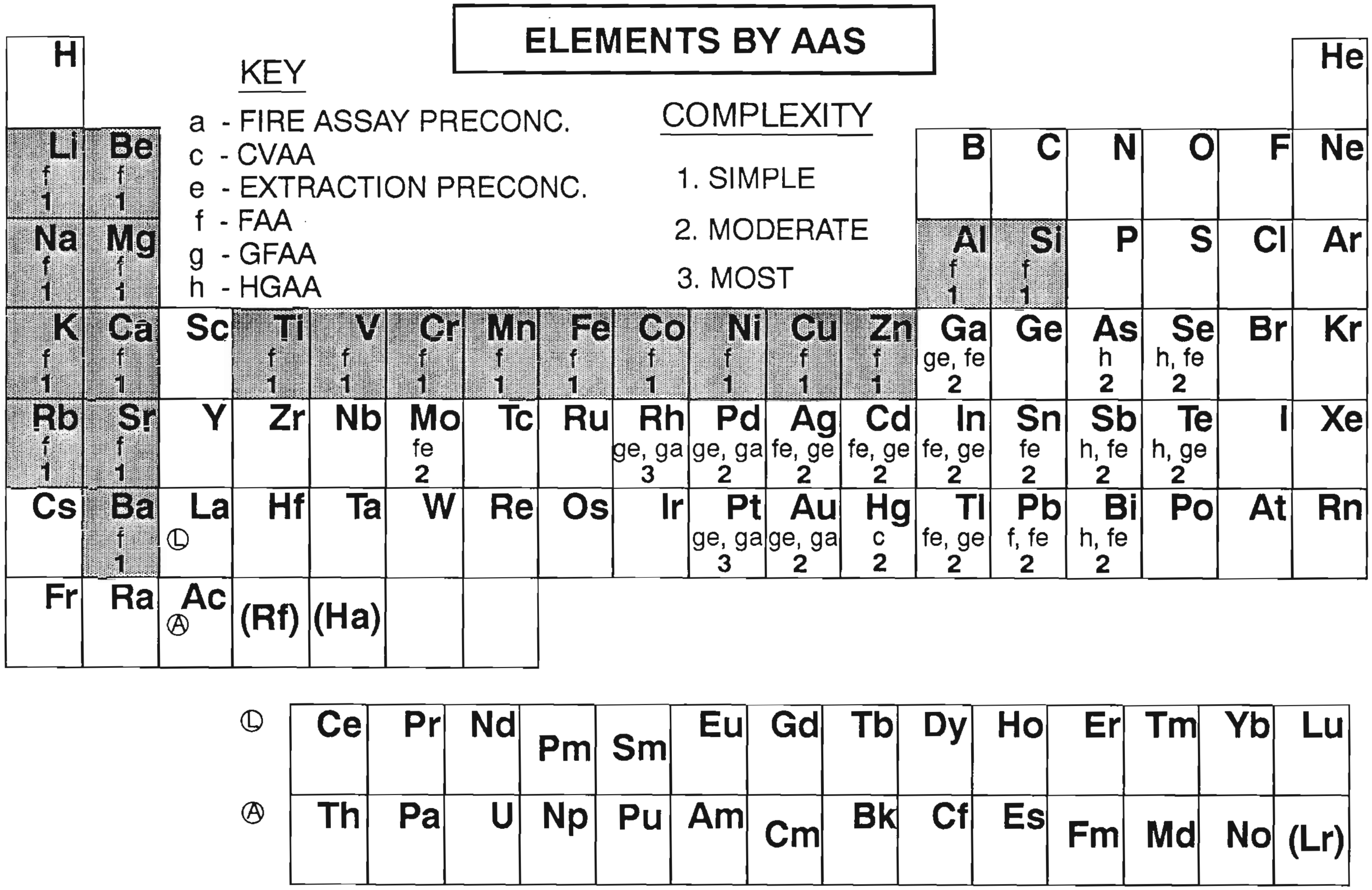


Hg vapour on Au foil and subsequent release of Hg into an absorption cell by rapid heating.

As for Hg, instrument manufacturers offer "front-end" generation systems to evolve the hydrides of As, Sb, Se, Te, Bi, Sn and Ge. The first three are commonly determined in geoanalytical labs by hydride generation (HG) AAS. Again like Hg, the most sensitive absorption lines of these elements lie in the 200 nm region where air and normal flame gases themselves absorb strongly. General practise involves formation of the hydride by the addition of a strong reducing agent, such as sodium borohydride, to an acid leachate (HCl-HNO_3; HF-$HClO_4$-HNO_3) and transfer of the vapour in a flow of argon into a heated (electrically or by air-acetylene flame) quartz tube situated in the light path of an AA spectrometer. Detection of the analytes to levels of about 0.1 ppm (in solid) is practical but care must be taken to avoid interferences which can be numerous and whose magnitude is specific to the operating conditions and generation system employed. Transition elements such as Cu, Ni, Co and precious metals suppress the signal by their reduction and subsequent adsorption and destruction of the analyte hydrides; a wealth of literature exists describing minimisation of interference by addition of reagents to prevent their reduction or by separation of analytes by coprecipitation on $La(OH)_3$ or $Fe(OH)_3$. The latter method is employed routinely at the GSC as it is not practical or possible to separate out samples containing > 0.1 % Cu etc.; over 5000 samples are analysed anually for As, Sb, Bi, Se and Te. Care is also necessary in ensuring that the analyte is in the appropriate valency state for reduction. Attempts to decrease detection limits to say, 10 ppb in the solid for Se and Te are hampered by the presence of mutual interferences (e.g., As on Te) and much work has concentrated on understanding these mechanisms, in the generation of the hydride, its transfer to the cell and radical formation (e.g., As-Te) in the quartz cell itself.

Graphite furnace (GF) AAS enjoys superior sensitivity over F-AAS by 1-3 orders of magnitude but suffers from more complex interferences and lower productivity. The last 5-8 years have seen a "rebirth" of this technique due to the following: improved furnace design (e.g., L'vov platform) to achieve atomisation into an isothermal atmosphere to minimise gas phase interferences; matrix modifiers (e.g., Pd, $MgNO_3$) proven to be of widespread application in negating chemical interferences; accurate background correction facilities; and sophisticated electronics for signal integration and output. Briefly, a sample aliquot (5-50 μl) is automatically injected into a graphite furnace (+/- matrix modifier) whereupon a progressive heating program is applied to dry (100-150°C), ash (400-1000°C)and atomise (1000-3000°C) the sample. Typically, each analysis requires 2 min. Unlike F-AAS, it is desirable to avoid HCl in the final sample matrix to negate Cl vapour phase interferences and so HNO_3 and, to a lesser extent, H_2SO_4 are preferred. The analysis of geological matrices by GF-AAS generally demands separation of the analyte from major concomitants by solvent extraction or coprecipitation. Elements not served well by F-AAS and thus requiring the sensitivity of GF-AAS include Ag, Cd, In, Sn, Tl and Pb. Probably the greatest need for GF-AAS lies in the determination of Au, Pt, Pd and Rh and undoubtedly the most common organic separation used in geochemical exploration is the extraction of Au as the chloro or bromo anion into MIBK (methyl isobutyl ketone). Separation of Au, Pt and Pd is also accomplished by Pb fire assay, leaving the analytes in a "clean" acidic solution for GF-AAS. The determination of Au and the PGEs is discussed in another section.

The elements annotated in the Periodic Table (Figure 5) can, for the most part, be determined easily by AAS to crustal abundance levels with different degrees of complexity reflecting the relative cost and productivity of analysis. In summary, F-AAS remains useful



ELEMENTS BY AAS

KEY

a - FIRE ASSAY PRECONC.
c - CVAA
e - EXTRACTION PRECONC.
f - FAA
g - GFAA
h - HGAA

COMPLEXITY

1. SIMPLE
2. MODERATE
3. MOST

H																	He
▨ Li f 1	▨ Be f 1											B	C	N	O	F	Ne
▨ Na f 1	▨ Mg f 1											▨ Al f 1	▨ Si f 1	P	S	Cl	Ar
▨ K f 1	▨ Ca f 1	Sc	▨ Ti f 1	▨ V f 1	▨ Cr f 1	▨ Mn f 1	▨ Fe f 1	▨ Co f 1	▨ Ni f 1	▨ Cu f 1	▨ Zn f 1	Ga ge, fe 2	Ge	As h 2	Se h, fe 2	Br	Kr
▨ Rb f 1	▨ Sr f 1	Y	Zr	Nb	Mo fe 2	Tc	Ru	Rh ge, ga 3	Pd ge, ga 2	Ag fe, ge 2	Cd fe, ge 2	In fe, ge 2	Sn fe 2	Sb h, fe 2	Te h, ge 2	I	Xe
Cs	▨ Ba f 1	La Ⓛ	Hf	Ta	W	Re	Os	Ir	Pt ge, ga 3	Au ge, ga 2	Hg c 2	Tl fe, ge 2	Pb f, fe 2	Bi h, fe 2	Po	At	Rn
Fr	Ra	Ac Ⓐ	(Rf)	(Ha)													

Ⓛ	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ⓐ	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	(Lr)

▨ Indicates "best" element by this technique

FIGURE 5 : *Sensitivities with respect to crustal abundances*

when only 3-4 elements are to be determined and sensitivity is adequate; its instrumentation is robust and highly skilled operators are not mandatory. AAS provides cost effective analysis for Au and its pathfinder elements As, Sb and Hg using GF-, HG- and CV-introduction methods. The detection capability of GF-AAS is rivalled only by the much more expensive and sophisticated technique of ICP-MS. A field-portable AA spectrometer, the AAZ, is made by Scintrex of Concord, Ont. and is based on atomisation from a tungsten filament with Zeeman background correction. Research is currently active in the analytical community into the direct analysis of slurried samples by GF-AAS and automated injection devices are now available. The obvious advantage here is elimination of the digestion step but limitations in geoanalysis include the inevitable small sampling feature (5-20 mg) and hence likely heterogeneity problem, the need for fine grinding (to say 10 μm) and the possibility of increased interferences from the vapourisation and atomisation of complex geological matrices.

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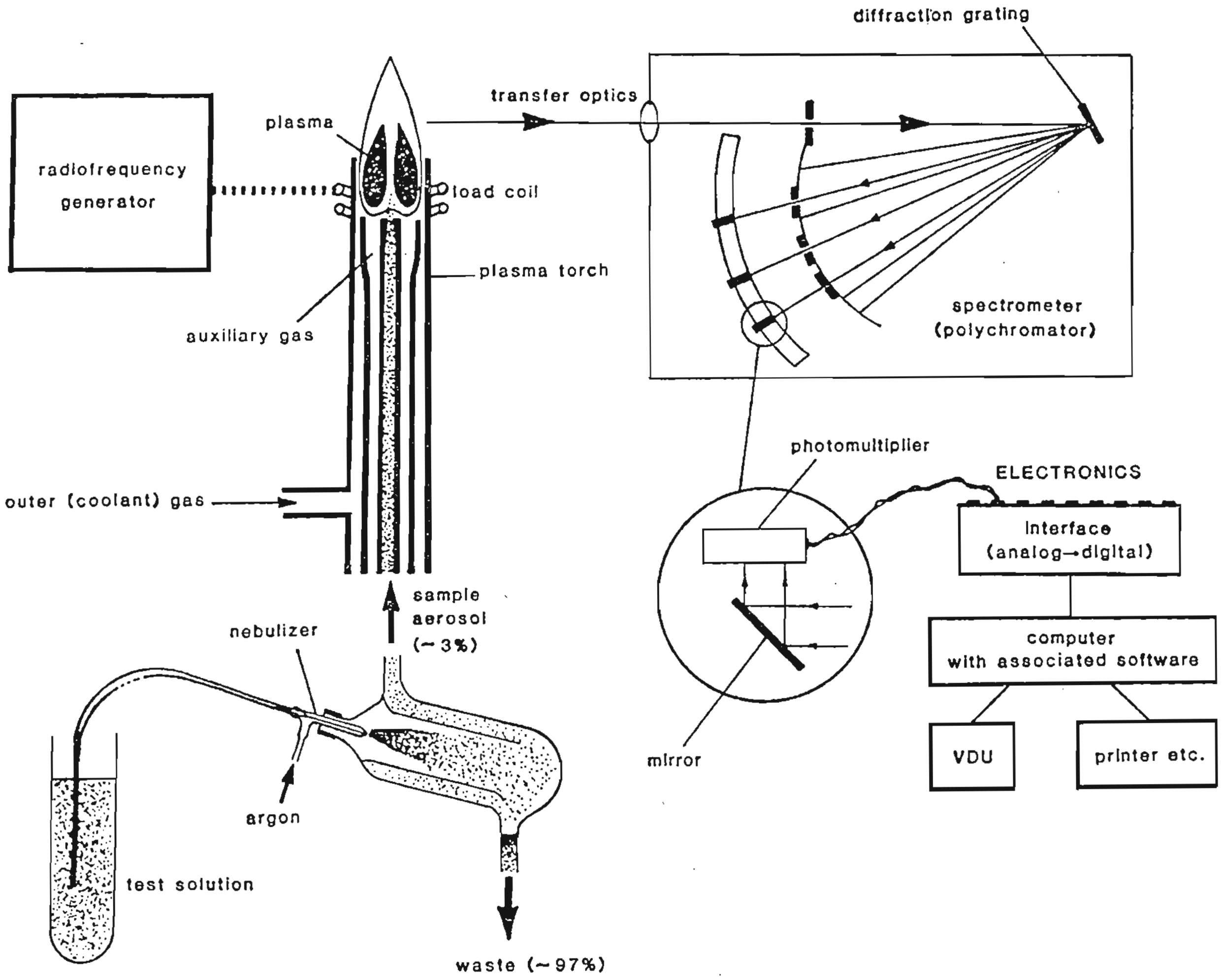
INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP-AES)

The first ICP emission spectrometer was introduced commercially in 1975 and rapidly became the workhorse of labs with a tradition of wet chemical analysis. The attraction over the established technique of AAS was the ability to determine 20-60 elements *simultaneously* in a cycle time of 2-3 min. Furthermore, the long linear dynamic range of 3-5 orders of magnitude meant that both major and trace elements could be determined on the same solution (i.e. no dilution). It remains firmly today as the leading instrument in geoanalytical labs, as is evident from company brochures.

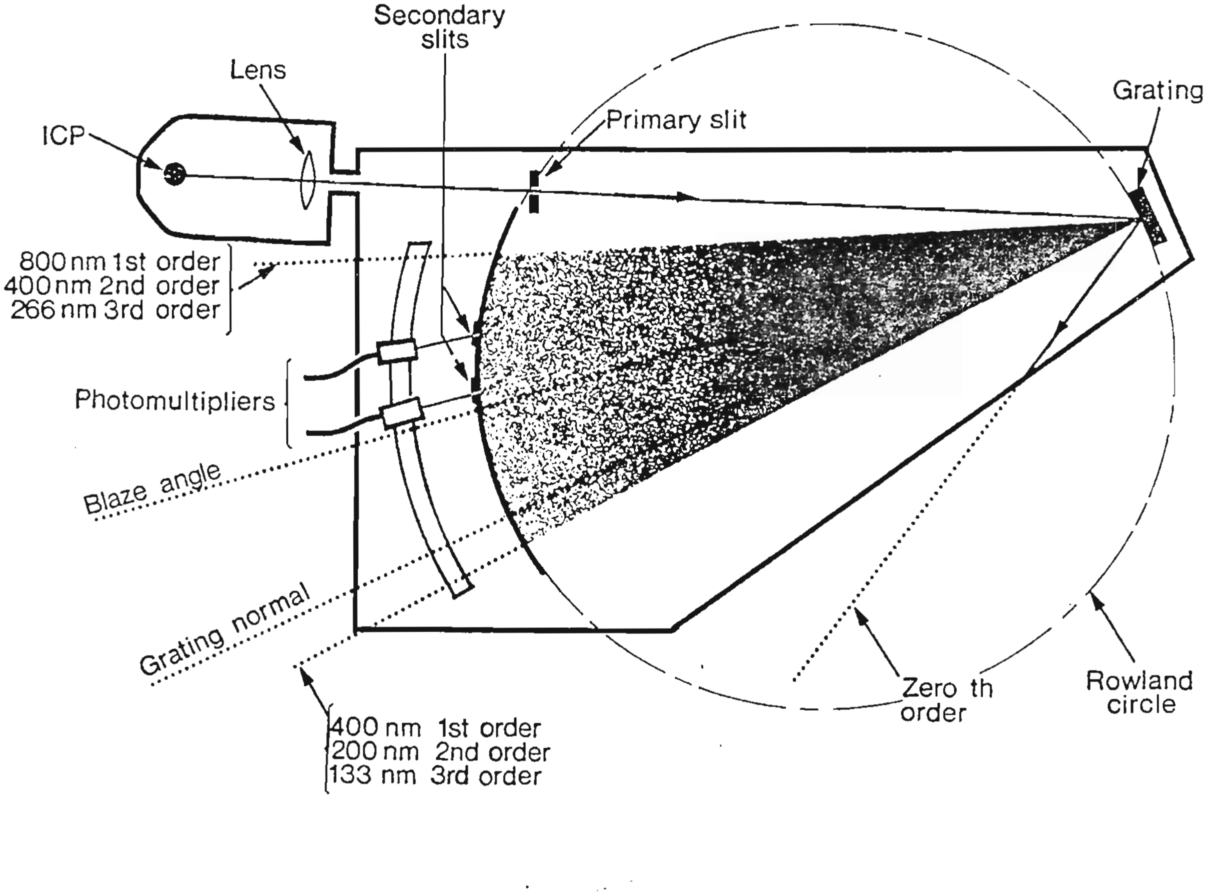
A schematic diagram of a conventional ICP simultaneous spectrometer is shown in Figure 6. The common means of sample introduction is the pneumatic nebuliser of concentric or cross-flow design but the efficiency of transfer to the ICP is only about 2%, most of the larger droplets ($>10\ \mu m$) being removed in the spray chamber. The plasma is a gas in which atoms are present in an ionised state. When a high frequency current flows in an induction coil, it generates a rapidly varying magnetic field within the coil. The interaction or *inductive coupling* of the oscillating magnetic field with flowing ionised gas generates the ICP "flame". The inductive heating of the flowing gas maintains plasma temperatures of 6000-10000^{0}K, much hotter than the nitrous oxide - acetylene flame. Argon is chosen as the plasma gas because: (1) it is inert and likely to suppress chemical interferences; (2) it is transparent in the U.V.-visible region; (3) it has a high IP (15.75eV), permitting detection of all elements that can be excited to emit lines in the U.V.-vis.; and (4) it has a moderately low thermal conductivity. The function of the ICP is to vapourise, dissociate, atomise and excite the sample, thereby promoting atomic and ionic line spectra as photons are emitted in energy transfer reactions. The torch comprises three accurately aligned concentric tubes of silica. The outer, coolant argon flow-rate is usually 10-20 l min^{-1} while the sample carrier flows at ca. 1 l min^{-1}. The auxiliary gas is employed to lift the

Figure 6: *Schematic diagram of a conventional simultaneous ICP emission spectrometer*



plasma off the torch, to prevent salt build-up on the torch tip and to nebulise organics. Two generator frequencies are offered: 27.12 or 40.68 MHz. The normal analytical zone, where emission is measured, is in a 4-5 mm window some 12-20 mm above the load coil. Spectrometers are capable of either simultaneous (polychromator) or sequential (monochromator) measurement. The simultaneous spectrometer is a direct reader design, usually based on the Pashen-Runge mounting (Figure 7).

Figure 7: *The optics of a polychromator in the Pashen-Runge mounting with the grating blazed for maximum reflection of 600 nm in the first order.[From Thompson and Walsh, 1989].*



Light from the ICP is focused on a fixed diffraction grating on the circumference of the

Rowland's circle where fixed exit slits are arranged to coincide with the diffracted lines of a suite of predetermined elements. Light passing through these slits is focused on individual photomultiplier tubes (20-60). [A spectrometer based on detection by a photodiode array is on the market but the number of units are few at present]. The sequential spectrometer offers the flexibility of line choice but at the expense of productivity. A scanning monochromator can be programmed to move rapidly from one line to another under computer control. It has been demonstrated that the analysis of 30 samples for 30 elements takes 2 hours on a simultaneous system compared to 6 hours on a sequential. Manufacturers today offer combined simultaneous-sequential spectrometers arranged at 90° to each other, viewing the same ICP; this provides maximum flexibility and speed. In order to measure spectra at wavelengths below 200 nm, the path of the spectrometer is either evacuated of air (absorbs in the vacuum-U.V.) or purged with nitrogen. Measurements are made from this region up to the Cs line at 852.12 nm.

Critical parameters to be optimised in ICP-AES include carrier gas flow-rate, plasma power and observation height in the flame. Chemical and ionisation interferences are of less impact than in AAS but spectral overlap is of greater concern in the absence of the "lock-and-key" effect created by the hollow cathode lamp. Hence, spectrometer resolution becomes important, especially in the analysis of geological samples which are complex matrices with Fe as a major element (emits > 1000 lines between 200 and 300 nm). There are now several comprehensive line atlases available for the ICP spectroscopist, e.g., by Winge et al., Wohlers, and Boumans and Vrakking. Where spectral interference cannot be avoided by judicious selection of an atomic or ionic line, mathematical correction factors for a particular instrument are computed using known standard solutions. There is general concensus that numerical uncertainty in these measured values is the limiting factor in ICP-AES geoanalysis for trace elements. Background emission interference is subtracted by measurement of intensity on either or both sides of the analyte line - this is trivial with flexible sequential systems while manufacturers of simultaneous units differ in design. Commonly, the polychromator entrance slit can be moved +\- .5 nm either side of its normal position, thereby shifting measurement at each detector off the analyte peak. Aluminium, for example, emits continuum radiation in the region 190-220 nm which must be corrected for measuring in this part of the spectrum. Physical\matrix interferences are caused by changes in nebulisation efficiency due, for example, to differences in salt content or acid concentration. Matrix-matching is only expedient when analysing a group of similar samples such as fairly pure limestones or silicates and therefore other methods of circumventing interferences have arisen. Normalisation to the intensity of an added internal standard (e.g., Y, Sc) compensates for nebulisation efficiency changes as long as that element behaves in the identical fashion to the analyte(s). An alternate approach is to calibrate using solutions directly prepared from rock\sediment\soil reference materials. These are digested in identical fashion to the unknowns, permitting automatic matching of the matrix. The disadvantage is the uncertain confidence that must be placed on the "recommended" values for SRMs, particularly for some traces. In general, interferences in geoanalysis by ICP-AES are reduced without much effort to manageable levels.

Solutions presented to the ICP can be derived from fusions or acid attacks. Lithium metaborate is in common use for total decomposition and is suitable for major and minor element determination but the necessity to incorporate a dilution factor of ca. 500 to keep the total salt content below 1% degrades detection limits for traces. The ease with which the

$LiBO_2$ fusion can be carried out coupled with the capability of ICP-AES has made this the method of choice for major and minor element determination, replacing the older method of fused disc\XRF in many geoanalytical labs. The precision obtained by ICP-AES (+\-1% relative) is inferior to that of XRF, especially for Si and to a lesser extent Al but is adequate for most geoanalytical purposes. Potassium is highly ionised in the zone usually chosen for viewing and, as its atom line is by far the most sensitive, problems in detection can arise when the sample contains <0.05% K. In this case, a lower dilution factor is desirable. Only one of the larger commercial labs in Canada still promotes fused disc\XRF over $LiBO_2$\ICP-AES for the classical whole rock package; the suite normally reported comprises SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, Fe_2O_3, MnO, Cr_2O_3, P_2O_5, TiO_2 (and LOI). These elements, with the exception of Si, are also determined following an HF-$HClO_4$-HNO_3-HCl attack but decomposition is not necessarily complete.

Acid digestions in commercial labs fall mainly into 2 categories: aqua regia (HCl-HNO_3) and HF-$HClO_4$-HNO_3-HCl. The latter is often referred to as "total" but it must be remembered that resistant minerals such as chromite, zircon, sphene and cassiterite are only partially attacked. Dilution factors following acid attack range from 20 to 100, compatible with the determination of about 30 elements at their crustal abundance. Table 4 lists the determination limits quoted by four large commercial labs using an acid digestion for trace elements together with those published by Thompson and Walsh (1989). The latter are significantly higher than the values arrived at by multiplying the 3σ ICP-AES detection limit for ideal, "clean" solutions by a typical dilution factor in order to account for variability introduced by the digestion (contamination, sample processing etc.) and the uncertainty encountered in applying correction procedures when analysing real solutions. The terms

Table 4. *Determination limits quoted by commercial laboratories for trace elements analysed by ICP-AES following an aqua regia or HF-$HClO_4$-HNO_3-HCl decomposition. Values in* $\mu g\ g^{-1}$.

Element	Lab				Thompson & Walsh*
	1	2	3	4	
Ag	0.1	0.2	0.2	0.1	1
As		5	5	3	
Ba	2	10	5	1	1
Be	0.2	0.5	0.5		
Bi	2	2	5	3	10
Cd	1	0.5	1	0.1	
Co	1	1	1	1	2
Cr	1	1	1	1	
Cu	1	1	1	1	2
Ga		10	2		
La	2	10	1		5
Li			1		2
Mo	1	1	1	1	10
Nb	2		1		10
Ni	1	1	1	1	5
Pb	2	2	2	2	20
Sb	2	5	5	2	10
Sc	0.2	1	1		1
U	5	10		5	
V	2	1	1		2
W	1	10	10	3	
Y	2		1		1
Zn	1	2	1	1	5
Zr	1		1		

* "realistic" determination limit, Thompson and Walsh, 1989.

"determination" limit and "quantitation" limit are generally defined to represent 6σ and 10σ, respectively. Of the elements listed in Table 4, those with determination limits at or near crustal abundances comprise Ba, Be, Co, Cr, Cu, Ga, La, Li, Mo, Ni, Pb, Sc, Sr, V, Y, Zn and Zr. Of these, low results due to incomplete digestion may arise for Ba, Be, Cr, Sr and Zr.

A landmark paper was published by Stan Church (USGS) in 1981 describing the analysis of a diverse suite of 54 reference materials for 40 elements. The decomposition was based on HF-$HClO_4$-HNO_3-HCl with modifications to ensure solubilisation of chromite-, phosphate- and carbonate- bearing samples. Fourteen standards solutions were designed to generate a matrix-matching calibration scheme to encompass the wide variety of materials analysed and an azeotropic acid mixture was employed for final dissolution to ensure constant acid strength. Data for several reference samples analysed this way are extracted in Table 5; Church found overall that agreement with accepted values for majors was within 2-3% while that for minors and traces lay in the range 5-10%. Of the 28 traces studied, 17 could be determined in crustal rocks. Precision normally obtained in analysis by ICP-AES is in the 1-2% range when measuring well above (>x10) the detection limit.

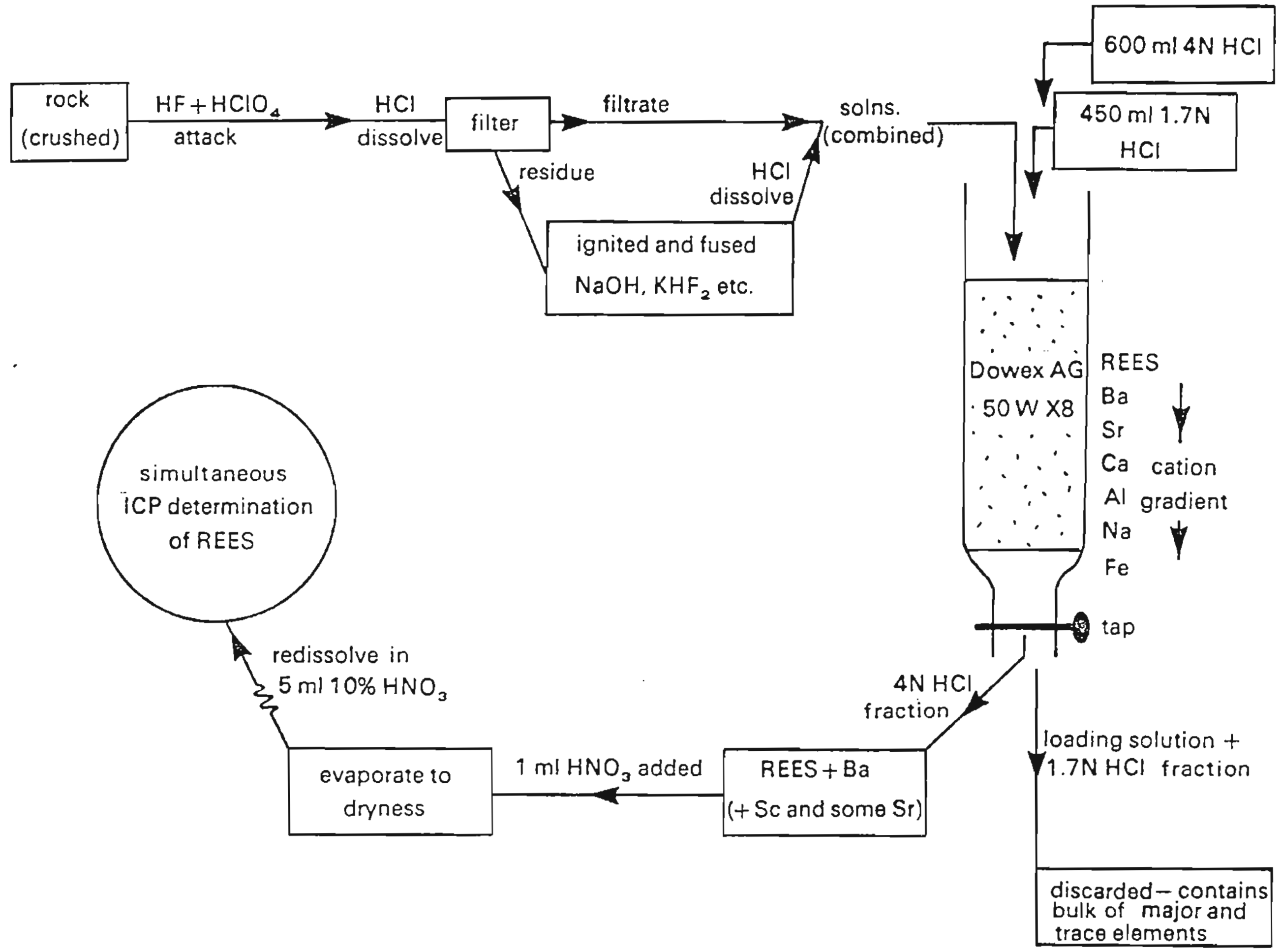
As in AAS, solvent extraction has been employed to preconcentrate trace elements prior to analysis. Using Aliquat 336 and MIBK as solvent, detection levels can be lowered to 0.01-0.1 $\mu g\ g^{-1}$ (ppm) for Cu, Pb, Zn, Co, Ni, Mn, Mo, As, Bi, Sb, Ag, Cd, Te and Tl. Preconcentration by ion-exchange, with the added advantage of separating spectral interferences, is used extensively for the REEs to achieve adequate sensitivity (DF of ca. 10). Figure 8 illustrates the procedure used by Walsh (Thompson and Walsh, 1989) to determine La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Any residue from the acid

Table 5. *Results for SRMs by ICP-AES/acid digestion from Church (1981).*

Element[1] or Oxide	STM-1	RGM-1	QLO-1	SDC-1	BHVO-1
	syenite	rhyolite	quartz latite	mica schist	basalt
Na_2O	8.90 ± 0.28	4.12 ± 0.13	4.21 ± 0.13	2.03 ± 0.07	2.39 ± 0.08
K_2O	3.86 ± 0.10	>4.3	3.37 ± 0.08	3.15 ± 0.08	0.546 ± 0.02
MgO	0.102 ± 0.003	0.283 ± 0.009	1.03 ± 0.03	1.75 ± 0.05	7.53 ± 0.23
CaO	1.14 ± 0.04	1.23 ± 0.04	3.18 ± 0.10	1.42 ± 0.05	11.24 ± 0.37
Fe_2O_3	5.30 ± 0.12	1.93 ± 0.04	4.37 ± 0.10	6.91 ± 0.15	2.37 ± 0.27
Al_2O_3	18.30 ± 0.65	14.06 ± 0.51	16.26 ± 0.59	15.65 ± 0.56	14.16 ± 0.51
TiO_2	0.132 ± 0.003	0.267 ± 0.007	0.606 ± 0.015	0.979 ± 0.024	2.75 ± 0.07
P_2O_5	0.160 ± 0.005	0.048 ± 0.002	0.264 ± 0.007	0.148 ± 0.005	0.280 ± 0.007
Li	35.1 ± 0.70	62 ± 1.24	24.1 ± 0.60	32.6 ± 0.65	2.0 ± 1.0
Be	9.8 ± 0.20	2.48 ± 0.05	2.0 ± 0.04	3.07 ± 0.06	1.36 ± 0.03
Sr	701 ± 14	102 ± 2.0	332 ± 6.6	182 ± 3.6	413 ± 8.3
Ba	580 ± 12	836 ± 17	1405 ± 28	644 ± 13	139 ± 2.8
La	153 ± 3.1	23 ± 0.5	27 ± 0.5	41 ± 1.0	17 ± 1.0
Ce	258 ± 7.7	32 ± 3.2	59 ± 3.0	88 ± 2.6	46 ± 3.0
Nd	78 ± 15	<20	<20	35 ± 7.0	26 ± 7.0
Sm	8.0 ± 1.6	<5	<5	6.7 ± 2.0	13.9 ± 1.4
Eu	4.0 ± 0.2	0.62 ± 0.3	1.5 ± 0.15	1.8 ± 0.1	2.6 ± 0.26
Gd	9.0 ± 0.5	3.1 ± 0.3	3.7 ± 0.4	7.4 ± 0.37	7.0 ± 0.35
Yb	4.3 ± 0.13	2.3 ± 0.07	2.3 ± 0.07	3.2 ± 0.10	2.1 ± 0.07
Zr	1340 ± 40	233 ± 7.0	192 ± 5.8	(59) ± 1.8	187 ± 5.6
U	<20	<20	<20	<20	<25
Th	<25	<25	<25	<25	<25
V	6.0 ± 1.0	12.0 ± 0.6	48.0 ± 1.5	94.8 ± 2.9	315 ± 9.5
Cr	9.0 ± 1.0	3.0 ± 1.0	3.0 ± 1.0	64.0 ± 1.9	294 ± 8.8
Mn	1750 ± 53	294 ± 8.8	725 ± 22	904 ± 27	1385 ± 42
Co	2.0 ± 1	2.5 ± 0.5	7.3 ± 0.4	17.3 ± 0.9	44.5 ± 1.4
Ni	5.2 ± 1.0	2.5 ± 1.0	5.5 ± 0.5	38.0 ± 1.1	131 ± 3.9
Cu	<1	9.7 ± 0.5	26.0 ± 1.3	27.3 ± 1.4	141 ± 4.0
Zn	248 ± 7.5	33.0 ± 1.0	63.3 ± 1.9	105 ± 3.2	109 ± 3.3
Mo	6 ± 2.5	<3	<3	<4	<5
W	<7	<7	<7	<7	<8
Ag	<2	<2	<2	<2	<2
Au	<3	<3	<3	<3	<3
Cd	<2	<2	<2	<2	<3
Sn	5 ± 2.5	6 ± 3.0	<3	<3	3 ± 2.0
Pb	20 ± 10.0	<23 ± 10.0	19 ± 10.0	22 ± 9.0	<11
Bi	<25	<25	<25	<25	<25
As	<6	<5	<6	<5	<5
Sb	<18	<14	<18	<18	<14
Se	<30	<30	<30	<30	<30

[1] Major elements expressed in weight percent oxide; others expressed in ppm.

Figure 8: *Schematic diagram of separation scheme for ICP-AES determination of the REEs. [From Thompson and Walsh, 1989].*



attack is fused with NaOH, KHF_2 or $LiBO_2$, the solutions combined and loaded onto the cation exchange resin to remove majors. Subsequent elution of the REEs and evaporation to a final volume of 5 ml results in ICP-AES analysis down to or below chondrite levels but care is still needed in determining inter-element spectral correction factors. The REEs emit a large number of atomic and ionic lines concentrated in the region 340-440 nm. Jarvis and Jarvis (1988) published a study comparing such ICP-AES data for 37 SRMs with results obtained by INAA, XRF and IDMS. The precision shown was generally better than +\-3% except at levels approaching determination limits (6σ); some of their data are shown in Table 6(a and b). The advances in sensitivity and coverage gained by implementation of this ICP-AES based method for the REEs compared to the previously established methods employing INAA and XRF have had a significant impact on petrogenetic modeling and geochemical exploration [see discussion in ICP-MS section]. Nevertheless, most commercial labs in Canada employ INAA for the REEs as the methods have been well documented and problems with incomplete digestion are circumvented.

Many papers have been published on HG-ICP-AES but in order to take advantage of the simultaneous feature of the technique compared to AAS, one must ensure that the decomposition employed is appropriate for the particular suite of analytes and that they are in their suitable valency states. The species As (III), Sb (III), Bi (III), Se (IV) and Te (IV) can all be reduced simultaneously to their hydrides from a strong HCl solution (>4M). As in AAS, interferences occur from elements such as Cu and Ni by co-reduction and subsequent adsorption of hydride or precipitation (as insoluble selenides, tellurides etc.); however, the replacement of the heated quartz cell by the plasma reduces the mutual vapour

Table 6a. *Wavelengths and detection limits of ICP-AES lines used for REE and Y determination (Jarvis and Jarvis, 1988).*

Element	Wavelength (nm)	Detection limit*1 (ng ml^{-1})	Quantitation limit*2 (μg g^{-1})	Chondrite (μg g^{-1})
La	398.85	2.6	0.087	0.329
Ce	418.66	8.7	0.29	0.865
Pr	422.29	3.8	0.13	0.122
Nd	430.36	5.2	0.17	0.630
Sm	359.26	1.8	0.062	0.203
Eu	381.97	0.26	0.009	0.077
Gd	335.05	2.1	0.069	0.276
Dy	353.17	0.65	0.022	0.343
Ho	345.60	0.56	0.019	0.076
Er	390.63	1.1	0.037	0.226
Yb	328.94	0.25	0.008	0.220
Lu	261.54	0.2	0.007	0.034
Y	371.03	1.5	0.05	ND

*1 Detection limits are based on 3 sigma standard deviations of blank intensities and are reported as concentrations in solution.

*2 Quantitation limits are equal to 10 sigma standard deviations and are reported as concentrations in the material analysed (allowing for the standard 1:10 dilution of the final REE solution).

Table 6b. *Concentrations of the REE and Y in USGS SRMs as determined by ICP-AES following an HF-HClO$_4$ digestion and ion exchange preconcentration. Values in μg g^{-1}.*

Element	AGV-1 andesite	BCR-1 basalt	BHVO-1 basalt	G-2 granite	GSP-1 granodiorite	QLO-1 quartz latite	RGM-1 rhyolite
La	37.6±0.6	23.6±0.6	14.7±0.4	88.6±4.8	177±2	26.4±0.2	23.1±0.4
Ce	69.1±0.5	52.5±0.7	37.5±1.01	167±9	431±3	52.1±0.6	47.6±0.7
Pr	7.82±0.07	6.26±0.09	4.99±0.02	15.2±0.1	50.0±0.4	5.31±0.70	4.77±0.07
Nd	31.0±0.3	27.5±0.5	23.7±0.2	50.8±0.4	197±1	21.2±0.4	18.2±0.3
Sm	5.49±0.02	6.04±0.04	5.45±0.09	7.07±0.09	25.8±0.2	4.21±0.06	3.65±0.07
Eu	1.66±0.01	1.96±0.02	1.98±0.04	1.47±0.01	2.91±0.02	1.30±0.02	0.67±0.01
Gd	4.49±0.09	6.23±0.01	5.50±0.07	3.66±0.18	11.7±0.2	3.58±0.43	3.39±0.05
Dy	3.39±0.03	5.99±0.04	4.90±0.03	2.04±0.01	6.17±0.04	3.57±0.07	3.41±0.05
Ho	0.68±0.01	1.25±0.01	0.94±0.01	0.38±0.01	1.08±0.01	0.76±0.01	0.72±0.01
Er	1.80±0.02	33.3±0.03	2.39±0.10	0.88±0.05	2.56±0.06	2.13±0.05	2.07±0.03
Yb	1.61±0.04	3.19±0.03	1.82±0.04	0.58±0.01	1.33±0.01	2.29±0.05	2.40±0.03
Lu	0.26±0.01	0.51±0.01	0.27±0.01	0.09±0.01	0.17±0.01	0.38±0.01	0.39±0.01
Y	18.3±0.4	33.4±0.5	23.2±0.5	23.2±0.3	22.8±0.3	22.8±0.3	22.7±0.4

Mean values and 1 sigma standard deviations based on single determinations of three separate sample solutions.

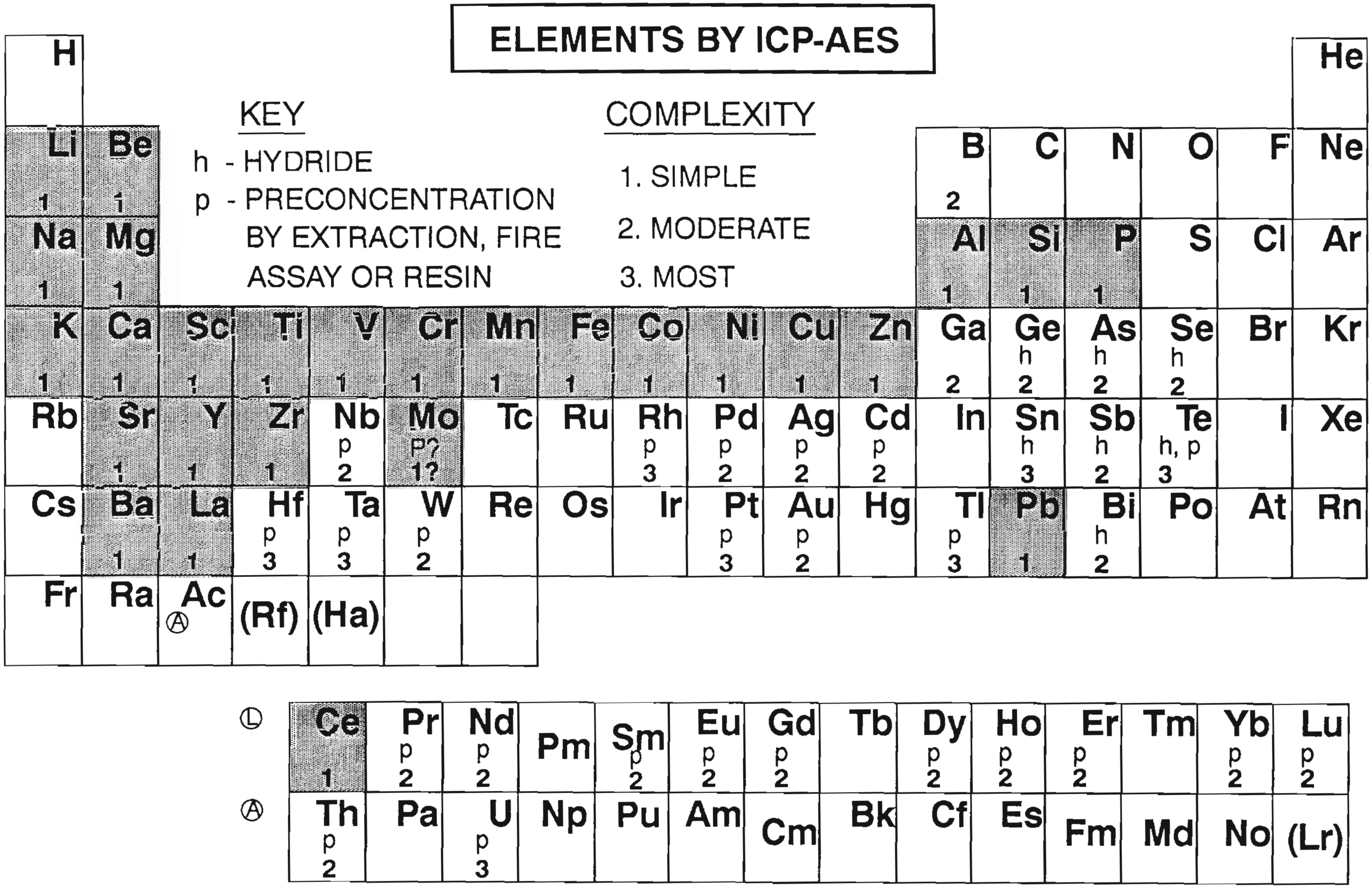
phase interference. A Canadian commercial lab offers the detection of As, Sb, Bi, Ge, Se and Te by HG-ICP-AES to a determination limit of 0.1 $\mu g\ g^{-1}$ following HF-aqua regia decomposition with the caveat that the method is unsuitable for samples containing >0.5% Cu or Ni. It is probably fair to say that most commercial labs offer only As, Sb and Bi by HG-AAS or HG-ICP-AES at this time.

In some spectrometers, the ICP is replaced by the direct current plasma (DCP) where an argon plasma discharge is maintained between two tungsten anodes and a cathode. DCP-AES has found limited application, probably owing to its generally inferior sensitivity compared to ICP-AES and its susceptibility to chemical interferences (inferior efficiency of atomisation).

Elements frequently determined by ICP-AES are shown in the Periodic Table, Figure 9. Straightforward analysis of an acid or fusion leachate is appropriate for the elements labelled "1" while preconcentration is generally required for those with a "2" unless a survey is intended to depict only "highs". A substantial improvement in sensitivity is needed to reach abundance levels for those labelled with a "3" and consequently costs can be significant. Boron of course is excluded from the $LiBO_2$ package and volatilises with HF; it can be determined after a Na_2CO_3-KNO_3 fusion which is compatible with other elements such as Mo and W. Research is currently being carried out in geoanalytical labs to extend the universality of the $LiBO_2$ fusion to include analysis for many more traces by employing an automated preconcentration procedure.

Suggested reading:

- Thompson, M. and Walsh, J.N., 1989. A Handbook of Inductively Coupled Plasma Spectrometry. Blackie, 316pp. [Very thorough,orientated to geological applications, ICP-AES



ELEMENTS BY ICP-AES

KEY
h - HYDRIDE
p - PRECONCENTRATION BY EXTRACTION, FIRE ASSAY OR RESIN

COMPLEXITY
1. SIMPLE
2. MODERATE
3. MOST

H																	He
▨ Li 1	▨ Be 1											B 2	C	N	O	F	Ne
▨ Na 1	▨ Mg 1											▨ Al 1	▨ Si 1	▨ P 1	S	Cl	Ar
▨ K 1	▨ Ca 1	▨ Sc 1	▨ Ti 1	▨ V 1	▨ Cr 1	▨ Mn 1	▨ Fe 1	▨ Co 1	▨ Ni 1	▨ Cu 1	▨ Zn 1	Ga 2	Ge h 2	As h 2	Se h 2	Br	Kr
Rb	▨ Sr 1	▨ Y 1	▨ Zr 1	Nb p 2	▨ Mo P? 1?	Tc	Ru	Rh p 3	Pd p 2	Ag p 2	Cd p 2	In	Sn h 3	Sb h 2	Te h, p 3	I	Xe
Cs	▨ Ba 1	▨ La 1	Hf p 3	Ta p 3	W p 2	Re	Os	Ir	Pt p 3	Au p 2	Hg	Tl p 3	▨ Pb 1	Bi h 2	Po	At	Rn
Fr	Ra	Ac Ⓐ	(Rf)	(Ha)													

Ⓛ	▨ Ce 1	Pr p 2	Nd p 2	Pm	Sm p 2	Eu p 2	Gd p 2	Tb	Dy p 2	Ho p 2	Er p 2	Tm	Yb p 2	Lu p 2
Ⓐ	Th p 2	Pa	U p 3	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	(Lr)

▨ Indicates "best" element by this technique

FIGURE 9 : *Sensitivities with respect to crustal abundances*

and ICP-MS].

- Montaser, A. and Golightly, D.W., 1987. Inductively Coupled Plasmas in Analytical Atomic Spectrometry. VCH, 660pp. [Detailed on principles and instrumentation, -AES, -AFS, -MS, applications general].
- Church, S.E., 1981. Geostand. Newsl., 5, 133. [Analysis of 54 SRMs for 40 elements by ICP-AES].
- Hall, G.E.M. and Vaive, J.E., 1986. Curr. Res., Geol. Surv. Can., Pap. 86-1A, p. 71-79. [Comparison of ICP-AES with XRF and AAS for geological SRMs].
- Jarvis, K.E. and Jarvis, I., 1988. Geostand. Newsl., 12, 1. [Analysis of 37 SRMs for REEs].
- Motooka, J.M., Mosier, E.L., Sutley, S.J. and Viets, J.G., 1979. Appl. Spectrosc., 33, 456. [Preconcentration by Aliquat 336-MIBK for traces in geologicals by ICP-AES].

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)

Since the advent of high resolution germanium detectors in the 1960s, INAA has played a major role in the determination of trace elements in geological samples. The technique is particularly sensitive for the REEs (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu), Sc, Co, Cr, Cs, Hf, Ta, Th, U and Au. Renewed interest in exploration for Au and the PGEs in the 1980s led to the widespread application of this technique in the analysis of rocks, sediments, soils and vegetation. Features such as the unrivalled simplicity of INAA, its flexibility to handle a range of sample weights (e.g., 1-30 g) and its ability for *direct analysis* without sample decomposition have encouraged the growth of commercial labs using nuclear facilities.

Samples are activated by irradiation with neutrons, usually in a reactor, thus producing radioactive isotopes by neutron capture-type reactions. Upon removal from the reactor, samples are allowed to decay or "cool" during which time unwanted short-lived activity (e.g., from ^{24}Na) diminishes. Specific isotopes are identified by their characteristic γ-ray energy or energies, normally in the range 60-1600 keV and they are quantified by measurement of the peak area. Calibration is carried out using one or more SRMs, irradiated and counted under identical conditions. Radiochemical NAA involves a separation procedure to isolate analytes from their matrix in order to achieve lower detection levels by 1-2 orders of magnitude; this time-consuming method is rarely used today in the routine analysis of geological materials.

The nuclear reactor depends upon the fission of ^{235}U in which the nucleus splits into isotopic fractions releasing high energy neutrons and energy. When moderated, these neutrons will take part in another reaction with ^{235}U to generate an additional 2.2 neutrons each. In a reactor, this chain reaction is controlled by selective absorption of neutrons with control rods thereby maintaining a fission equilibrium. Water is employed to moderate or decrease the energy of the neutrons from their high state of about 2 MeV through elastic collisions. Neutrons used in activation can be classified according to their kinetic energy into three groups: *thermal*, of low energy in the range 0-0.5 eV; *epithermal*, at 0.5-10 keV; and *fast*, at energies greater than 10 keV. Most INAA measurements are based on thermal neutrons which efficiently promote (n, γ) reactions. Epithermal neutrons, about 2% of the thermal flux, are isolated by a cadmium foil liner of 1 mm thickness which absorbs neutrons below 0.5 eV. Some elements which are preferentially activated by epithermal neutrons include U, Ta, Sb, Sr, Br, Rb, Ba, Mo, Au and Ir. Fast neutrons are not generally employed for analysis. The stability and intensity of the neutron flux are important parameters in INAA; an adequate flux is in the range 10^{11}-10^{13} n cm^{-2} s^{-1}. The *neutron capture cross-section* of an isotope is defined as the probability it (the target nucleus) will absorb a neutron and is measured in *barns* (one equals 10^{-24} cm^2).

Figure 10 illustrates a typical neutron capture (n,γ) reaction and the subsequent radiation that is emitted. The capture gamma-rays emitted usually have very short half-lives in the order of ms and can be measured during irradiation (prompt gamma activation analysis, PGAA). Boron and Gd can be determined by PGAA. The product nuclide of an (n,γ) reaction has an atomic number (z) that is unchanged but the atomic weight has increased by one unit. It is the measurement of the gamma-rays emitted during the decay of this radioactive nuclide to a stable state which forms the basis of INAA. Although there are numerous types of radioactive decay, the largest number proceed through beta-emission (Figure 11). The isotope (Ce-141) returns to a stable state by converting a neutron to a proton with simultaneous ejection of a beta-particle. This transition results in a product isotope of the same atomic weight but with an atomic number greater by one (Pr-141). The 145 keV gamma-ray identifies Ce and its intensity is proportional to its concentration. The half-lives of radionuclides and their associated gamma-ray (and other such as x-ray) energies are well documented.

The instrumentation required to measure a gamma spectrum comprises three parts: (1) the detector, invariably a Ge crystal which becomes ionised by the gamma photons and so generates an electronic signal; (2) electronic amplification; and (3) a multi-channel analyser to sort and store detected pulses (Figure 12). These counting systems can be established at locations remote from the reactor and irradiated samples shipped under license to these sites. Semiconductor detectors (Ge) are superior in resolution to scintillation (NaI) and gas-filled alternatives; Ge is ideal because of its purity, high atomic number, and

Figure 10: *Schematic diagram showing gamma-rays emitted after thermal neutron capture.*

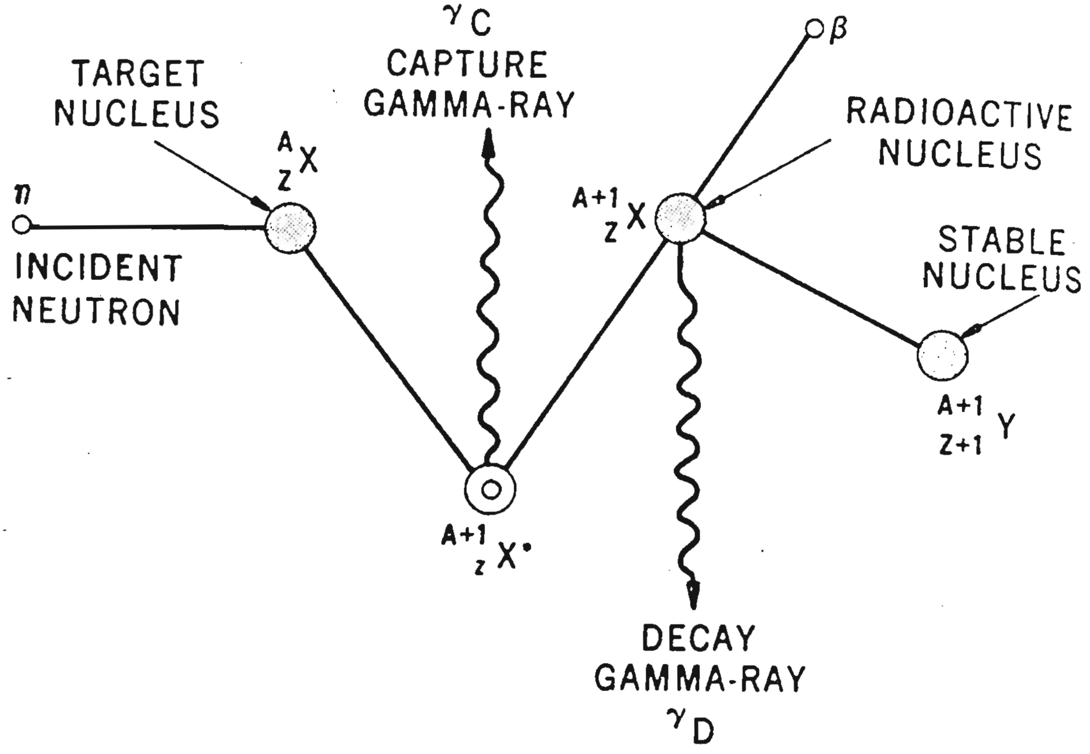
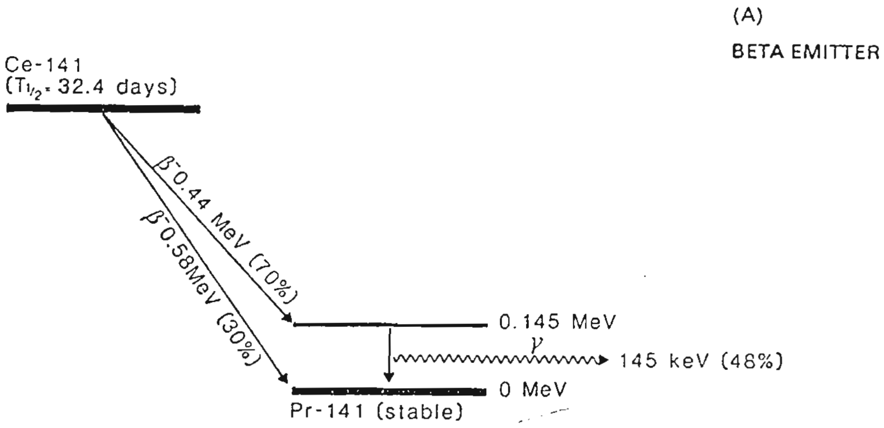


Figure 11: *Decay of unstable Ce nucleus by conversion of a neutron to a proton with ejection of a beta particle (electron). [From Potts, 1987].*



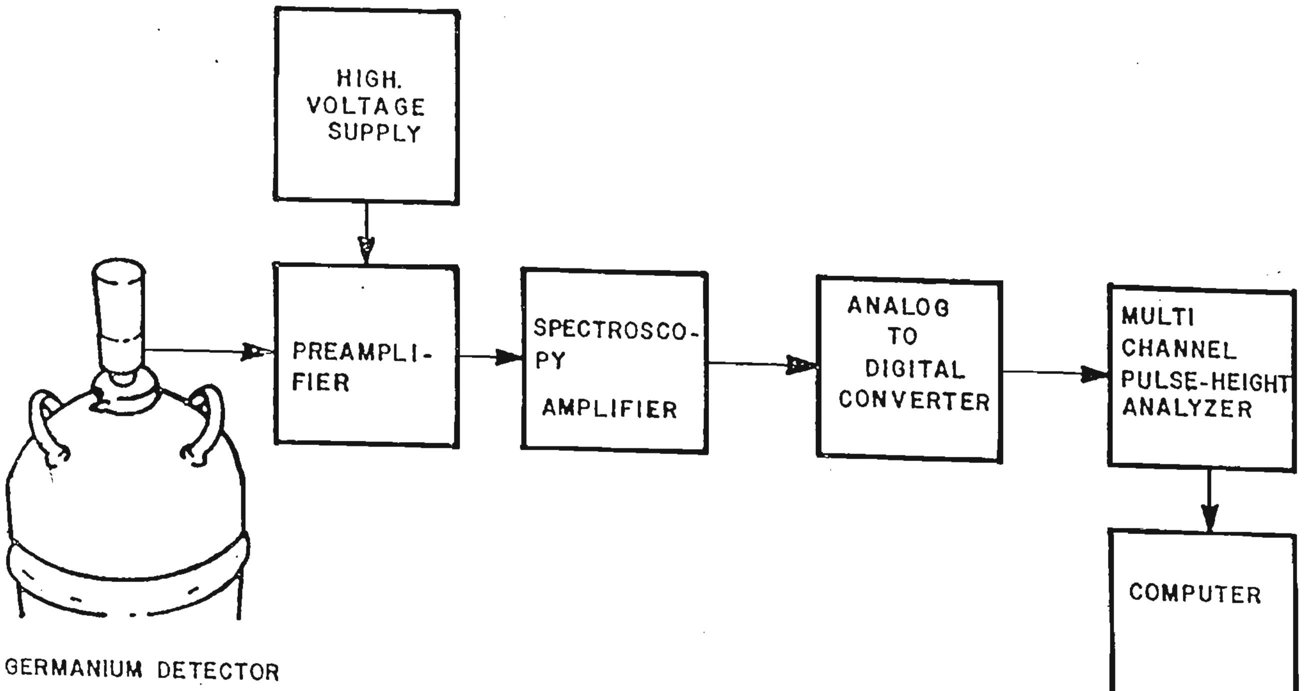
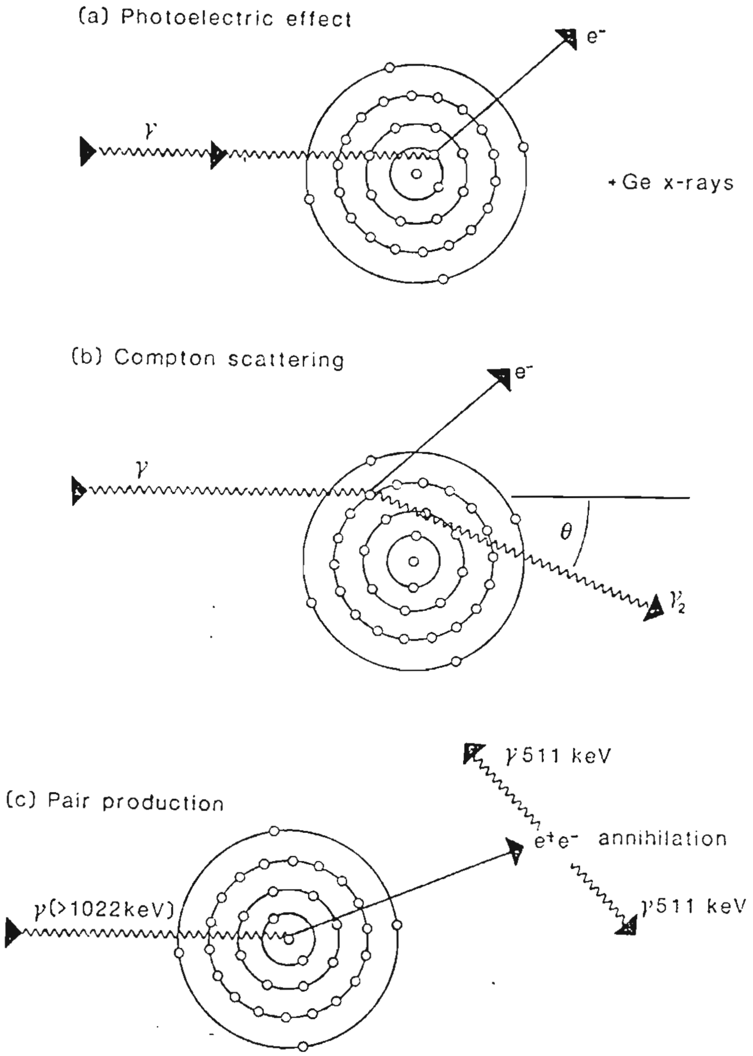


Figure 12: *Counting system to measure gamma-ray spectrum in INAA.*

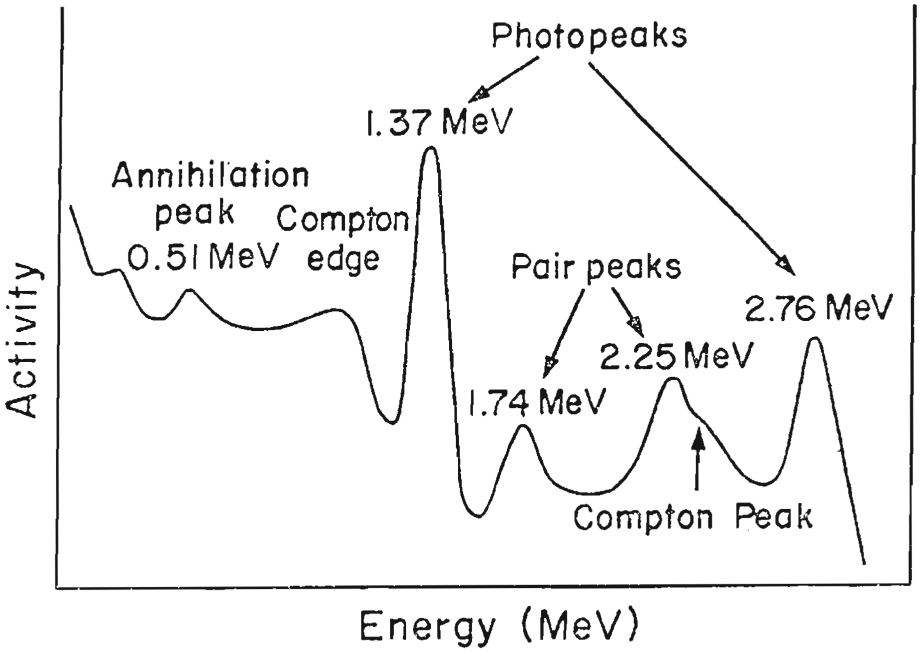
the low energy required to ionise electrons from valence to conduction bands. Lithium atoms are drifted into the Ge crystal lattice to compensate for the presence of any impurity atoms; "hyperpure" Ge, the result of developments in refining technology, does not need Li. *Coaxial* detectors are most suitable for measurement of high energy gamma radiation (300-2000 keV) while *planar* crystals are appropriate at the low energy region (60-300 keV). Detectors are mounted in an ultra-high vacuum environment to prevent surface contamination of the crystal surface and cooling to -196°C is employed to minimise electronic noise. Photons interact with matter to produce ionisation principally via three processes: (1) *photoelectric effect*, the total absorption of a photon by an atom with complete transfer of energy to the electron; (2) *Compton scattering*, partial transfer of energy to an electron with emission of a lower energy gamma-ray; and (3) *pair production*, creating an electron-positron pair at energies above 1022 keV (Figure 13). These processes are illustrated in the gamma-ray spectrum for ^{24}Na in Figure 14; Compton scatttering in the detector is the main cause of high background below the energies of most photopeaks used for analysis in INA. Detector efficiency and resolution are important parameters. The latter is defined as the full width at half the intensity maximum (FWHM) of a gamma photopeak at a given energy, usually specified at 1332 keV from ^{60}Co for coaxial detectors and 122 keV from ^{57}Co for planar designs. There are various methods by which photopeak areas are measured (Covell's, Wasson's etc.) which will not be discussed here. INAA is unusual in that it is common practice to calibrate each batch of samples by including only one SRM. The calibration is then the straight line drawn between the activity of the standard and the origin; this naturally places a high degree of confidence on the recommended values for the SRM. Alternatively, high purity chemical reagents can pipetted onto a silica substrate, irradiated

Figure 13: *Interaction of gamma radiation with a Ge detector by: (a) photoelectric effect, (b) Compton scattering, (c) pair production. [From Potts, 1987].*



and counted. Factors used in the calibration equation include the photopeak area, weight of sample, correction for the difference in flux density at the sample site versus the standard site, a term to account for the amount (exponential) of radioactive decay which has occurred for the sample and standard, and variations in counting geometry between sample and standard.

Figure 14: *Gamma-ray spectrum of Na-24 obtained with a NaI(Tl) detector. [Muecke, 1980].*



Samples are weighed (e.g., 1-30 g) into snap-cap polyethylene (low blank value) vials and organised into batches with the insertion of flux monitors which can be attached to each vial or take the form of nichrome or iron wires running along a batch. Typically, in the generation of data for the "Au +" package discussed later, samples are stacked in bundles and irradiated at the McMaster Reactor for 20 min. in a neutron flux of 4×10^{12} n cm^{-2} s^{-1}. Following a 7-day delay period, samples are mounted on an automatic changing table and counted for 15 min. at a distance of 1 cm from the detector. A lab control sample is analysed at a frequency of 1 in 20 to check for errors. Sensitivity can be improved if desired by increasing sample weight, irradiation time, neutron flux (positioning in the reactor), and counting time; however, this can give rise to high background levels and spectral interferences. Precision in peak area quantification, based on Poisson counting statistics, is influenced by the background counts, particularly as signals approach detection levels.

INAA is remarkably free of interferences as matrix effects are small. Likely the two most important sources of inaccuracy are spectral overlaps and errors in maintaining reproducible sample geometry. The most prominent photopeak interferences in geoanalysis, extracted by Potts (1987) from comprehensive tables, are listed in Table 7. Faced with such an overlap, one can: (1) select an alternative gamma photopeak of the isotope; (2) employ a peak fitting program; or (3) recount the sample after a suitable decay period during which the interfering activity has largely disappeared. Very accurate sample positioning is required for low activity monitoring when the distance to the detector is less than 20 mm. Self-shielding of neutrons occurs during irradiation when a sample contains high concentrations of an isotope having a high neutron capture cross-section. The worst offenders in this regard are elements such as Gd, Eu and B which fortunately are not major constituents of geological materials. At energies below 100 keV, self-absorption of gamma-rays becomes increasingly important so there is some advantage in forming the samples into thin discs rather than cylinders. The formation of ^{235}U fission products during irradiation creates interferences on neutron capture isotopes. Isotopes suffering from this type of overlap include ^{95}Zr, ^{99}Mo, ^{140}La, ^{141}Ce and ^{147}Nd; correction factors can be computed to overcome these effects.

Table 7: *Photopeak interferences in INAA. [From Potts, 1987].*

Analytical photopeak			Interfering photopeak		
	keV	Decay intensity (%)		keV	Decay intensity (%)
^{169}Yb	63.12	(45.0)	*^{181}Hf	63.20	(5.6)
^{182}Ta	67.75	(41.3)	^{182}Ta	67.20	(5.2)
^{153}Sm	69.67	(5.25)	*^{153}Gd	69.60	(2.6)
^{187}W	72.00	(11.9)	^{187}W	71.20	(1.1)
^{170}Tm	84.26	(10.0)	*^{182}Ta	84.68	(2.7)
^{160}Tb	86.80	(13.40)	*^{233}Pa	86.61	(1.8)
^{233}Pa	94.66	(9.60)	^{169}Yb	93.62	(2.4)
^{153}Gd	97.50	(30.0)	*^{153}Sm	97.43	(0.73)
^{233}Pa	98.44	(15.50)	^{239}Np	99.50	(15.0)
^{153}Sm	103.18	(28.3)	*^{153}Gd	103.20	(21.8)
			^{239}Np	103.70	(24.0)
			^{233}Pa	103.86	(0.59)
^{177}Lu	112.95	(6.60)	^{182}Ta	113.67	(1.9)
			^{175}Yb	113.80	(1.8)
^{181}Hf	133.05	(43.0)	^{131}Ba	133.61	(2.9)
^{141}Ce	145.45	(48.0)	^{175}Yb	144.86	(0.32)
			*^{233}Pa	145.40	(0.44)
^{177}Lu	208.36	(11.0)	^{239}Np	209.75	(3.2)
^{239}Np	228.19	(10.72)	^{182}Ta	229.32	(3.6)
^{51}Cr	320.07	(9.83)	^{147}Nd	319.40	(2.2)
^{175}Yb	396.32	(6.21)	^{233}Pa	398.50	(1.3)
^{187}W	479.57	(23.4)	^{154}Eu	478.30	(0.21)
^{122}Sb	564.08	(71.0)	^{134}Cs	563.26	(8.4)
			*^{152}Eu	563.97	(0.52)
^{134}Cs	604.66	(97.60)	^{124}Sb	602.71	(98)
^{95}Zr	756.72	(54.8)	*^{154}Eu	756.70	(4.1)
^{140}La	815.80	(22.32)	^{154}Eu	815.60	(0.53)
^{59}Fe	1099.22	(56.5)	^{160}Tb	1102.59	(0.54)
^{65}Zn	1115.52	(50.75)	^{182}Ta	1113.38	(0.40)
			*^{160}Tb	1115.12	(1.6)
^{46}Sc	1120.52	(99.99)	*^{182}Ta	1121.28	(35.0)
^{154}Eu	1274.80	(35.50)	^{182}Ta	1273.75	(0.67)
^{59}Fe	1291.56	(43.2)	^{182}Ta	1289.17	(1.4)
^{24}Na	1368.55	(100)	*^{124}Sb	1368.21	(2.6)
^{140}La	1596.20	(95.47)	^{154}Eu	1597.30	(1.7)

A major application of INAA remains the determination of the REEs and other elements of importance in petrogenetic and tectonic studies such as Sc, Hf, Ta, Th and U. A typical multi-element package, based on long-lived isotopes, offered by commercial labs is shown in Table 8; the two sets of detection limits are termed "exploration" and "research", the latter costing about three times the former. Not all REEs are determined to chondrite levels due to lack of sensitivity (e.g., Gd, suffers Th interference) but fortunately analysis for critical elements such as Eu is sensitive and accurate. The precision of INAA is excellent, aided greatly by the minimum sample manipulation required. Contamination is not of the concern it is in other techniques and any introduced after irradiation would not be measured in any case. The 1980s saw the development "Au+" package where about 33 elements could be determined with Au at little additional expense on a maximum sample weight of one assay ton. The elements offered are more or less those listed in Table 8 but detection limits for this cost-effective package are slightly inferior for some elements (Hf, La, Ni, Se). Obviously data for a substantial number of these elements would normally be below detection (e.g., Ir, Se, Zn). The determination of Au by INAA is particularly advantageous in light of the fact that the common aqua regia attack employed for solution based techniques can be partial (matrix dependent), as can Pb fire assay if precautions are not taken for certain matrices. Furthermore, 30 g of sample can be accommodated. Only recently has INAA been rivalled (by ICP-MS) in its ability to determine the PGEs following a NiS fire assay preconcentration and separation procedure. This avoids the interference of Ca on Pt, removes the possibility of fission products from U and generally reduces the background to promote better detection capability. Typically, analysis is performed to lower limits of: 0.1 ng g^{-1} for Ir; 1 ng g^{-1} for Au and Rh; 3 ng g^{-1} for Os; and 5 ng g^{-1} for Pt, Pd,

Table 8. *Exploration and research packages of long-lived isotopes offered by INAA laboratories. Values in ppm unless otherwise noted.*

	Detection Limit			Detection Limit	
Element	Explor.	Res.	Element	Explor.	Res.
Ag	5	2	Ir	5 ppb	1 ppb
As	2	1	Mo	5	2
Au	5 ppb	2 ppb	Na_2O	0.01%	0.001%
Ba	100	20	Ni	200	50
Br	1	0.5	Rb	20	10
CaO	0.5%	0.2%	Sb	0.2	0.1
Co	1	0.1	Se	3	0.5
Cr	2	0.5	Sr	500	100
Cs	0.5	0.2	Ta	1	0.5
Fe_2O_3	0.02%	0.005%	W	3	1
Hf	0.5	0.2	Zn	40	10
Rare earth and actinide elements					
Sc	0.1	0.01	Tb	0.5	0.1
La	0.5	0.1	Yb	0.2	0.05
Ce	3	1	Lu	0.05	0.01
Nd	5	3	U	0.5	0.1
Sm	0.1	0.01	Th	0.5	0.2
Eu	0.2	0.05	Dy	0.5	0.5

Ru, and Re. Two irradiations are required because of the short half-life of ^{104}Rh (4.41 min.); Rh is counted for about 200-500 s following an irradiation time of 5 min. and decay of 60 s. Samples are irradiated further for ca. 16 h and Pd counted after a decay of ca. 4 h. The remaining isotopes are counted after about 7-9 days.

Another area of impact by INAA is in the analysis of vegetation and humus. This matrix is ideal because of the insensitivity to such elements as C, N, H and O, thus creating a low background. The organic material is macerated, compressed into a briquette and shrink-wrapped. The weights accommodated have been increased from 8 g to 30 g to improve sample representivity. As many as 35 elements can be determined after a 5-7 day decay (Na activity decreases); detection limits normally quoted for vegetation are shown in Table 9 (those for humus would be about a decade higher). Besides being an inexpensive, accurate and productive method of analysing vegetation, INAA avoids ashing where volatiles can be lost and the considerable problems of dissolving copious amounts of organic matter are negated. Elements such as Pb, Cu, Ni and Cd are not well served owing to lack of sensitivity.

INAA is an ideal technique for the analysis of heavy mineral concentrates. It avoids the need to subdivide or pulverise the sample which may lead to a loss of Au; the entire sample can be encapsulated. The determination of U by delayed neutron counting saw great advances in the 1970s when automated pneumatic rabbit systems became widespread. A small fraction of the U fission products formed on irradiation decays by the emission of neutrons. The half-life of neutron emission lasts from a fraction of a second to a minute. The technique involves irradiation for about 60 s, removal via the rabbit system and counting using BF_3 spectrometers. About 2400 samples a day can be analysed down to 0.1 $\mu g\ g^{-1}$ U.

Table 9. *Elements and their detection limits in vegetation by INAA. Values in ppm unless otherwise noted.*

Element	Detection limit	Element	Detection limit
Au	0.1 ppb	Sb	5 ppb
Ag	0.2	Sc	0.01
As	0.01	Se	0.1
Ba	5	Sr	10
Br	0.01	Ta	0.05
Ca	0.01%	Th	0.1
Co	0.1	U	0.01
Cr	0.3	W	0.05
Cs	0.05	Zn	2
Fe	50	La	0.01
Hf	0.05	Ce	0.1
Hg	0.05	Nd	0.3
Ir	0.1	Sm	0.01
K	0.01%	Eu	0.05
Mo	0.05	Tb	0.1
Na	50	Yb	0.05
Ni	2	Lu	0.01
Rb	1		

The simplicity, productivity, relative freedom from matrix effects and particularly the absence of need for decomposition procedures, which can lead to both loss of analyte and contamination, ensure INAA a continuing important role in geochemical analysis. Its capability in determining the REEs, Au, As, Sb, Hf and Ta and the other elements shown in Figure 15 clearly demonstrates that it is a technique complementary to others such as ICP-AES and XRF whose strength lies in analysis for the majors and base metals.

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ELEMENTS BY INAA

KEY

p - PGAA
d - DNC
a - ASSAY PRECONCENTRATION

SENSITIVITY

1. HIGH
2. MODERATE
3. LOW

H																	He
Li	Be											B p 1	C	N	O	F	Ne
▨ Na 1	Mg											Al	Si	P	S	Cl	Ar
K 3	Ca 3	▨ Sc 1	Ti	V	▨ Cr 1	Mn	Fe 2	▨ Co 1	Ni 3	Cu 3	Zn 3	Ga	Ge	▨ As 1	Se 3	▨ Br 1	Kr
▨ Rb 1	Sr 3	Y	Zr 3	Nb	Mo 2	Tc	▨ Ru a 1	▨ Rh a 1	▨ Pd a 1	Ag 3	Cd 3	In	Sn 3	▨ Sb 1	Te	I	Xe
Cs 2	▨ Ba 1	▨ La 1	▨ Hf 1	▨ Ta 1	▨ W 1	▨ Re a 1	▨ Os a 1	▨ Ir a 1	▨ Pt a 1	▨ Au (a) 2 (1)	Hg 3	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac Ⓐ	(Rf)	(Ha)													

Ⓛ	▨ Ce 1	Pr 3	▨ Nd 1	Pm	▨ Sm 1	▨ Eu 1	▨ Gd (p) 1	Tb 2	▨ Dy 1	Ho 3	Er 3	Tm 3	▨ Yb 1	▨ Lu 1
Ⓐ	▨ Th (d) 1	Pa	▨ U d 1	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	(Lr)

▨ Indicates "best" element by this technique

FIGURE 15 : *Sensitivities with respect to crustal abundances*

X-RAY FLUORESCENCE SPECTROMETRY (XRF)

Following instrumental development in the 1960s, XRF became widely used for the routine analysis of rocks for majors and a select suite of traces, namely Sr, Rb, Y, Nb and Zr. The availability of extremely stable high power X-ray tubes and the development of mathematical procedures to correct for absorption-enhancement effects have resulted in such excellent precision in silicate analysis that figures of merit are essentially limited by the degree of sample inhomogeneity. Analysis of silicates and carbonates by ICP-AES following $LiBO_2$ fusion does not yet rival the precision obtained by fused disc XRF for the major elements. Samples are prepared as fused discs or pressed powders and excited with X-rays; this interaction results in the ionisation of analyte atoms by ejection of discrete orbital electrons. As the atom falls back to a stable state, fluorescence X-rays characteristic of that element are emitted and their intensity measured and compared with standard samples. Conventional instrumentation for XRF analysis is based on the wavelength dispersive spectrometer, though energy dispersive X-ray detectors became available in the mid 1970s.

The mechanism of XRF is demonstrated in simple form in Figure 16. A high energy primary X-ray photon interacts with a K orbital electron in the Fe atom, causing it to be ejected. In order to regain stability, an electron from the L shell (or M) falls down the potential gradient to fill this vacancy and the surplus energy is emitted as a secondary X-ray of well-defined energy. This is termed a Kα line; if the transition occurred from an M subshell, it would be labelled a Kβ line and would be less intense. Thus the series of analytically important lines are the K-, L- and M- where the letter denotes the shell vacated and filled. The orbital energy level diagram and the observed transitions for Fe are shown in Figure 17. Selection of lines for quantitation is much more straightforward than for AES

Figure 16: *Schematic representation of the mechanism of XRF of an Fe atom.*

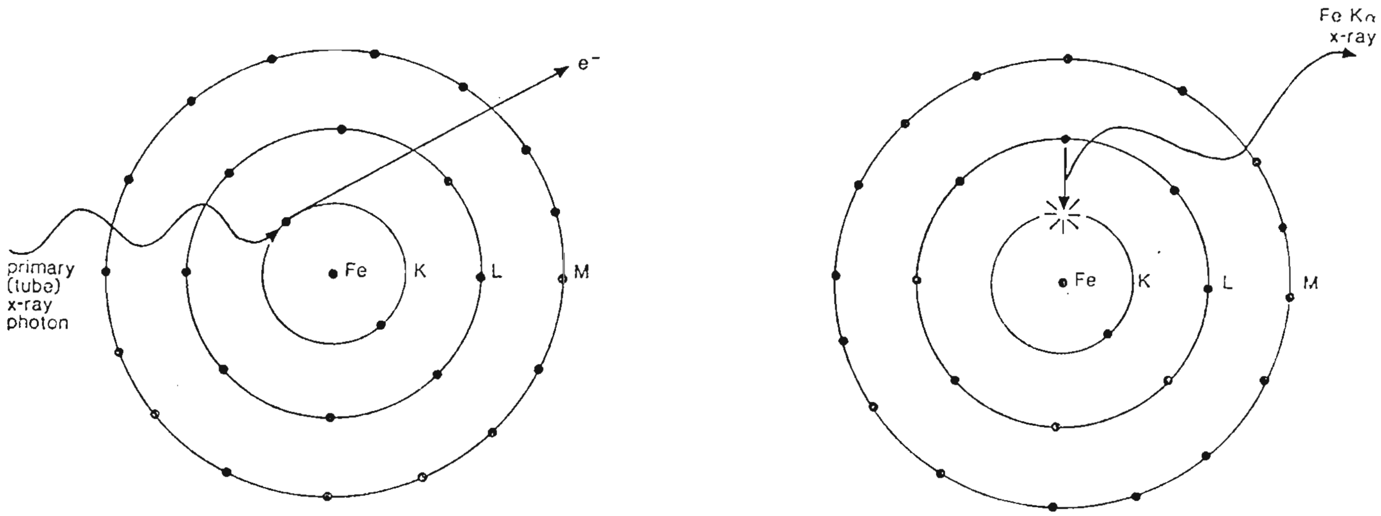
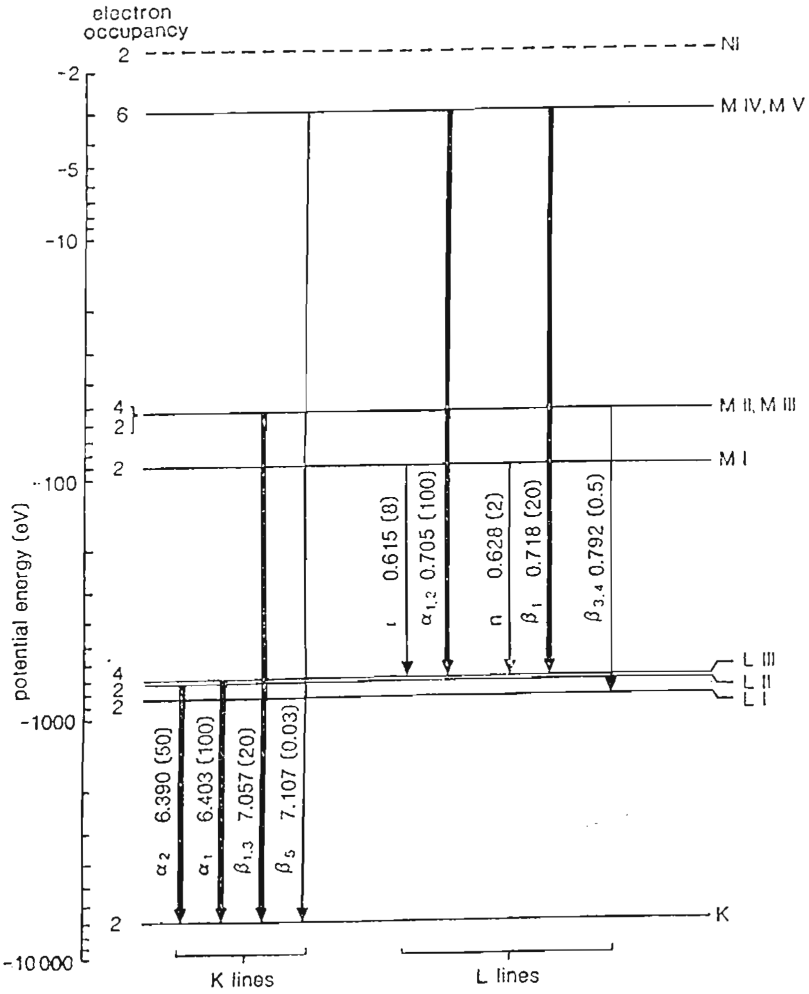


Figure 17: *Orbital energy level diagram for an Fe atom. [From Potts, 1987].*



for example and depends on the following: (1) energy should be in the range 1-25 keV for optimal detection by modern instrumentation; (2) within a series, line of maximum intensity is best (e.g., $K\alpha_{1,2}$ for Na to Mo and $L\alpha_{1,2}$ for Ba, REEs, Pb, Th, U); and, (3) presence of spectral overlap, though rare, would dictate another choice. As inner orbital shells are involved in the transitions, XRF analysis is independent of oxidation state or coordination number. Clearly, only X-ray photons that exceed the ionisation energy of the appropriate orbital electron can cause fluorescence. This is illustrated in Figure 18 by plotting the intensity of X-rays transmitted through a thin (Ti or Ba) metal foil as a function of energy. With increasing energy, the proportion of transmitted photons increases until the *absorption edge* is reached, an abrupt discontinuity representing the threshold above which primary photons are capable of ionising an orbital electron. *The mass attenuation coefficient* of that element describes the degree of attenuation of an X-ray beam at a given energy.

The primary photons can interact with atoms principally in two ways besides the photoelectric effect above, and these contribute to undesirable background intensities. Consider first the X-ray tube (Figure 19). Electrons emitted from an incandescent W filament are accelerated through a large potential and strike the metallic (e.g., Cr, Rh, Mo, Ag) target anode. This results in two types of X-ray emission: (1) X-ray fluorescence characteristic of the target material; and (2), continuous X-ray spectrum (*the bremsstrahlung effect*), caused by interaction between primary electron and outer orbitals with energy from zero up to the operating potential of the tube. A small fraction of primary X-rays are radiated from the sample without change in energy, creating *Raleigh scatter* of continuum and characteristic tube radiation and hence superimposing a background on measured analyte spectra. High atomic number elements are more efficient in promoting Raleigh

Figure 18: *Variation of mass attenuation coefficient over the range 3-8.5 keV showing the absorption edges due to Ti K and Ba L(I), L(II) and L(III) transitions. [From Potts, 1987].*

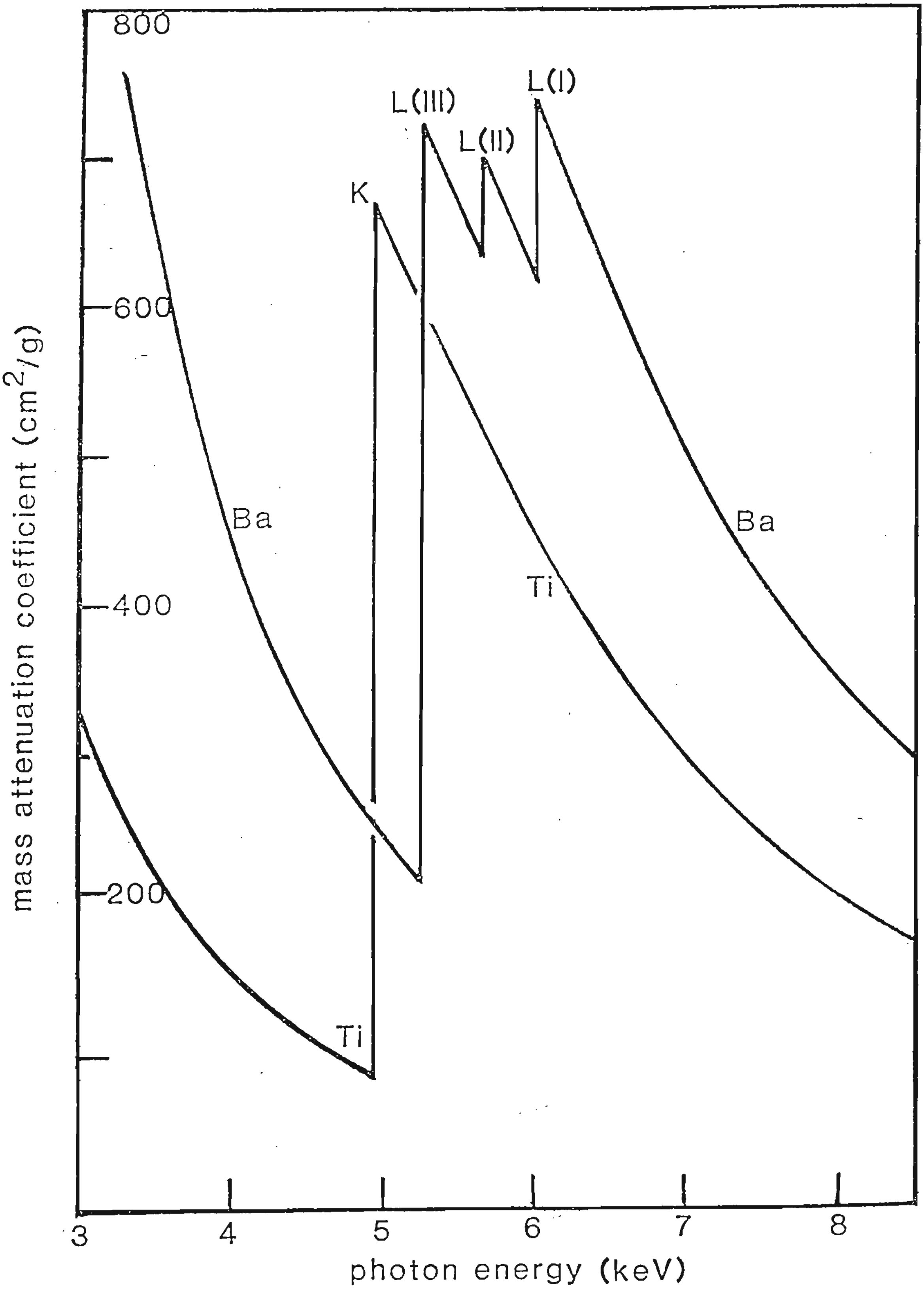
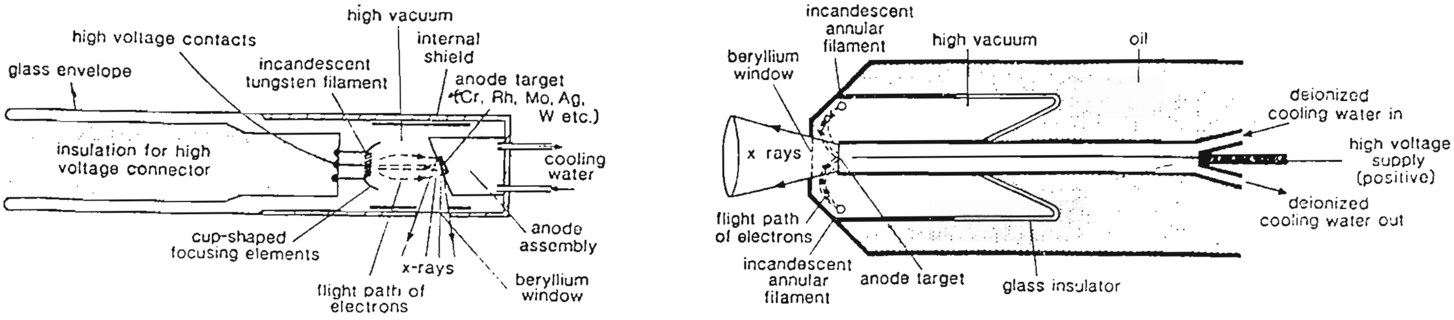


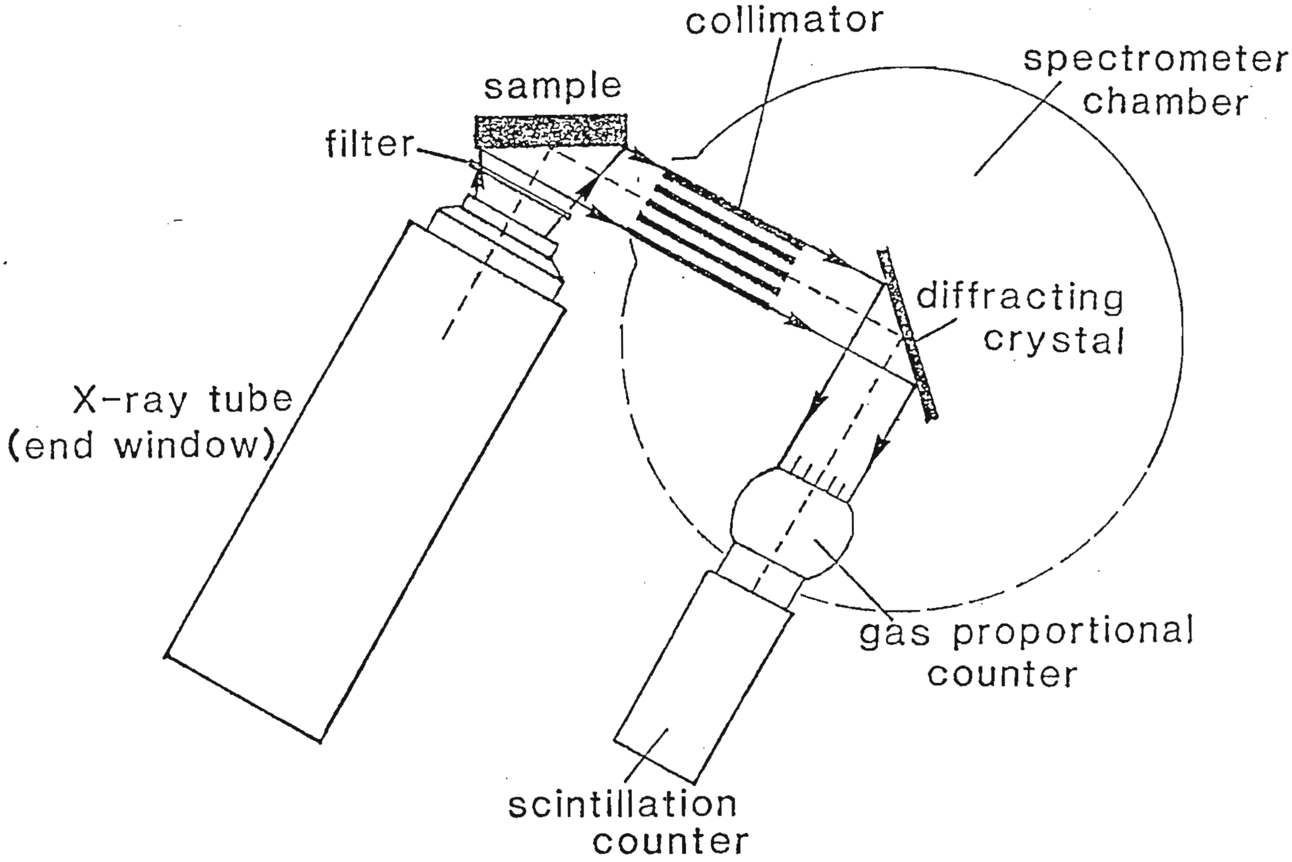
Figure 19: *The side- and end-window x-ray tube. [From Potts,1987].*



scattering than lighter ones. The *Compton scatter* spectrum is also caused by a fraction of the tube radiation being emitted by the sample but at lower energies dependent on the scatter angle. Samples with a low mean atomic number have a greater incidence of the Compton scatter effect. These effects can be reduced by insertion of a beam filter (Al or Cu) to attenuate characteristic tube lines but this is at the expense of elemental sensitivities and is done in exceptional situations.

A schematic diagram of a wavelength X-ray spectrometer is shown in Figure 20. Side-window X-ray tubes, operated up to 100 kV, are preferable to the end-window design in the excitation of the K lines (>20 keV) of some heavier elements such as Sb, Sn and Cd. Rhodium anode tubes serve universally in the analysis of geologicals for both majors and traces. Chromium tubes are preferred for application to majors specifically while Mo, W, Au, Ag and Co tubes are employed for particular trace elements. Cooling is necessary for modern high power tubes operated up to 3 kW. A variety of crystals are available for

Figure 20: *Schematic arrangement of a wavelength dispersive X-ray spectrometer.*



diffracting (Bragg's equation) the emitted X-rays and are selected as a function of X-ray energy. For example, LiF, combining high dispersion and intensity, is widely used for the K lines of K and above while Ge is preferred for P, S and Cl. In a sequential spectrometer, a goniometer mechanism is required to maintain the precise angular relationship between the diffracting crystal and the X-ray counter with respect to the sample source such that for the angle of incidence at the diffracting crystal of θ, the total angle of diffraction is 2θ. X-ray counters convert each X-ray photon into an electronic signal for counting and storage. The gas proportional counter is used to detect X-rays of energies up to 6-8 keV while the scintillation counter is effective above this range; both are mounted in tandem along the axis of the diffracted beam. Errors due to dead time and pulse height depression, appreciable effects above count rates of 10^4 cps, are corrected for in routine procedures.

The background signal contribution is measured at a position adjacent to the analyte peak, sometimes on both sides and interpolation is used. For a simultaneous spectrometer, with a discrete number of fixed channels, background corrections must be made either by separate measurements on a blank sample or by calibrated extrapolation of count rate measurements from one or two designated background channels. Spectral overlaps are few, the more serious being As Kα on Pb Lα and Rb Kβ on Y Kα. In these cases where lines cannot be resolved, correction factors are computed. All XRF measurements on bulk samples are subject to non-linear effects resulting from the attenuation, or infrequently enhancement, of fluorescence X-ray intensities by interaction with the sample matrix. These effects comprise mainly: (1) attenuation as the beam penetrates the sample, dependent upon photon energy (low suffers more) and matrix composition (greater for high atomic number); and, (2) attenuation of the fluorescence photons emerging from the sample. Many mathematical models, based either on fundamental principles or empirically determined, have been developed to account for these matrix effects (e.g., Lachance-Trail alpha coefficients, Rasberry-Heinrich algorithm).

There is a critical depth below the surface of a sample beyond which fluorescent X-ray photons are effectively absorbed. The magnitude of this critical penetration depth depends on the photon energy and on the mean mass attenuation coefficient of the sample. For example, for the Kα lines of Na and La in a silicate powder they are estimated to be 0.005 mm and 10.6 mm, respectively. Thus, for a powder sieved to pass 60 μm, the fluorescence signals from the lightest elements (Na Kα to Ca Kα) will be derived from a single monolayer. It is unlikely that this mass of sample would adequately represent the bulk and distortions may arise from heterogeneity along the surface of a compressed powder. Heavier elements are much less effected as the signal is acquired from a larger fraction of material. Hence the heavier trace elements may be determined in samples prepared as pressed pellets while for the majors it is essential that the mineralogical constituents of the sample are broken down.

Powder pellets are prepared by mixing the sample (having been sieved to pass a 200 mesh screen) with a suitable binder (e.g., methyl cellulose and polyvinylpyrrolidone) and compressing the mixture in a die at a pressure of 15-20 ton in^{-2} to form a disc about 4-6 mm thick and 30-50 mm in diameter. Either flat surface can be analysed after drying. Most fluxes used to prepare glass discs are based on lithium tetra- and\or meta-borate (20:80 mixture is popular) as it is available in a pure state and its constituents are not normally detected by XRF. The sample and flux are mixed at a ratio of ca. 1:5 and fused in Pt-5%Au crucibles at 1000-1150 °C for about 20 min. with agitation to ensure homogeneity. The disc is formed by pouring the melt into a circular mould and quenching as a flat disc by flattening with a preheated plunger or, by pouring the melt into a preheated casting dish which is then cooled. Semi-automated systems are available to carry out this task. "Low dilution" glass discs, prepared at a ratio of 1:2 rather than 1:5 are used to determine a suite of trace elements in addition to the majors. Problems arise in the fusion of mineralised samples. Elements such as As, Sb, Se, Te, Hg, Cd and S as sulphide are likely to be volatilised. This can partially be overcome by adding an oxidant (lithium nitrate) in the flux. Pt-ware is ruined by attack from mineralised samples containing sulphides. Hence the fusion based method is normally reserved for the "whole rock" analysis of silicates and to a lesser extent carbonates, chromites and barites.

It is general practice to calibrate with as many SRMs as possible, in part to minimise the effects of errors arising from uncertainties in "recommended" values. All count data are normalised against a drift monitor. The accuracy obtained will depend upon the reliability of the attenuation-enhancement correction procedure employed and the calibration protocols used. The data extracted from the literature by Potts (1987) indicates the accuracy and precision obtained by three XRF labs for the majors following a fusion (Table 10). A compromise must be made between obtaining the highest precision, from long count times, and maximum sample throughput. Data for trace elements, also from Potts (1987), are shown in Table 11; these are based on pressed pellets with the exception of Lee and McConchie who used low dilution glass discs. In the analysis of exploration samples, where the fraction of sulphide or oxide is not more than a few %, silicate based calibration and correction procedures will serve. However, at higher concentrations there is a lack of well characterised SRMs to match; synthetic pressed powders have not yet found widespread

Table 10: *Analysis of glass discs for major elements by WD-XRF. [From Potts, 1987].*

	Andesite USGS: AGV-1				Diabase USGS: W-2				Andesite N-1005			
	Gladney *et al.* (1983)		Lee and McConchie (1982)		Abbey (1983)	Schroeder *et al.* (1980)			Harvey *et al.* (1973)			
	Expected (% oxide)	CV (%)	Analysed (% oxide)	CV (%)	Expected (% oxide)	Analysed (% oxide)	*A* CV (%)	*B* CV (%)	Analysed (% oxide)	*C* CV (%)	*D* CV (%)	
SiO_2	59.25	0.49	59.25	0.13	52.81	52.89	0.61	0.68	59.15	0.27	0.18	SiO_2
TiO_2	1.06	2.4	1.05	0.19	1.06	1.08	0.37	0.87	0.72	0.37	0.44	TiO_2
Al_2O_3	17.15	0.99	16.99	0.16	15.49	15.45	0.84	0.70	17.47	0.36	0.24	Al_2O_3
Fe_2O_3	6.76	2.8	6.81	0.16	10.86	10.94	0.30	0.49	5.73	0.19	0.42	Fe_2O_3
MnO	0.096	4.2	0.095	2.1	0.167	0.17	1.8	1.17	0.107	0.10	0.23	MnO
MgO	1.53	3.3	1.54	0.78	6.39	6.60	0.61	2.8	2.79	1.43	2.15	MgO
CaO	4.94	1.4	4.89	0.12	10.89	11.15	0.27	0.60	5.42	0.14	0.21	CaO
Na_2O	4.25	1.4	4.30	1.4	2.21	1.92	2.6	11.4				Na_2O
K_2O	2.90	1.7	2.95	0.14	0.63	0.60	0.83	(0)	2.28	0.18	0.24	K_2O
P_2O_5	0.48	3.1	0.49	0.1	0.14	0.15	6.7	4.6	0.244	0.08	0.23	P_2O_5
Total	98.42		98.37		100.65							Total

CV = coefficient of variation = 100.standard deviation/mean analysis (%).

(i) USGS: AGV-1. Analysed data (Lee and McConchie) was obtained on 1 : 2 low dilution glass discs excited with a chromium x-ray tube operated at 50 kV for count times of 10 to 100 s per element. Data represents mean and CV in 10 analyses. Expected data are the 'consensus' values of Gladney *et al.*; the CV was calculated from residual data remaining after discarding outliers.

(ii) USGS: W-2. Analysed data (Schroeder *et al.*) was obtained from samples prepared as glass discs by fusing in the ratio 1 : 5 with heavy absorber flux. A chromium tube was used to excite samples at 60 kV for count times of 20 to 100 s per element. Coefficient of variation *A* was calculated from the analysis of six separate glass discs. Coefficient of variation *B* was calculated from ten analyses of the same glass disc of USGS: W-1 carried out over ten working days. W-1 and W-2 have almost identical major element compositions. These data are compared with expected compositions for W-2 taken from Abbey (1983).

(iii) Andesite N-1005 (a Nottingham University in-house reference sample) was prepared as 1 : 5.4 glass discs with heavy absorber flux and excited with a chromium tube at 40 to 60 kV for 20 to 40 s per element. Coefficient of variation *C* represents the arithmetic mean of the standard deviation of five replicate measurements on six discs and is a measure of instrumental precision. Coefficient of variation *D* represents the standard deviation derived from the average analysis of each glass disc and therefore is a measure of additional errors caused by sample preparation.

favour. Synthetic standards, however, for glass discs have found wide acceptance in XRF analysis for silicate exploration samples, iron concentrates, chromitites, barites and REE minerals.

The typical classical "whole rock" package offered by commercial labs comprises the determination of : (1) SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, Fe_2O_3, MnO, Cr_2O_3, P_2O_5, TiO_2 to 0.01 %; (2) Ba, Nb, Rb, Sr, Y and Zr to 10 $\mu g\ g^{-1}$; and (3) at extra cost Cu, Zn, Pb, Ni, Co, Mo, U and Th to 10 $\mu g\ g^{-1}$. Detection limits for the trace elements improve in the

Table 11: *Analysis of powder pellets for trace elements by WD-XRF. [From Potts, 1987].*

	Basalt CRPG : Br				Andesite USGS : AGV-1				Galway Granite JW6012			Amphibolite BL3571			
	Govindaraju and de la Roche (1977)		Schroeder *et al.* (1980)		Gladney *et al.* (1983)		Lee and McConchie (1982)		Leake *et al.* (1969)			Leake *et al.* (1969)			
	Expected (ppm)	CV (%)	Analysed (ppm)	CV (%)	Expected (ppm)	CV (%)	Analysed (ppm)	CV (%)	Analysed (ppm)	*A* CV (%)	*B* CV (%)	Analysed (ppm)	*C* CV (%)	*D* CV (%)	
Sc									4.2	34	50	15.9	12.9	9.8	Sc
V	235	39	240.0	1.8	123	4.8	121	4.3	5.5	75	17	181.9	8.1	2.8	V
Cr	380	21	287.1	0.7	12	13			58.9	8.8	3.1	795.5	1.2	0.5	Cr
Co	50	24	56.2	2.8	15.1	4.0			(0.1)			55.2	22	29	Co
Ni	260	28	259.5	0.5	17	12	22	12.7	1.4	174	506	608.4	3.0	1.2	Ni
Cu	72	38	80.0	1.7	60	5.0	63	3.0	33	21	12.5	85.7	4.4	4.7	Cu
Zn	150	25	135.1	0.8	88	1.1	82	2.4	36.7	9.0	3.7	85.1	2.5	2.3	Zn
Ga	20	76			20	7.5			18.3	6.0	9.7	13.0	13.5	11.5	Ga
Rb	47	36	46.5	1.2	67	0.7	64	4.5	265.5	1.4	1.2	20.4	4.6	4.2	Rb
Sr	1320	22	1363.8	0.2	662	0.7	646	1.0	20.6	3.1	3.2	267.4	0.7	0.7	Sr
Y	30	40	31.2	1.3	21	14	26	13.0	32.1	4.4	3.6	9.5	7.0	3.9	Y
Zr	250	29	251.1	3.8	225	4.0	260	2.2	75.3	8.6	5.0	62.3	6.5	4.9	Zr
Nb	100	11	114.7	1.2	15	10			19.2	10.1	11.1	3.5	106	29	Nb
Ba	1050	20	1056.4	0.6	1221	0.7	1200	0.5	61.7	13.1	7.7	244.4	5.1	3.5	Ba
La	80	40			38	3.9			10.3	16	19.2	9.6	18.6	37.5	La
Ce	140	13			66	4.5			36.1	11.6	17.9	51.9	11.3	14.0	Ce
Nd					34	7.4			9.3	47	21	9.0	41	39	Nd
Sm					5.9	4.2			8.6	51	63				Sm
Pb	8	63			36	6.9	34	9.1	76.8	5.0	3.9	5.9	65	63	Pb
Th					6.50	2.8			62.1	6.2	6.1	6.6	73	24	Th
U					1.89	6.6			3.6	150	105				U

CV = coefficient of variation = 100 × standard deviation/mean analysis (%).

(i) CRPG : BR. Data of Schroeder *et al.* were obtained by exciting powder pellets at 60 kV with a tungsten tube for count times of 40 to 130 s per element line. Results are the average of 40 analyses carried out over a 10 day period. These data are compared with expected compositions compiled by Govindaraju and de la Roche; coefficients of variation were calculated from all submitted data, without rejection of outliers.

(ii) USGS : AGV-1. Analysed data (Lee and McConchie) were obtained by exciting a 1 : 2 low dilution glass disc with a chromium or molybdenum tube at 35 to 60 kV, using count times of 50 to 100 s per element. The coefficient of variation was calculated from 10 replicate analyses. Data are compared with 'consensus' values of Gladney *et al.*, the corresponding coefficients of variation being calculated from published analyses, after rejection of outliers.

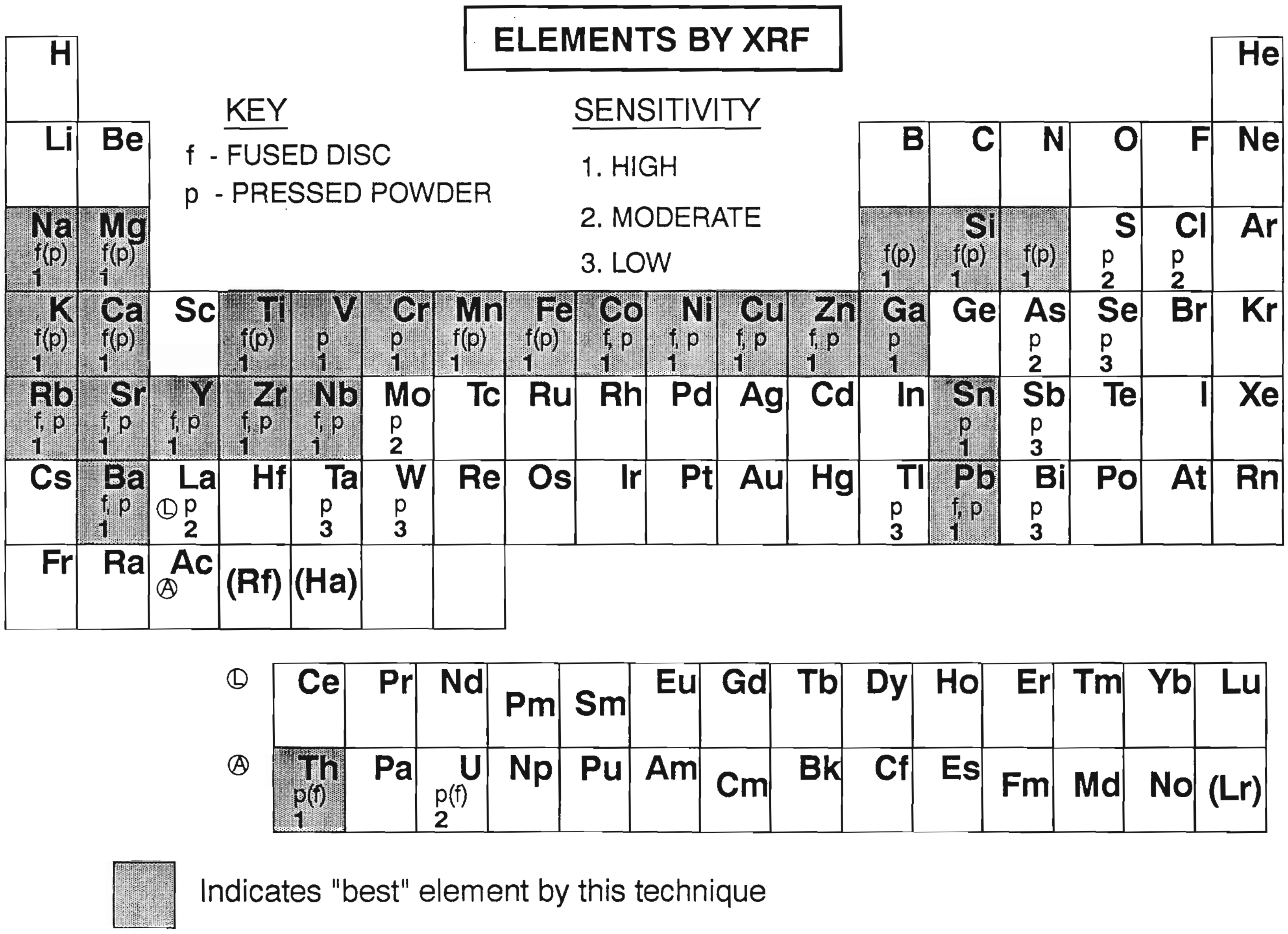
(iii) JW6012 and BL3571 are two in-house reference samples analysed by Leake *et al.* (1969). Data represent the average of a total of 36 to 48 analyses of 12 pellets of these materials, together with the corresponding coefficients of variation (*A* and *C*). Samples were excited with molybdenum or tungsten tubes operated at 50 to 100 kV (2 kW generator). Count times were 30 to 100s. Coefficients of variation (*B* and *D*) were obtained from 9 to 30 replicate analyses of the same sample pellet.

pressed powder package, shown in Table 12. The Periodic Table (Figure 21) shows the relative sensitivity of elements commonly determined by XRF with respect to Clarke values.

The energy dispersive XRF differs from WD in that, instead of being based on a Bragg diffracting crystal, the spectrometer uses a solid state lithium drifted Si detector to measure *simultaneously* all energies emitted by the sample. Potts et al. (1985) found that in

Table 12. *Elements determined by pressed pellet XRF, offered by a commercial laboratory. Values in ppm.*

Element	Detection limit	Element	Detection limit
As	3	S	50
Ba	20	Se	3
Bi	3	Sr	2
Cl	50	Sn	5
Co	2	Ta	5
Cu	2	Tl	5
Fe	3	Th	2
Ga	3	Ti	5
Mo	2	U	2
Nb	2	W	5
Ni	2	Y	2
Pb	2	Zr	3
Rb	2	Zn	2



ELEMENTS BY XRF

KEY
f - FUSED DISC
p - PRESSED POWDER

SENSITIVITY
1. HIGH
2. MODERATE
3. LOW

H																	He
Li	Be											B	C	N	O	F	Ne
▨ Na f(p) 1	▨ Mg f(p) 1											▨ f(p) 1	▨ Si f(p) 1	▨ f(p) 1	S p 2	Cl p 2	Ar
▨ K f(p) 1	▨ Ca f(p) 1	Sc	▨ Ti f(p) 1	▨ V p 1	▨ Cr p 1	▨ Mn f(p) 1	▨ Fe f(p) 1	▨ Co f, p 1	▨ Ni f, p 1	▨ Cu f, p 1	▨ Zn f, p 1	▨ Ga p 1	Ge	As p 2	Se p 3	Br	Kr
▨ Rb f, p 1	▨ Sr f, p 1	▨ Y f, p 1	▨ Zr f, p 1	▨ Nb f, p 1	Mo p 2	Tc	Ru	Rh	Pd	Ag	Cd	In	▨ Sn p 1	Sb p 3	Te	I	Xe
Cs	▨ Ba f, p 1	La Ⓛ p 2	Hf	Ta p 3	W p 3	Re	Os	Ir	Pt	Au	Hg	Tl p 3	▨ Pb f, p 1	Bi p 3	Po	At	Rn
Fr	Ra	Ac Ⓐ	(Rf)	(Ha)													

Ⓛ	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ⓐ	▨ Th p(f) 1	Pa	U p(f) 2	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	(Lr)

▨ Indicates "best" element by this technique

FIGURE 21 : *Sensitivities with respect to crustal abundances*

analysis for the heavier trace elements, the performance in terms of detection limits, precision and ease of operation of ED and WD XRF were equivalent. However, ED XRF is inferior in analysis for the lighter major elements. This instrumentation has not yet gained a solid position in commercial geoanalytical labs.

In summary, XRF is applicable to the determination of elements from Na to U at concentrations in the ppm to % range but is limited in the variety of matrices studied, silicates being by far the most common. Matrix corrections require special attention in unusual samples and the lack of well characterised similar SRMs is a hindrance. The technique is easily adaptable to automation and sample preparation is simple, without problems associated with dissolution and discs or pellets can be stored for repeat analysis. XRF is an exemplary technique in analysis for the major elements and the traces Rb, Sr, Y, Zr, Nb, Pb and Th and performs well for Co, Ni, Cu and Zn. There has been a trend in Canadian labs to abandon this workhorse in favour of ICP-AES but the precision of XRF in the above determinations is outstanding in silicate and carbonate matrices and its capabilities considerable in routine automated analysis.

Suggested reading:

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INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS)

The first commercial ICP-MS instrument was introduced by Sciex in 1983, followed shortly by VG in the U.K. Perhaps an indication of the acceptance of the technique is the fact that three Japanese manufacturers have now added the instrument to their product line. Although over 400 units have been sold world-wide, only one major commercial geoanalytical lab in Canada uses the technique routinely. The attractive features of ICP-MS are simple spectra, wide linear dynamic range (10^4-10^5), flexibility, the ability to measure isotope ratios as well as elemental concentrations, and excellent detection limits in solution in the range 0.01-0.1 ng ml^{-1} for most elements. Its high sensitivity make it a very exciting technique for ultra-trace analysis; it is not suitable for major element determinations. A schematic diagram of the spectrometer is shown in Figure 22. The "front end" is identical to ICP-AES but here the ions produced in the plasma are actually being sampled for measurement in the mass spectrometer. The ion beam passes through the sampler (made of Ni, Cu or Pt) into a pressure region of 1 Torr and then through the skimmer to the ion lenses at about 10^{-5} Torr. Ions of selected m/z (mass/atomic number) range leave the mass analyser and are deflected into a channel electron multiplier (CEM) for detection in a pulse-counting mode. Measurements are made by either scanning a chosen range of the mass spectrum for a fixed time or "sitting" on an analyte peak for a specified count time before advancing to the next peak. Unit mass resolution is easily achieved.

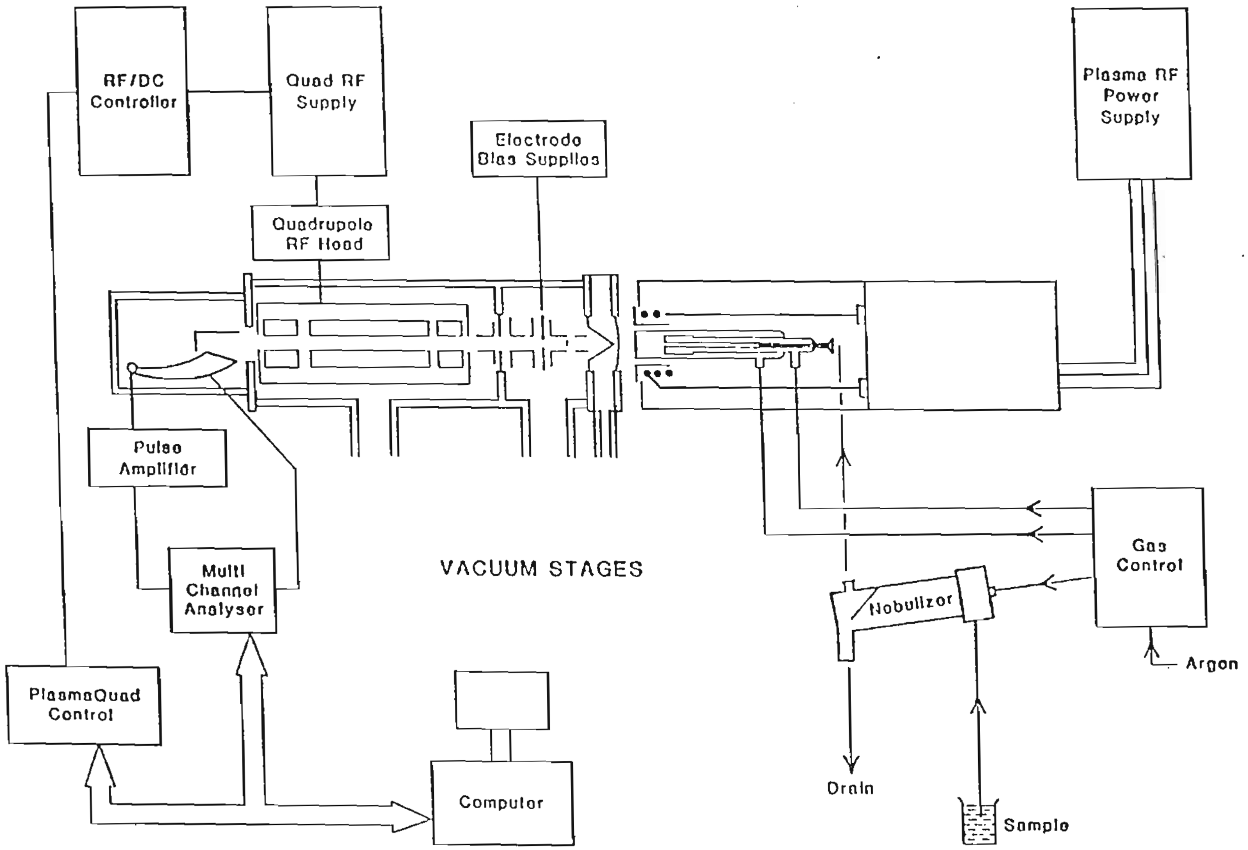

Figure 22: *Schematic diagram of an ICP-Mass Spectrometer.*

Spectral interferences are far fewer than in ICP-AES and are relatively easy to predict. These mass overlaps are due to isotopes of another element, oxides (MO^+), doubly charged ions, hydroxides and polyatomic ions formed from matrix elements and the plasma (e.g., ArO^+ on $^{56}Fe^+$). Fortunately almost every element has an isotope which is free from mass overlap by another element. Oxide and hydroxide formation is minimised by judicious setting of operating conditions, particularly the plasma power and carrier gas flow rate. When the magnitude of this interference remains significant, mathematical corrections can be computed. Non-spectral or "matrix-induced" interference is more problematic and, in simple terms, is manifested by a change in analyte signal due to other elements present in the sample solution. For example, salt deposition on the sampler and skimmer cause a reduction in sensitivity which worsens with time . There is an "ion sampling" effect where the relative proportions of ions initially sampled does not remain constant through the skimmer and lens system. The lighter the analyte and the heavier the concomitant (interferent), the greater is the degree of interference. Hence, the effects of elements such as Pb and U (matrix elements) on analytes such as Li and B can be severe. Elements below mass 80 tend to suffer the most interferences and care is needed in this region.

Calibration strategies naturally are chosen with anticipation of the types of interferences which may arise. Selection of one or more internal standards which would behave in a similar fashion to the analytes in changing matrices is now a common strategy. Thus, an internal standard is close in mass and ionisation potential to the analyte and, of course, does not exist to any degree in the sample matrix. The best internal standard one can choose is an isotope of the analyte but, other than in very precise work, calibration by isotope dilution is not yet widespread. Calibration by the method of standard addition is little used because it is time consuming. The choice of acid in which the sample is presented to the nebuliser is not the popular HCl used in ICP-AES because Cl forms polyatomic ions which create spectral interference such as ClO (on V) and ArCl (on As); hence HNO_3, which forms species that already exist in the plasma, is now employed more frequently.

To date, there have been three areas of major impact of ICP-MS in geoanalysis, in the determination of: REEs; Au and PGEs ; and a group of refractory elements not well served by more established techniques, namely Hf, Ta, Mo, W, Zr and Nb. Extracted from Jarvis (1989) in Table 13 is a comparison of detection (3σ) and quantification (10σ) limits for the REEs by ICP-MS with those by ICP-AES, INAA and XRF.

Table 13: *Comparison of detection limits by ICP-MS with other techniques. [From Jarvis, 1989].*

	ICP-MS				ICP-AES‡	INAA§	XRF¶‖
Element	Detection limit/ ng ml^{-1}	Quantification limit*/ µg g^{-1}	Quantification limit†/ µg g^{-1}	Element	Quantification limit‖/ µg g^{-1}	Quantification limit/ µg g^{-1}	Quantification limit/ µg g^{-1}
^{139}La	0.075	0.125	0.00125	La	0.044	0.83	1.17
^{140}Ce	0.1	0.17	0.0017	Ce	0.145	2.50	1.10
^{141}Pr	0.09	0.15	0.0015	Pr	0.065	—	1.03
^{146}Nd	0.2	0.35	0.0035	Nd	0.085	7.7	0.87
^{147}Sm	0.2	0.25	0.0025	Sm	0.031	0.17	0.77
^{153}Eu	0.06	0.10	0.001	Eu	0.005	0.08	0.73
^{157}Gd	0.1	0.15	0.0015	Gd	0.035	6.5	0.67
^{159}Tb	0.03	0.05	0.0005	Tb	—	0.15	0.67
^{163}Dy	0.1	0.20	0.002	Dy	0.011	—	0.63
^{165}Ho	0.04	0.05	0.0005	Ho	0.010	2.83	0.60
^{167}Er	0.06	0.10	0.001	Er	0.019	—	0.57
^{169}Tm	0.01	0.02	0.0002	Tm	—	0.57	0.57
^{172}Yb	0.06	0.10	0.001	Yb	0.004	0.23	0.57
^{175}Lu	0.05	0.10	0.001	Lu	0.004	0.17	0.50
^{89}Y	0.10	0.20	0.002	Y	0.025	—	1.63

* 500× dilution.
† 5× dilution.
‡ Jarvis and Jarvis.[18]
§ Potts *et al.*[19]
¶ Robinson *et al.*[20]
‖ 10× dilution.

The higher quantification limits in the ICP-MS column are based on a large dilution factor of 500 where the method involves only an acid digestion and subsequent dilution (0.2 g in 100 ml). However, if the REEs are separated from their matrix as they must be in analysis by ICP-AES (DF=5), then limits better than 4 ppb are obtained, far superior to ICP-AES. Besides sensitivity, the advantage of ICP-MS is that *all REEs* are determined at useful levels. *However, a consideration of great importance when comparing ICP-MS (or for that matter, ICP-AES) data and INAA data for the REEs is the decomposition method used.* Chondrite plots are shown for the same 5 igneous rocks in: Figure 23 by direct INAA; and Figure 24 by ICP-MS following an HF-$HClO_4$-HNO_3-HCl attack. The plots in Figure 24 are misleading, suggesting a light REE enrichment and no Eu anomalies. Analysis by ICP-MS after a $LiBO_2$ fusion agreed with INAA data; the heavier REEs were fractionated into refractory minerals (e.g., zircon) which were not attacked by the acid mixture.

In many cases the critical factor in computing the detection limit in a method based on ICP-MS is not the sensitivity of the analytical technique but the random contamination to the blank level created in the sample preparation procedure. Such an example is the determination of Au, Pt and Pd following Pb-FA and dissolution of the Ag prill. Results, from Simpson et al. (1990), for stream sediments analysed in this manner with a barren granite for "blank" control are shown in Table 14. A particularly "clean" flux (i.e. low in Au, Pt and Pd) and furnace were used for the fire assay and hence the blank levels for Au and Pd in particular, though measurable, were lower than might normally be encountered in high volume work. The actual solution detection limits for the analytes by ICP-MS are better than 0.1 $\mu g\ l^{-1}$ (ppb) and, with a dilution factor of 1, these would translate to about 1 ppb in the sediment. This is the case for Pt for which contamination is usually minimal (Table 14) but detection levels are degraded by the blank for Au and, to a lesser extent, for Pt.

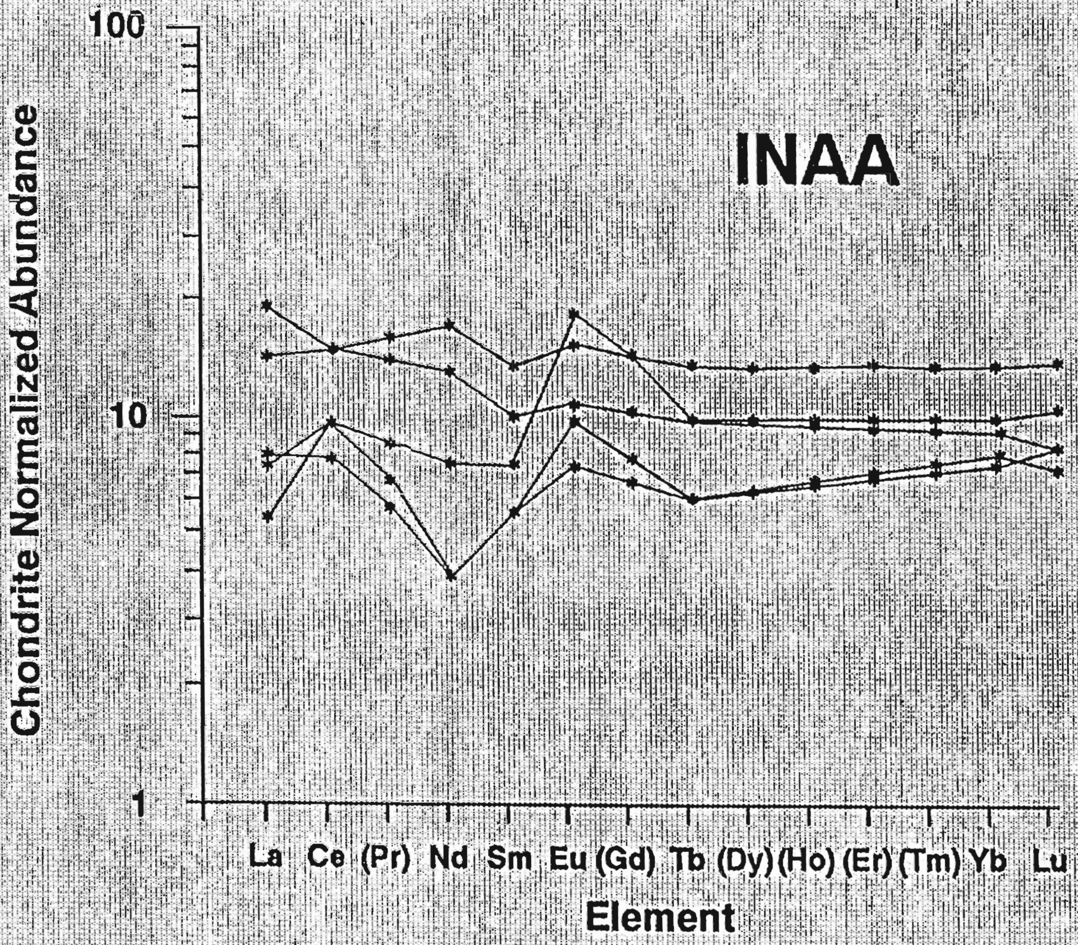

Figure 23: *Chondrite plots for REES by direct INAA.*

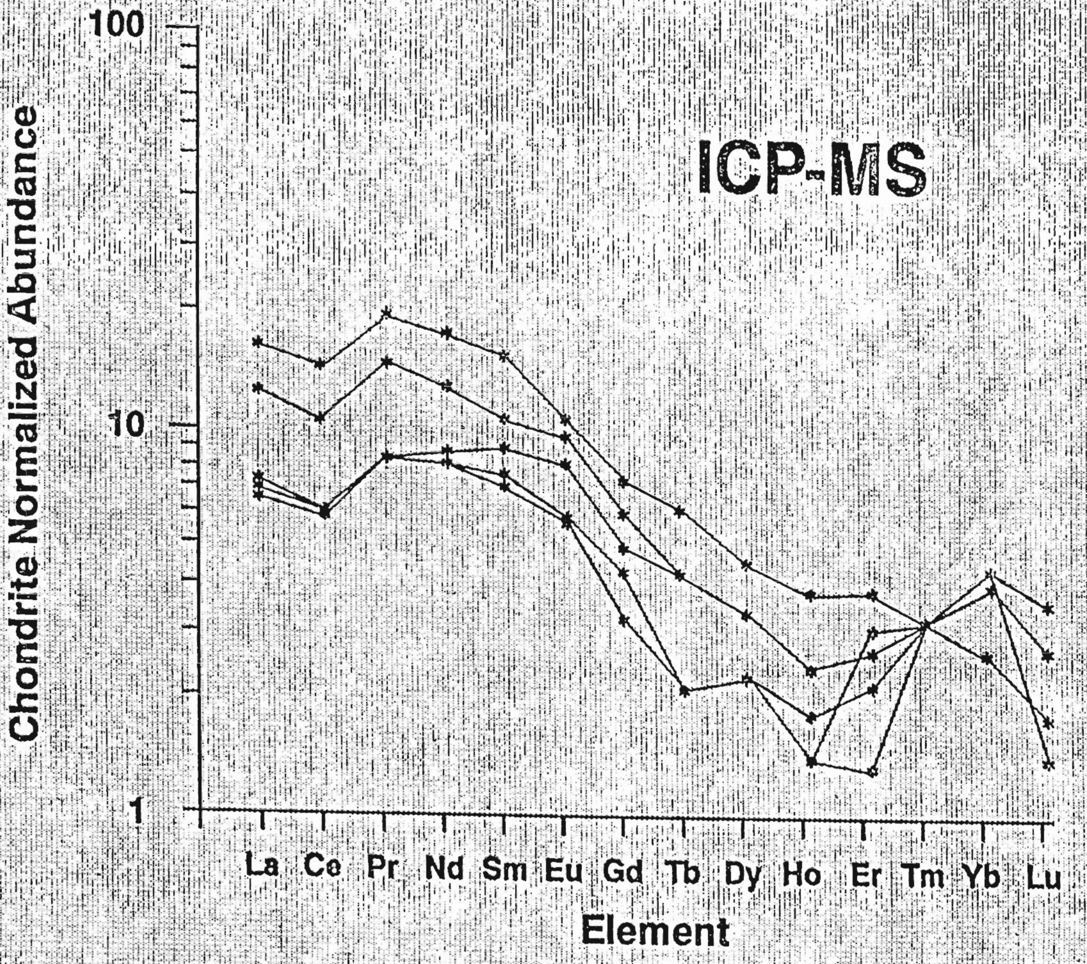

Figure 24: *Chondrite plots for REES by ICP-MS and HF acid digestion.*

ANALYSIS OF STREAM SEDIMENTS BY PbFA/ICP-MS (IN PPB)

SAMPLE	Au	Pt	Pd
3c	1.7, 2.1	1.6, 1.3	2.4, 3.0
69c	1.6, 1.5	1.7, 1.4	2.3, 2.0
190c	1.4, 1.9	1.3, 1.3	1.7, 1.7
65c	4.7, 3.8	2.9, 2.6	3.8, 3.7
45c	11, 13	3.5, 3.4	5.5, 5.3
18c	2.9±0.5 (n=5)	1.4±0.2	2.2±0.2
granite	0.73±0.35 (n=8)	0.06±0.04	1.80±0.13
DL (10g)	1	0.1	0.4
cf. DL* (10-30g)	1-5	5-10	1-2

* Commercial labs

TABLE 14. *: Analysis of sediments by Pb-FA / ICP-MS*

Nevertheless, the improvement in sensitivity for Pt (with a detection limit of 0.1 ppb compared to 5-10 ppb by ICP-AES) and for Pd should have considerable implications in geochemical exploration methods for these PGEs. The other package now determined by ICP-MS is that mentioned in the "Au and PGE" section following, based on NiS fusion which collects all PGEs. The alternative technique, INAA, is slightly inferior in sensitivity for Pt, Pd, Ru and Re and turnaround time is much longer.

The powerful sensitivity of ICP-MS benefits in two ways the determination of those elements of low natural abundance: detection limits below "background" can be achieved so that background *itself* can be estimated reliably; and efficiency and, therefore, cost can be improved so that multiple analytical techniques need not always be employed. For example, in the past one would have chosen XRF to determine Zr and Nb and INAA to determine Hf and Ta. These now form part of a larger package (including Mo and W) based on $LiBO_2$ fusion and ICP-MS where detection levels as low as 20 ppb in the sample can be reached.

Current research in ICP-MS centres on alternative sample introduction techniques to replace the inefficient nebuliser, to obviate interferences caused by concomitants in solution and to increase the present upper limit tolerated of 0.1-0.2% in total dissolved salts. Flow injection is solving the last problem. Laser ablation is being investigated in numerous geological labs but sample representivity remains in question at this point. Undoubtedly, the use of ICP-MS will grow in commercial labs as the need for lower detection levels in geochemical exploration is recognised.

Suggested reading:

- Hall, G.E.M., 1989. In: M.Thompson and J.N. Walsh, Handbook of Inductively Coupled Plasma Spectrometry. Blackie, Glasgow and London, p.238-268. [Review of state-of-the art of ICP-MS in geoanalysis].

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- Hall, G.E.M. and Plant, J.A., 1991, in press. [High field strength elements including REEs by ICP-MS].

- Jackson, S.E., Fryer, B.J., Gosse, W., Healey, D.C., Longerich, H.P. and Strong, D.F., 1990. Chem. Geol., 83, 119. [Au and PGEs by NiS-ICP-MS].

- Jarvis, K.E., 1989. J. Anal. At. Spectrom., 4, 563. [REEs by ICP-MS].

- Simpson, P.R., Robotham, H. and Hall, G.E.M., 1990. Trans. Inst. Min. Metall., 99, B183. [PGEs at low levels, applied study].

Au and the PGEs

Renewed interest in exploration for Au, Pt and Pd in the 1980s stimulated research into improving analytical methods for these elements, both in the area of decomposition\separation and instrumental measurement. The low abundance of Au and the PGEs requires the use of sensitive analytical techniques; a comparison of detection limits in pure solutions is shown in Figure 25 for F-AAS, GF-AAS, ICP-AES and ICP-MS.

Au

A number of options are available in selecting the method by which Au is to be determined, the choice being governed by the sample matrix, mineralogy, representative weight and detection limit required to meet objectives. Because of the "nugget" effect, a much larger weight than suffices for other trace elements is taken for analysis; this is usually

Figure 25: *Detection limits in ppb for Au and the PGEs by solution based techniques.*

DETECTION LIMITS

	Au	Pt	Pd	Rh	Ru	Ir	Os
F-AAS	10	120	20	6	160	360	120
GF-AAS*	0.1	0.5	0.1	0.1	2	2	6
ICP-ES	4	30	40	10	20	20	50
ICP-MS	←	0.05	→	0.15			→

* based on 50 μl

a minimum of 10 g but it has been common to use about one assay-ton (29.166 g). When heterogeneity is particularly problematic, the "metallics sieve analysis" can be employed. A sample of about 250 g is sieved to a certain mesh size (e.g., 150 mesh) dependent upon the grain size typical of the material; the entire "plus" sample is analysed and a sub-sample (e.g., 30 g) representative of the "minus" fraction is analysed. Both results are reported as well as the weighted average. This approach is naturally much costlier than analysis of a 10 g sample. Alternatively, but of similar expense, cyanidation of sample weights up to about 2 kg can be employed to negate the nugget effect but it must be remembered that this leach extracts only free Au.

The direct determination of Au to detection levels of 5 ppb in 10-30 g samples is achieved by INAA. Analysis at the 412-keV gamma-ray is relatively free of interference and many other elements can be determined for little additional cost. Other advantages of INAA for Au include: little risk of contamination as sample handling is minimal; no loss of Au as decomposition steps are absent; result is independent of mineralogy; and, the sample is not destroyed. Self-shielding is not a problem on Au grain sizes below 200 μm.

Other analytical techniques require dissolution and separation of Au which is accomplished by acid extraction or well established Pb fire assay (Pb-FA); commercial labs offer these methods based on ICP-AES, DCP-AES, ICP-AFS, F-AAS, GF-AAS or ICP-MS to a determination level of 1 ppb on a 10-30 g sample. Two oxidising acid leaches are in common use : aqua regia and Br_2-HBr. Prior to digestion, the sample is roasted at about 600^oC to volatilise sulphur and oxidise organic matter, both of which would otherwise coprecipitate Au from solution. To avoid the presence of interferences at the analytical stage, separation of Au from matrix elements is effected by solvent extraction into MIBK, or coprecipitated on Te or Hg. However, in an extensive study by Hall et al. (1989), it was demonstrated that the aqua regia extraction for Au is not always complete, the degree being dependent upon sample matrix. Residues left after an aqua regia attack on 157 rock samples were analysed for Au by INAA; as much as 50% of the total Au was found in these residues. When the aqua regia extractable Au result was added to the residual Au, results agreed well with direct INAA of the sample (Figure 26). This low bias in acid extractable Au compared to INAA Au is also evident in a "round-robin" study of five reference materials, soils and rocks, which were analysed by major North American labs. The data, illustrated in Figure 27, show that "wet chemical" Au, determined by a variety of analytical

Figure 26: *Comparison of results for Au: direct INAA versus aqua regia extractable Au and aqua regia extractable Au plus residual Au determined by INAA. [From Hall et al., 1989].*

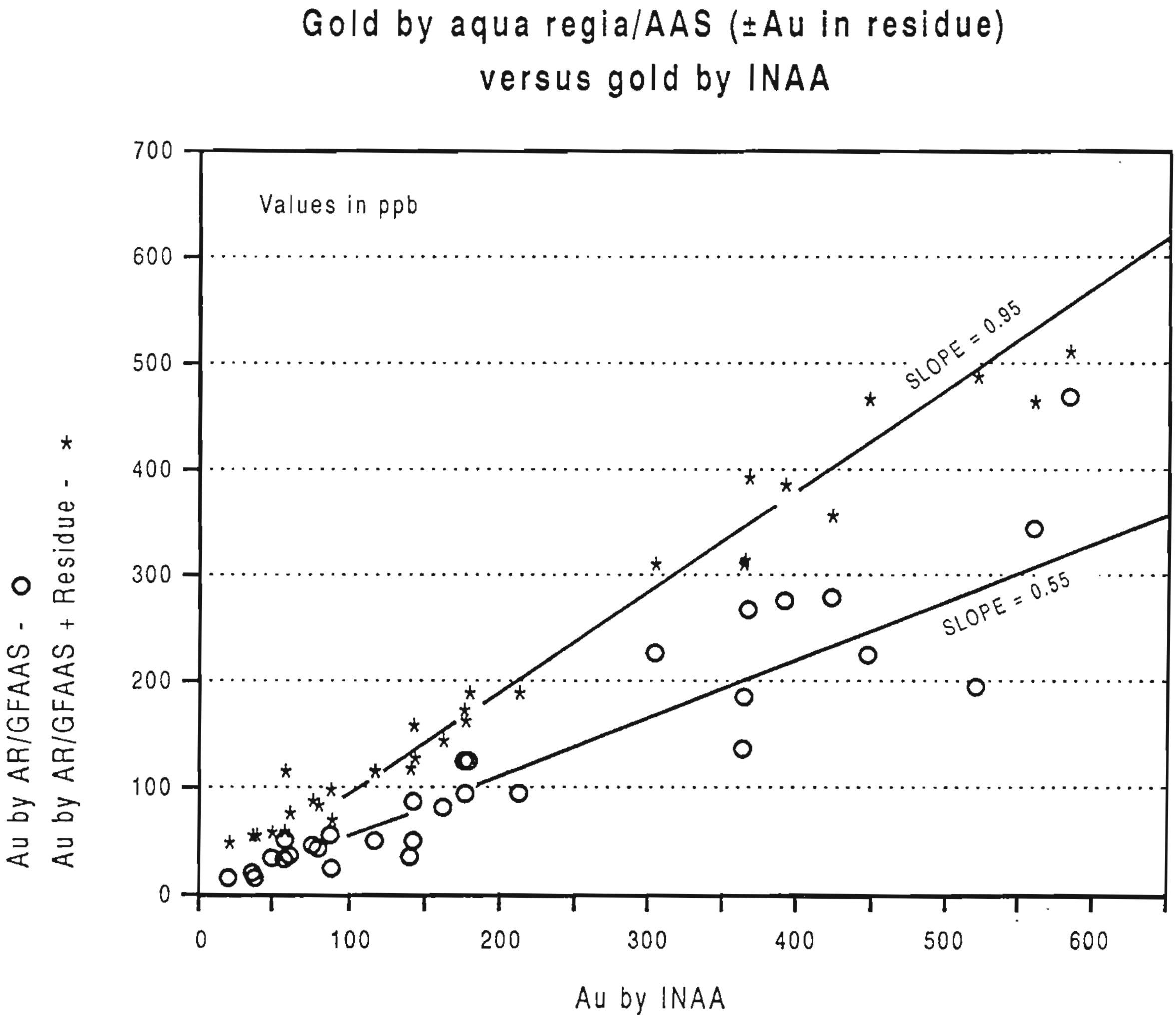
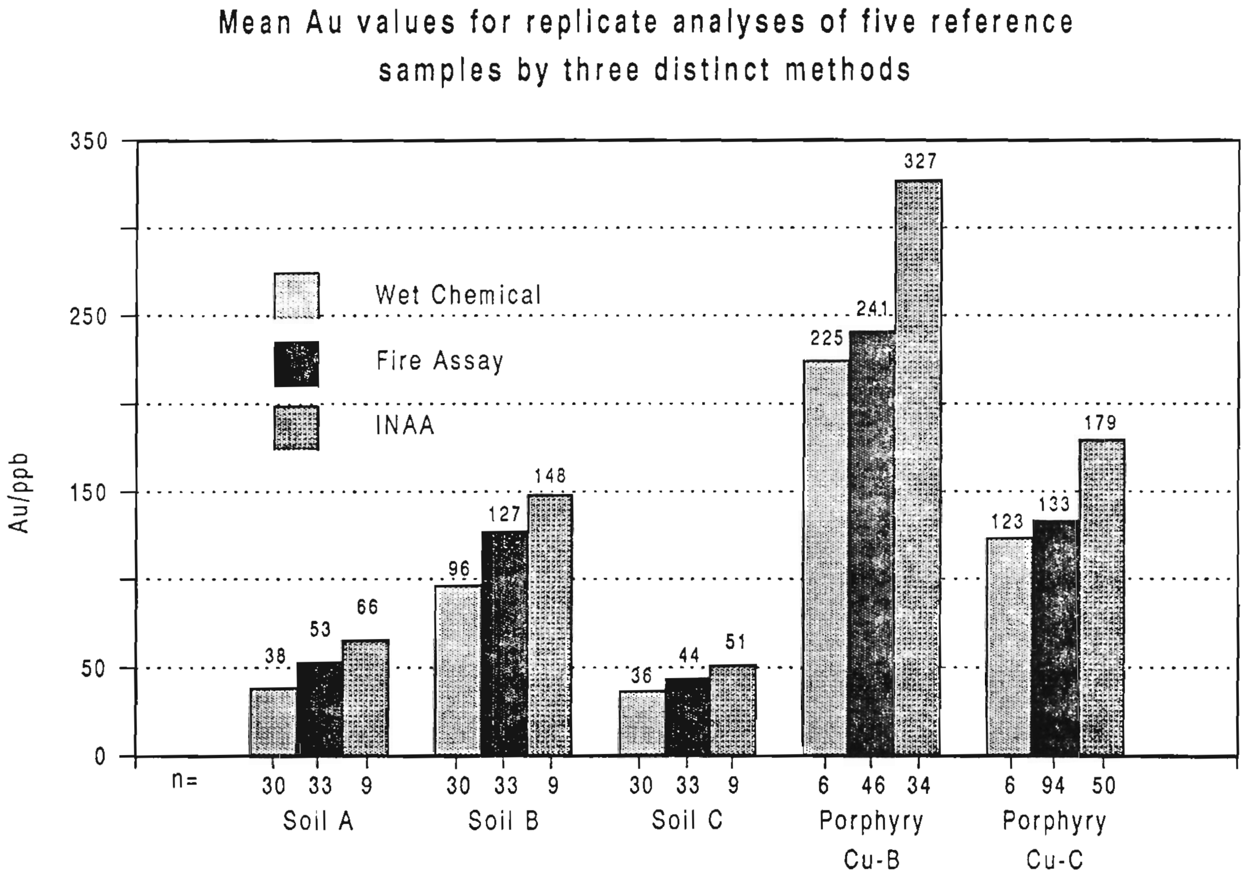


Figure 27: *Results for Au in five reference samples analysed by major North American labs using methods based on INAA, Pb fire assay and acid digestion. [From Hall et al., 1989].*



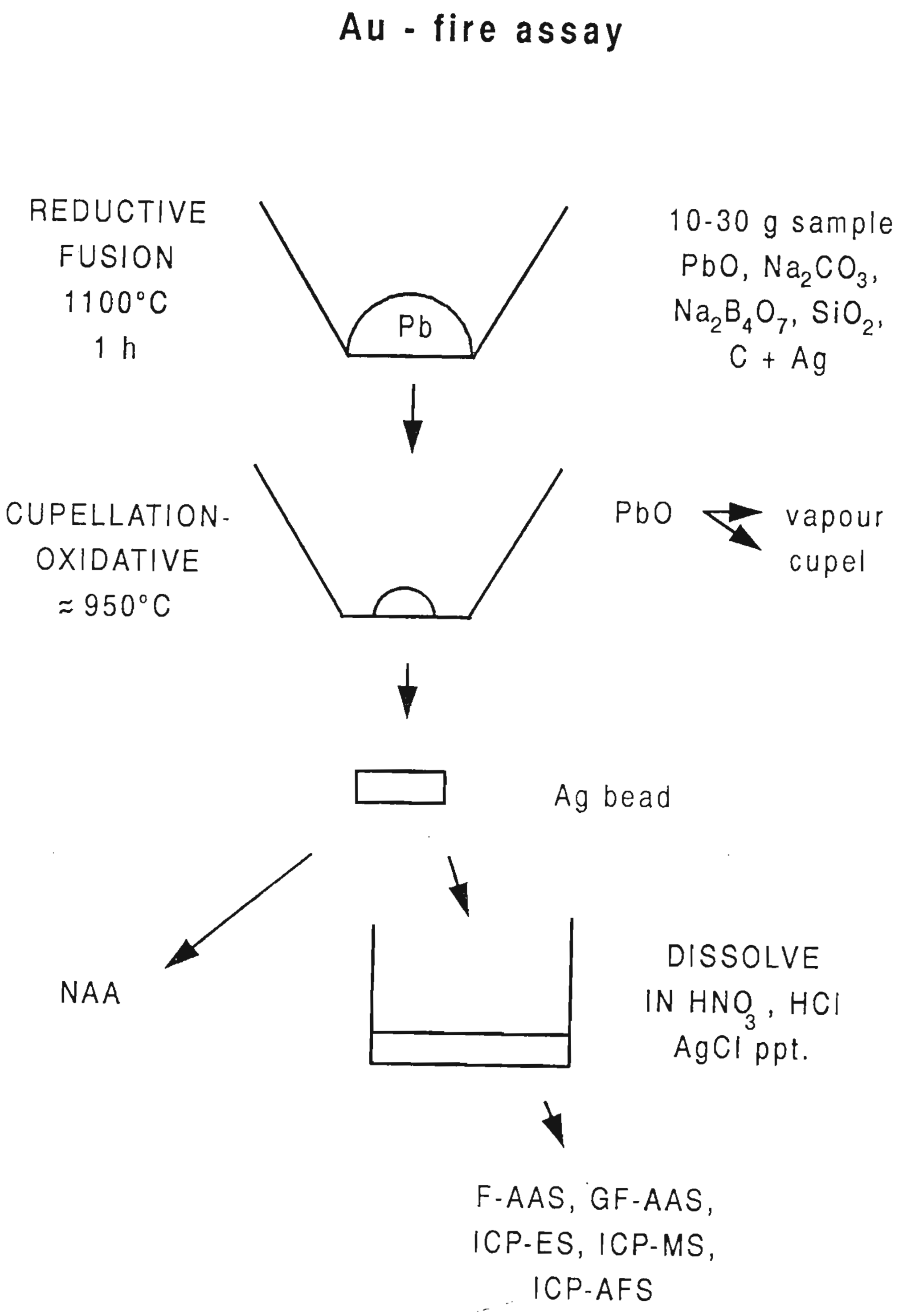
techniques is significantly lower than "fire assay" decomposed Au and INAA Au.

The classical Pb-FA procedure is illustrated schematically in Figure 28. It is important that the sample be finely divided, say, to -200 mesh, to ensure intimate mixing with the flux constituents. Typically, a suitable mixture for up to 30 g of sample would consist of 140 g of premixed flux, 10-20 g of SiO_2 and 3-5 g of flour. The quantities of the last two depend on the nature of the sample. Sulphides and arsenides are pretreated by roasting at 600-800°C to oxidise and volatilise S and As to prevent formation of a matte during fusion. Nitre (KNO_3) is added to samples containing appreciable amounts of Pb and S; for those high in Cu or Ni, either the flux composition is altered or an HCl leach is carried out prior to fusion. Conditions during the reductive fusion must be well controlled; thus it is apparent that experienced personnel are needed to obtain full collection of Au in the Pb button. Ag is normally employed to collect Au (and PGEs) during cupellation when the Pb is driven off; the prill is dissolved in HNO_3, Ag precipitated out with HCl and the solution analysed by AAS or ICP-AES normally.

PGEs

Essentially there are two "packages" offered by commercial labs for the PGEs: one is based on Pb-FA with collection in Ag for Au, Pt and Pd; and the more comprehensive is based on NiS-FA for Au, Pt, Pd, Rh, Ru, Os, Ir (and Re). The FA procedures effectively extract, separate and preconcentrate the analytes. The techniques used following dissolution of the Ag prill are commonly ICP- or DCP-AES, GF-AAS and less frequently ICP-AFS and ICP-MS. Detection limits reported are in the 1-5 ppb range for Au, 2-10 ppb for Pt and 2 ppb for Pd. As mentioned above, skill and experience are critical in the fusion and cupellation steps. Rh is not collected in Ag but can form part of a "package" with Pt and Pd

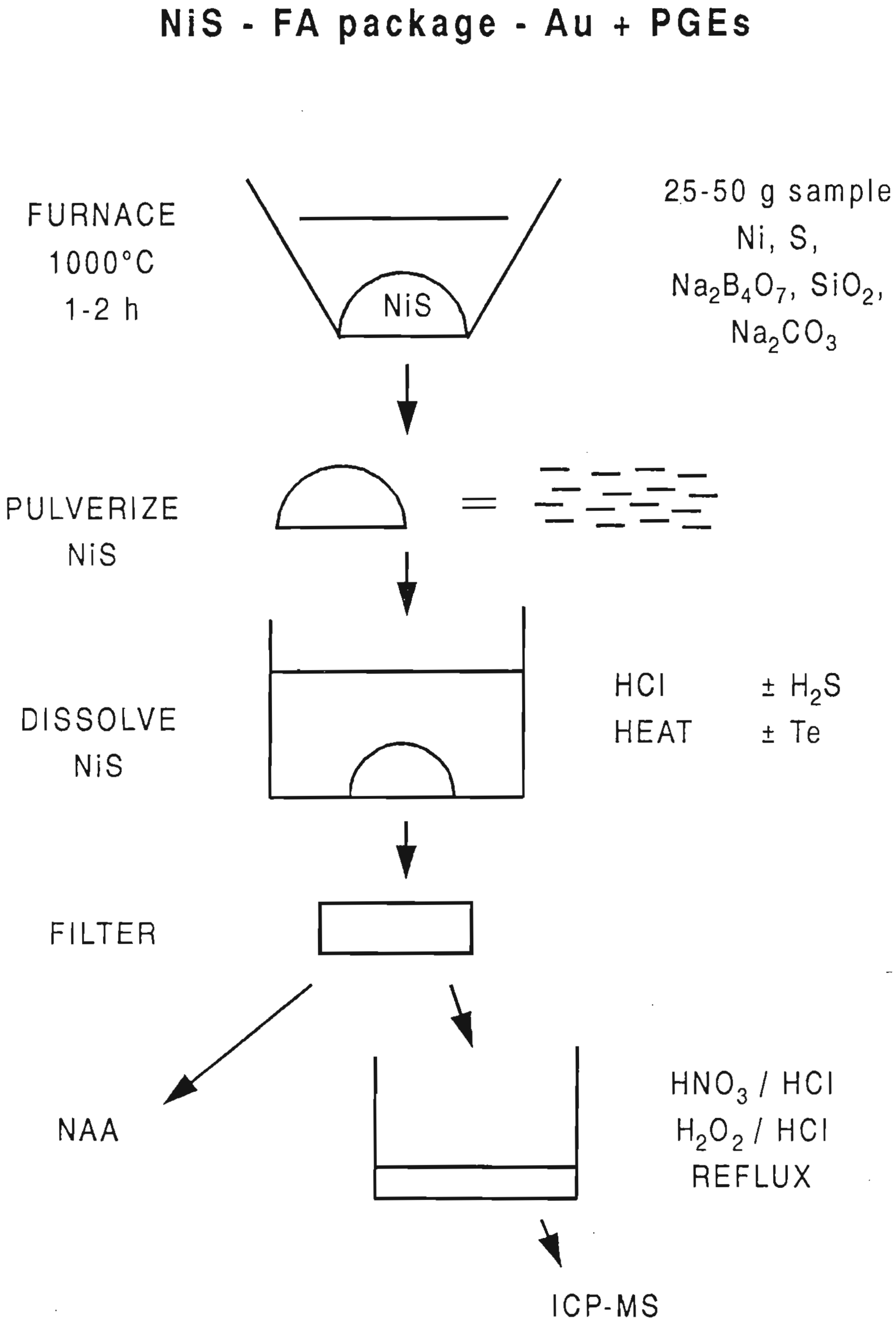
Figure 28: *Schematic diagram of the classical Pb fire assay procedure.*



when the collection is made in Au. Os and Ru are volatilised in the cupellation step.

The NiS-FA process is illustrated in Figure 29. The obvious advantage of this fusion is that it can be used for all the PGEs, though there are numerous reports that its collection for Au is low and inferior to Pb-FA. Large sample weights, often up to 50 g, can be accommodated but some modifications to the fusion are still necessary. The amounts of Ni and S in the flux are reduced accordingly for samples high in these elements. It is routine in some labs to analyse an aliquot of sample for Ni, Cu, Cr and S in order to design the fusion parameters. A lower weight must be taken for Cu-rich (ca. 10%) samples to prevent formation of CuS. A high concentration of Zn can lead to a poor fusion and low recoveries; apparently Zn prevents the NiS button from settling and proper separation is not achieved. The addition of H_2S or Te during dissolution of NiS in HCl hinders any loss to solution of the analytes, especially Au and Pd. Currently, most labs offering this service analyse the residue by INAA, though analysis by ICP-MS will become more prevalent when the instrumentation is more widely distributed. Two irradiations and three decay periods are required in INAA, resulting in a turnaround time of about 10 days. Routinely, Au and Rh are reported to 1 ppb; Pt, Pd, Re and Ru to 5 ppb; Os to 3 ppb; and Ir to 0.1 ppb. Detection limits are degraded by high concentrations of Au, Sb and Cu. If analysis is to be by ICP-MS, the sulphide residue is dissolved under reflux in $HNO_3\backslash HCl$ or $H_2O_2\backslash HCl$; care must be taken to prevent loss of Ru and Os by volatilisation of their oxides. Here detection limits for Pt, Pd, Re and Ru have improved over INAA to 1 ppb. High amounts of Cu degrade the detection limit for Rh. Some research labs are currently engaged in an attempt to lower the mass of the NiS button from 15-25 g to less than 1 g to improve the practicality of the method and reduce costs; however, this may well impede recovery of analytes. The

Figure 29: *Schematic diagram of the NiS fire assay procedure.*



cost of the complete NiS package is about six times that of the Pb-FA for Au, Pt and Pd. [See ICP-MS section for further discussion on PGEs].

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- Hoffman, E.L., Naldrett, A.J., Van Loon, J.C., Hancock, R.G.V. and Manson, A., 1978. Anal. Chim. Acta, 102, 157. [NiS package by INAA].

WATERS AND VEGETATION

Waters have not been used a great deal in geochemical exploration in North America. Until the advent of ICP-MS, it was possible in an inexpensive way to analyse for major constituents and only a few trace elements such as U and B which might be of interest to the explorationist. U can be determined easily to $<0.1\ \mu g\ l^{-1}$ by laser induced fluorescence using the Scintrex (Concord, Ont.) UA-3 analyser. Table 15 lists the detection limits for waters by ICP-AES with and without the need to preconcentrate to reach natural levels in rivers. Methods incorporating a twenty-fold or greater preconcentration by solvent extraction, coprecipitation, ion exchange or evaporation are therefore required and normally the cost would be prohibitive. Henshaw et al. (1989) analysed 250 lakes from the Eastern U.S. by direct ICP-MS for 49 elements and found that sensitivity was sufficient to allow determination of more than half these elements. The summary statistics are shown in Table

Table 15: *Typical elemental detection limits by ICP-AES for waters with comparison to concentrations in rivers and open sea. [From Thompson and Walsh, 1989].*

Element	*Wavelength* (nm)	*Detection limit**	*Median concentrations*		*EEC maximum admissible concentrations* (*or * = guide levels*)
			River	*Sea*	
Elements readily determined directly					
Na	589.0	20	6300	10.5×10^{6}	1.8×10^{5}
K	766.5	60	2300	3.8×10^{5}	1.2×10^{4}
Mg	279.1	70	4100	1.3×10^{6}	5×10^{4}
Ca	317.9	40	15000	4×10^{5}	1×10^{5}*
Sr	407.8	1	50	8000	
Ba	455.4	2	20	30	100*
Fe	259.9	10	100	(10)	200
B	249.7	1	10	4600	
S	180.7	80	3700	8.8×10^{5}	8.3×10^{4}
Si	288.2	30	1300	3000	
Elements mostly determined after 20 × preconcentration					
Li	670.8	2	3	170	
Be	313.0	0.1	0.4?	(6×10^{-4})	
V	311.1	2	0.9	2	
Cr	267.7	3	1	(0.05)	50
Mo	281.6	4	1.5	10	
Mn	257.6	10	15	(2)	50
Ni	231.6	8	1.5	2	50
Cu	324.8	2	3	3	100*
Zn	202.5	8	20	10	100*
Al	308.2	40	—	10	200
P	178.3	10	20	70	2182
Elements not determined after 20 × preconcentration					
Co	228.6	7	0.1	0.1	
Ag	328.1	2	0.3	0.04	10
Cd	226.5	2	0.03	0.1	5
Hg	194.2	5	0.07	0.03	1
Pb	220.3	20	3	0.03	50
As	193.8	20	2	3	50
Sb	206.8	90	1	0.5	10
Bi	223.1	30	0.005	0.02	
Se	196.1	80	0.2	0.4	10
Te	214.3	20	?	?	

Table 16: *Summary statistics for ICP-MS analysis of lake waters in Eastern U.S. study. [From Henshaw et al., 1989]*

element	% of lakes with detectable concn	% of lakes with determinable concn	maximum measured concn
Be	2	0	0.44
B	100	62	16.5
Al	94	75	698
Ca	100	100	9170
V	53	12	0.93
Cr	3	0	0.46
Fe	90	100	727
Mn	100	99	368
Co	74	39	1.6
Ni	53	3	2.1
Cu	37	7	7.0
Zn	56	8	432
Ga	3	0	0.06
Ge	1	0	0.11
As	43	1	2.0
Se	1	0	4.6
Br	42	3	86[b]
Rb	100	100	2.8
Sr	100	100	56
Y	71	48	1.2
Zr	14	0	0.10
Mo	8	2	1.6
Rh	3	0	0.03
Cd	7	1	0.79
Sn	1	0	0.26
Sb	17	0	0.16
I	89	46	14
Cs	19	1	0.15
Ba	100	100	41
La	54	29	1.2
Ce	61	29	1.9
Pr	43	15	0.23
Nd	26	6	0.82
Sm	4	0	0.15
Dy	4	0	0.14
Ho	2	0	0.04
Tl	8	0	0.41
Pb	50	13	5.2
U	18	1	0.57

[a] Nb, Ru, Pd, Te, Er, Eu, Gd, Tm, and Th were not detected in any lakes. Ag is not reported, because of uncertainty due to Cl added in spiking solution. [b] Br concentration using subsequent calibration (see text).

16. Hall et al. (1988) analysed spring waters for Mo and W by ICP-MS and found concentrations above 0.1 $\mu g\ l^{-1}$ to indicate areas of known Mo and W occurrences. Thus, it appears that ICP-MS is the tool needed to evaluate the usefulness of waters in geochemical exploration.

For the most part, the analysis of vegetation is well served by INAA, either as a pressed pellet, or preconcentrated as an ash for the determination of involatile elements. Though the detection limit by INAA for Au in vegetation is adequate (0.1 ppb in the pellet), that for Pt and Pd is not. A method based on ICP-MS was developed by Hall et al. (1990) whereby detection limits below 1 ppb in the ash for Au, Pt and Pd could be achieved by taking less than 50 g of dry sample (cf. 1 kg required for Pt by conventional methods). More research is needed to design cost-effective methods to determine elements such as Se, Te, some REEs, Ag, Ni, Th and Hg.

Suggested reading:

- Hall, G.E.M., Jefferson, C.W. and Michel, F.A., 1988. J. Geochem. Explor., 30, 63. [Mo and W in waters by ICP-MS].
- Hall, G.E.M., Pelchat, J.C. and Dunn, C.E., 1990. J. Geochem. Explor., 37, 1. [Au, Pt, Pd in vegetation by ICP-MS].
- Henshaw, J.M., Heithmar, E.M. and Hinners, T.A., 1989. Anal. Chem., 61, 335. [Surface waters by ICP-MS].

SUMMARY COMMENTS

There are other analytical techniques in use which, in the author's opinion, do not warrant in depth discussion here. For example, electrochemical techniques such as anodic stripping voltammetry (ASV) and detection by an ion selective electrode (ISE) are employed for specific purposes in geoanalytical labs. Fluoride is measured by its ISE, directly in waters or in a leachate following an alkaline fusion. Alternatively, it can be determined together with Cl and S by ion chromatography (IC) following pyrohydrolysis of the sample. IC is used routinely to determine F, Cl, S, Br, P and N species in waters. A field portable ASV unit is currently under evaluation at the GSC and to date has performed well in the analysis of waters and acid leachates for Zn, Cu, Pb and Cd; applications for Au, As and Ni will be forthcoming.

This article gives the geologist a guide as to the relative merits of today's common analytical methods. *However, it is up to the user of analytical data to ascertain the validity of those numbers. All too often, the geologist relies upon the laboratory's quality assurance and control program.* That is not to say that such programs are inadequate but they may not always suit the types of sample matrices submitted or be rigorous enough to satisfy the demands of the particular survey. Normally a laboratory will evaluate a new method by its application to well characterised SRMs, available commercially from a number of organisations such as the U.S.G.S., CANMET and NIST (formerly the National Bureau of Standards, U.S.). It will then standardise its own internal controls against these for their frequent insertion in sample batches. Where facilities are available, the geologist should develop and standardise his\her own bulk control samples which are similar in matrix generally to the samples of interest. Replicate data for these controls will allow computation of precision and accuracy of the methods used and determination of whether the analytical variability is insignificant compared to the geochemical variability. Communication between the lab and the geologist is of paramount importance, an understanding of the nature of the samples and program objectives will allow the lab manager to judiciously advise on the choice of analytical methods to be employed.

Publications covering a variety of analytical methods are listed below. Phil Potts' comprehensive recent book has been invaluable in writing this paper. A special issue of the Journal of Geochemical Exploration dedicated to analytical methods and directed towards the geochemist as reader will be published in 1992. A journal which every geochemist should subscribe to is Geostandards Newsletter, published twice a year in France by the International Working Group on standards and edited by K. Govindaraju. Its special issue of 1989 contains comprehensive data on 272 geostandards and regular issues give the reader an appreciation of the state of the art of current techniques and methods applied to SRMs. Most of the analytical journals contain annual (or bi-) reviews covering recent literature in specialised topics. Advances in each technique (e.g., ICP-AES, ICP-MS) regardless of discipline or application are discussed while others focus on the type of sample analysed. For example, Analytical Chemistry publishes a review entitled "Geological and Inorganic Materials" biennially and a similar update can be found in the Journal of Analytical Atomic Spectrometry.

General reading:

- Fletcher, W.K., 1981. Analytical Methods in Geochemical Prosecting. Handbook of Exploration Geochemistry, Vol.1, 255pp.
- Mizuike, A., 1983. Enrichment Techniques for Inorganic Trace Analysis. Springer-Verlag, Berlin, 144pp.

Potts, P.J., 1987. A Handbook of Silicate Rock Analysis. Blackie, Glasgow and London, 622pp.

- Van Loon, J.C. and Barefoot, R.R., 1989. Analytical Methods for Geochemical Exploration. Academic Press, San Diego, 344pp.

PAPER #9

THE MANAGEMENT, ANALYSIS AND DISPLAY OF EXPLORATION GEOCHEMICAL DATA

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Abstract

Procedures are outlined that assist in the management, analysis and display of exploration geochemical data. Topics presented include: microcomputer software; quality control procedures; the concepts of background and threshold, and their estimation; map preparation; univariate data inspection; simple regression analysis; weighted sums; and a concluding section on developing a strategy for use of the tools described. The benefits of disaggregating large data sets into more manageable and interpretable subsets are discussed, and the graphical advantages and statistical requirements for logarithmic data transformations are reviewed. The techniques presented are illustrated using a small stream sediment data set. Attention is focused, where possible, on simple graphical procedures, and on non-parametric, median and percentile based, methods that are resistant to the effects outliers and anomalies may have on estimating the parameters of geochemical background. The importance of fully utilizing the geological and geochemical knowledge concerning the survey area available to the geochemist or geologist undertaking an interpretation is stressed. The point is made that computer procedures can significantly assist the interpretational task; however, computers can not and should not replace the careful inspection of the data in the light of all available geological knowledge in the development of an interpretation that recognizes the geochemical dispersion processes active in a survey area.

Résumé

Les méthodes utilisées pour la gestion, l'analyse et la présentation des données géochimiques d'exploration sont examinées. Les sujets abordés sont notamment : les logiciels de micro-ordinateurs; les méthodes de contrôle de la qualité; les concepts de fond et de seuil et leur évaluation; l'inspection de données à une variable; l'analyse par régression simple; les sommes pondérées; et une série de conclusions sur la façon d'élaborer d'une stratégie pour utiliser ces outils. Les avantages à diviser les grandes séries de données en sous-séries plus faciles à gérer et à interpréter sont abordés. On examine également les avantages des méthodes graphiques et les caractéristiques statistiques nécessaires pour procéder à des transformations logarithmiques des données. Les techniques présentées sont illustrées en utilisant une petite série de données sur des sédiments de ruisseaux. L'accent porte, autant que possible, sur des méthodes graphiques simples et des méthodes non paramétriques, basées sur les médianes et les percentiles, qui résistent bien aux effets des valeurs anomales sur l'estimation du fond géochimique. On met l'emphase sur l'importance pour le géochimiste ou le géologue qui entreprend une interprétation, d'utiliser toutes les connaissances géologiques et géochimiques dont il dispose au sujet de la région où s'effectue le levé. On souligne que les méthodes informatiques peuvent faciliter considérablement l'interprétation; cependant, les ordinateurs ne peuvent pas et ne devraient pas remplacer l'inspection soignée des données à la lumière de toutes les connaissances géologiques disponibles afin d'élaborer une interprétation qui permette de déterminer les processus de dispersion géochimique dans une zone d'étude.

Introduction

How much are your data worth? The results are finally back from the lab, how much has been spent so far? There was sample collection - maybe even a flight in and out, shipping, sample preparation and then analysis. It all adds up only too fast, and what comes next? Just run a finger down the columns and look for the high numbers? Surely, all the time, effort and money spent so far deserves a bit more consideration than that.

There is a history of almost thirty years of applying computers and statistics to the management, analysis and display of geochemical data. Some procedures are complex and sophisticated, and in the past many have been applied needlessly when simpler procedures would have sufficed. The purpose of this presentation is to illustrate some simple procedures that will help get value out of expensively acquired data and aid interpretation.

Firstly, some microcomputer software will be discussed. This may seem like putting the cart before the horse, however, it is these tools that make a thorough job possible. Quality control procedures will be reviewed. Then, what is meant by threshold and how are appropriate values chosen? What are some different ways of looking at the data, how can the data be plotted so that they will reveal any unusual situations that may be indicative of mineralization? Are there any simple numbers or indices that can be calculated to indicate if the data hold information of use in exploration? What maps can be plotted that will assist identifying areas worthy of further exploration effort? Finally, some more advanced and newer procedures that are proving useful to geochemists will be briefly mentioned.

The assumption is made that the geochemist has access to a microcomputer. Twenty-five years ago calculations were made with slide-rules and log-tables, and histograms and graphs were tediously plotted by hand. Luckily those days are past, now microcomputers can be used to remove the drudgery from inspecting data and permit a far more thorough look at them.

Data Management

Geochemical data can be viewed as a simple table. The columns contain the attributes of geochemical samples, i.e., number, location, perhaps field data, e.g., soil type or stream size, and the laboratory results. The rows are the different samples in the survey.

This table could be entered with a text editor or word processing package, either neatly laid out in columns or as a continuous string with commas between each separate piece of data. In a neatly laid out table any lack of information is indicated by an empty space, or an abbreviation, e.g., n.d. or i.s.; in a continuous string an empty space would be indicated by a comma occurring immediately after the previous comma. These two styles are known as fixed format and free format respectively. A fixed format table is easier to read if it is printed; a free format table takes up less computer storage space. Before proceeding mention must be made of the problems associated with using characters, e.g., nd, n.d., is, i.s., etc., in fields of a data table that are normally numeric. These may look nice in a printed table, but many computer packages will balk at such characters. If it is planned to use characters in these ways select computer software for plotting and calculations with care.

Similar consideration has to be given to less-than-detection level data. For processing these are commonly indicated by values of ½ or ⅝ the detection limit. This is often adequate at the time of the project, but consideration has to be given to the problem of archival files and databases. As new and improved analytical methods become available detection limits fall; in archival files it is essential to know if a value of 1 ppm is a real observed value, or an indicator value which really means <2 ppm. Again, care must be taken in selecting DBMSs and designing databases for across project use.

There are better ways of working than simply having the data as a "typed" table, the table can be maintained by software that extracts the rows and columns that need to be accessed. Database Management Systems (DBMS), e.g., dBase, Paradox, Rbase, etc., were written to maintain and work with tables like those in geochemistry. Spread sheet programs, e.g., Excel, Lotus, Quattro Pro, etc., can also be used; these have the advantage that calculations can be undertaken inside the spread sheet to compute ratios and other useful numbers. However, probably the most useful tool is a data plotting and statistics package that also has some data management capabilities. Two examples of commercially available packages that meet this requirement are Statgraphics and Systat. In the examples that follow Systat has been used to plot the diagrams and maps, and to undertake additional calculations, sort the data and compute some statistics.

Today, many geochemical laboratories make data available in a computer-readable form, either on a diskette or over a telephone link. Data entry into any computer system is tedious and error-prone, the fewer times it has to be done the better. Therefore a further criterion in selecting microcomputer software is that it can import data from a fixed- or free-format external file. Another important consideration is that software be available to merge tables. The analytical data will come from a laboratory, but if maps are to be plotted the geographic coordinates will likely come from elsewhere. These two data tables, possibly together with some simple field observations, e.g., soil or till depth and colour, stream width and depth, etc., will need to be merged. If a lot of such work is expected it may be better to use two microcomputer packages, one for data management and another for the data analysis and display. The important thing to remember in selecting software is to consider the different processing scenarios that will be encountered and ensure that the selected software meets the geochemical requirements.

Perhaps one of the greatest benefits from microcomputer use in data management is that it helps preserve survey data. By having the data organized onto diskettes, value is added, and as a result people take greater care of them. How often has an old report been recovered and all the data not been found? Interests change, new commodities become important, and what is now critical information was lost as it was not considered of prime importance when the work was originally undertaken. If there was a diskette filed with the report how different life would be. In the information age it is likely that organized data on diskette will make a property or project more attractive to a "buyer" than another of equal geological merit for which the data are a "mess".

Quality Control

Canadian contract geochemical laboratories have an enviable reputation for high data quality. Even so, sample preparation and analytical mistakes and accidents can and do happen. It is ultimately the responsibility of the geologist or geochemist managing a survey to ensure the data quality; it is no excuse to say, "... well, those were the numbers the lab gave me".

An equally important, and often numerically larger, source of geochemical data variability is in the field at the sampling site. In fact for many of the elements routinely determined in the laboratory the true analytical variability is relatively minor; problems only arise when the application of procedures is inconsistent, e.g., changes in reagents, concentrations, and reaction times and temperatures.

The quality of geochemical data may be described in terms of accuracy and precision, the latter being divided into analytical and sampling-and-analytical precision.

Accuracy

Accuracy is the proximity of the results to the ultimate truth; it is most important in lithogeochemical surveys and assay-like work where the total amounts of a metal or compound are being determined. For example, accuracy is vital to good rare-earth-element (REE) work where chondrite-normalized data are being compared with external reference plots indicative of various genetic settings (Hall, 1990). Another example is the computation of petrochemical indicators and ratios, e.g., Nb/Y, Zr/TiO_2, etc., used to type volcanic environments. Inaccurate data can lead to totally misleading conclusions and wrong exploration decisions. With the use of non-total chemical attacks, absolute accuracy has less meaning. However, if data from surveys undertaken over several years are to be compared, it is essential that accuracy, in the form of long-term precision, be maintained. The only way of monitoring accuracy is by the inclusion of reference materials. For lithogeochemical surveys it is best to prepare one or more in-house control reference (CR) samples and then submit sub-samples of these with internationally certified reference materials (ICRMs) for replicate analysis. If the results for the ICRMs agree with the published values, the in-house CR samples and their mean values may be used as sub-standards in future work. With non-total analyses it is often sufficient simply to analyze sub-samples of large prepared CR samples of the sample materials to be employed in the projected survey work. These replicate analyses establish the levels of the elements of interest by the analytical procedure(s) to be used. It must be stressed that CR samples be of the routine survey sample material and have been prepared using preparation procedures similar, if not identical, to those to be employed in the surveys. By ensuring the CRs have the same mineralogical properties as the survey material, they will respond similarly to the survey material to any procedural changes or variability. In both cases, CR samples are included with the routine survey samples and the results monitored to ensure accuracy is maintained. Monitoring is best undertaken graphically, where the results for the CRs are plotted against batch number and/or date of analysis or report. The former is better as it ties back to a laboratory entity, Figure 1. In this example, control lines (UL & LL), based on the data for the first 3 batches, have been inserted at the mean ± 2 standard deviation limits to act as a guide for recognizing subsequent out-of-control analyses. Once out-of-control results are found, it is the geologist or geochemist's responsibility to assess their importance to the project and discuss the problem with the laboratory.

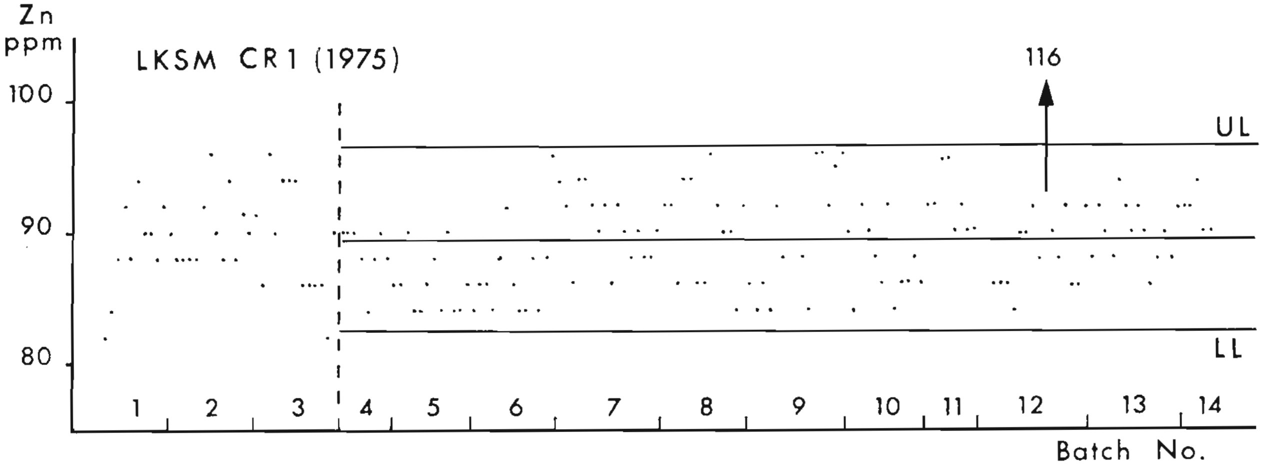
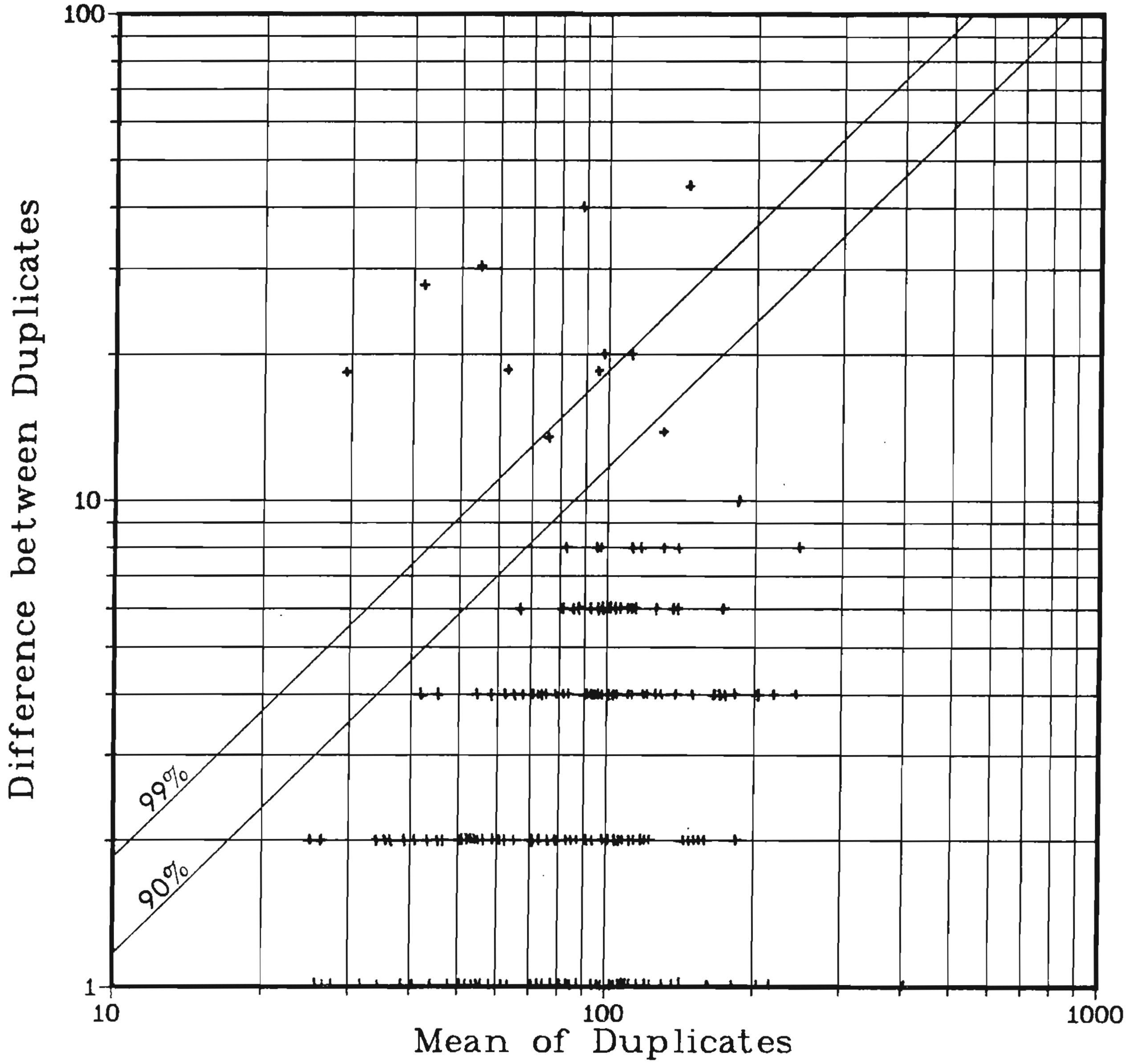


Figure 1. *Example of a Lake Sediment Control Reference quality control plot.*

Precision

Precision is a measure of the repeatability of data. It has nothing to do with absolute accuracy; data may be very precise but quite inaccurate. In most surficial material geochemical surveys, precision has always been of greater concern than accuracy. Precision is routinely assessed by including duplicate samples, i.e., samples collected at the same site or prepared from the same field sample, submitted for analysis with different sample numbers. Again, precision is best monitored graphically, an effective procedure is that proposed by Thompson and Howarth (1978), see Figure 2. In this log-log plot the difference between the duplicate analyses (y-axis) is plotted against their mean (x-axis). Both Thompson and Howarth (1978) and Fletcher (1981) discuss these plots and the placement of control lines on them (Appendix A). It is often sufficient simply to plot the data in the

Analytical Precision Control Chart



Project: Manitoba NGR NTS 64 J, K, N & O

Determination: Zn

Precision: ± 10%

Batch: All

Date: Nov 1975

Notes: Reverse Aqua Regia attack, AA finish

Figure 2. *Example of a Lake Sediment analytical precision quality control plot.*

order of analysis, i.e., time, and look for any inconsistencies. If a batch of 4 or 5 duplicates plot with large differences, relative to their means, out of character with the previous data it would be wise to discuss the problem with the laboratory. Different situations arise whether the duplicates are analytical or sampling-and-analytical. If the duplicates are analytical the cause will likely be in the laboratory, or a gross error in sample preparation. However, if the duplicates are sampling-and-analytical the geochemist has to carefully consider the problem and determine if the source of variation could be at the sampling site or in field procedures.

Quality Control Analyses

The question arises, how frequently should CRs and duplicates be inserted, and how many different CRs of a similar type? It is counter-productive to have suites of more than 3 CRs. The more CRs in a suite the less frequently each gets analyzed, and it is the repeat analyses upon which the quality control procedure relies. As to frequency of insertion, quality control is an overhead, and the answer is in the geologist's or geochemist's hands. A common frequency is 5% for each control type, i.e., a CR and a duplicate in every block of 20. If the rate is lowered, larger batches may need re-analysis if problems are found; on the other hand, if the rate is increased the cost of the overhead goes up. The above recommendation covers only analytical duplicates; field duplicates should also be considered, especially when surveys are being undertaken for precious metals or elements that occur in discrete mineral grains. In these situations the nugget effect comes into play and can introduce a large amount of variability. If resources are limited, it would be better to include a field-and-analytical duplicate and a CR rather than an analytical duplicate and a CR. Ultimately exploration geochemistry is a field science, and it is necessary to know the reliability of the field work.

Field Data Quality Control

Finally, quality control procedures should be applied to field locations and data. The simplest procedure for locations is to plot back the sample points, preferably at the scale of the field maps and compare the two maps. In the case of field data, many DBMS packages permit input values to be checked against ranges or thesauri of valid entries; any out of range or incorrect entries are refused and flagged for attention.

Quality control is a necessary part of good exploration practice. It is essential to be confident that differences observed in data acquired at different times and in different batches are due to real geological and geochemical causes and not variations in procedure. Without that confidence, one may hesitate to recommend additional expenditure on a project, or, one may recommend expenditures on a feature that is later found to be due to procedural variability.

Threshold

The concept of threshold is as old as geochemical prospecting and much has been written about it, both as a concept, and on its estimation. Intimately related to threshold are the concepts of background and anomaly. Threshold is the "line" dividing the two, and a simple working definition is:

"Threshold is the outer limit of background variation".

Note the use of the word "outer" rather than the more traditional "upper". As geochemists have gained access to data for more elements, many significant negative patterns are being recognized, and a pathfinder element negative anomaly is as useful as a positive one. This definition implies that the background data occur as a cloud of points. These are clustered around some "average background", and the concept of a cloud implies that the data also have a spread; they may occur in a tight mass, or more diffusely. These two data attributes are a numerical expression of the geochemical concepts of background level and relief.

It must be stressed that in many cases there is no single threshold in a survey area unless it is restricted to a single geochemical landscape. By geochemical landscape is meant a unique bedrock - surficial environment combination. Each geochemical landscape will have an appropriate threshold that is a function of the geochemical background of the bedrock and the surficial processes that have influenced the element in its journey from the bedrock to the sample medium. The situation in fresh bedrock surveys is simpler as surficial environment is not a factor.

In some instances a single threshold may be used, but this should be proven by studying the data for the different geochemical landscapes and convincing oneself that the different thresholds are so similar that a single value is valid. In general, single thresholds are most often acceptable for elements that occur in the rocks dominantly in their exploitable form(s). For example, gold, platinum metals, tin (cassiterite and stannite), tungsten (scheelite and wolframite) and molybdenum (molybdenite). The situation for base metals, nickel and cobalt is more complex as varying amounts of these elements occur in major rock-forming minerals as well as in potential ore minerals. Therefore, the geochemical patterns observed are due to both rock-forming and mineralizing processes.

Estimation of Threshold, Target Information Available

The estimation of thresholds is a much misunderstood process. There has been a history of misuse of numerical procedures to replace what should be a rational geochemical decision. Hawkes and Webb (1962) stated:

> "A fully dependable value for threshold can come only from an orientation survey in an area of known geology and mineralization, conducted and interpreted by a geologist experienced in geochemical interpretations. There is as yet no real substitute for a competent visual estimate based on a comparison of the geochemical patterns given by a series of tentative threshold values, correlated with the known distribution of metal in the bedrock".

In other words, carry out an orientation survey in and around an area of known mineralization of the type being sought; plot up the data and review it in the light of the known geology (bedrock and surficial); try several threshold levels and select that which best indicates the presence of the mineralization.

This ideal situation is often impossible to satisfy. One may not have access to a good orientation site because of ownership, or one may simply be looking for a deposit type in a geologically favourable area where one of its type has yet to be found. In these situations appropriate data analysis can be of assistance.

To provide an example of the procedures to be described the Zn and Fe data from a small test set of Norwegian stream sediment data will be used. These data have been employed by several authors to compare numerical procedures (Howarth and Sinding-Larsen, 1983; Garrett, 1989a), and consists of data for 25 sites where a suite of 6 elements (Zn, Cu, Pb, Fe, Mn, Cd) were determined; no map scale was provided in the original publication. The stream network can be seen in Figure 3, where the 6-element data are plotted as "trees" (Kleiner and Hartigan, 1981; Garrett, 1983). The salient geochemical features of interpretational importance are, a) Zn-Cd-Cu mineralization on a left bank tributary of the main southwest-northeast flowing stream, as indicated by prominent Zn-Cd-Cu "tree branches" (Fig. 3); and b) a swampy area below the lower lake where "trees" with disproportionately large Fe-Mn "branches" (Fig. 3) mark areas where Fe and Mn enter the main stream in groundwaters and are precipitated as fresh hydroxides capable of adsorbing metal ions.

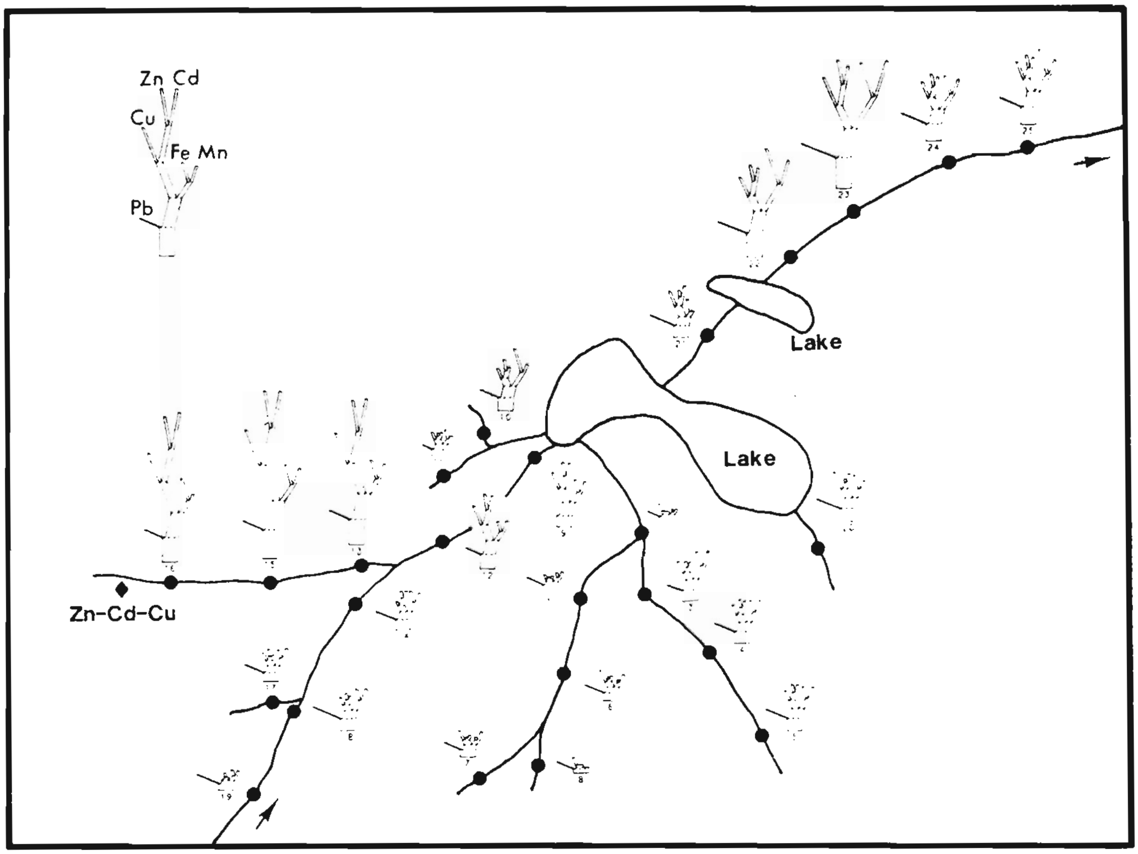


Figure 3. *Norwegian test data (Howarth and Sinding-Larsen, 1983) displayed as Kleiner-Hartigan (1981) trees.*

Although histograms have been used extensively in the past by geochemists, far better ways of presenting data for inspection are available today. The major problems with histograms are two-fold. Firstly, the starting point and bin-widths are arbitrary, and by choosing different values alternate representations of the data are be obtained. Secondly, the behaviour of individual data items is hidden, thus a variety of subtle but important features may be lost to the interpreter.

Two improved procedures are the cumulative probability plot, and the Tukey box-plot (Systat, 1990). Figure 4 demonstrates these plots for Fe. The box of the box-plot defines

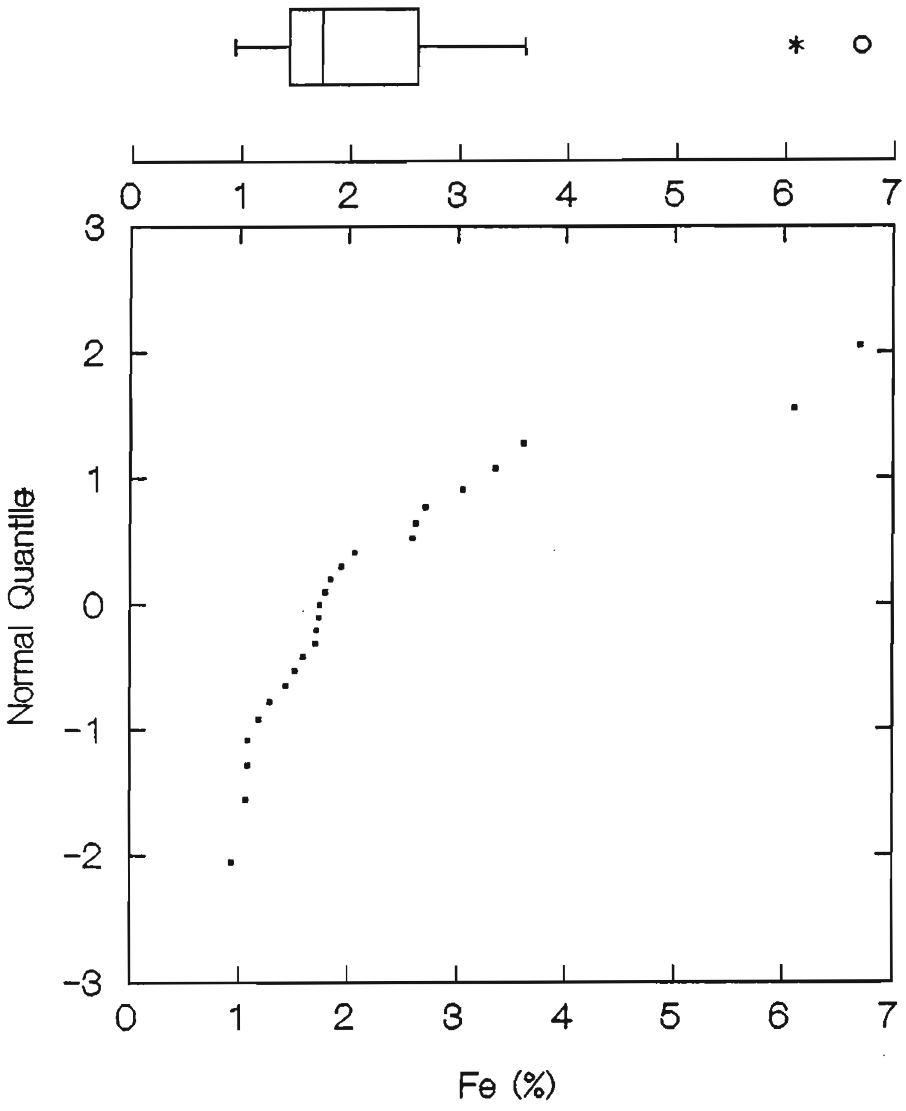


Figure 4. *Norwegian test data, Tukey box-plot and cumulative probability plot for Fe.*

the middle 50 % of the data, the bar is plotted at the data-set median and the box extends to the upper and lower "hinges" of the data. These "hinges" are the medians of the upper and lower halves of the data, and are approximately equal to the 1st and 3rd quartiles and the 75th and 25th percentiles. The difference between the two "hinges" is known as the Hspread or midrange, and the "whiskers" extend from the "hinges" to the upper and lower "fences", which lie (1.5xHspread) beyond the "hinges" or to the maximum or minimum value, whichever comes first. Therefore, if no points plot beyond the whisker ends there are no extreme values. Extreme values are plotted as asterisks up to (3xHspread), and open circles beyond. These extreme values, known as outliers, are worthy of inspection. The box-plot in Figure 4 indicates 2 extreme values. However, the cumulative probability plot reveals more information. The two extreme values are obvious, but of interest to the geochemist

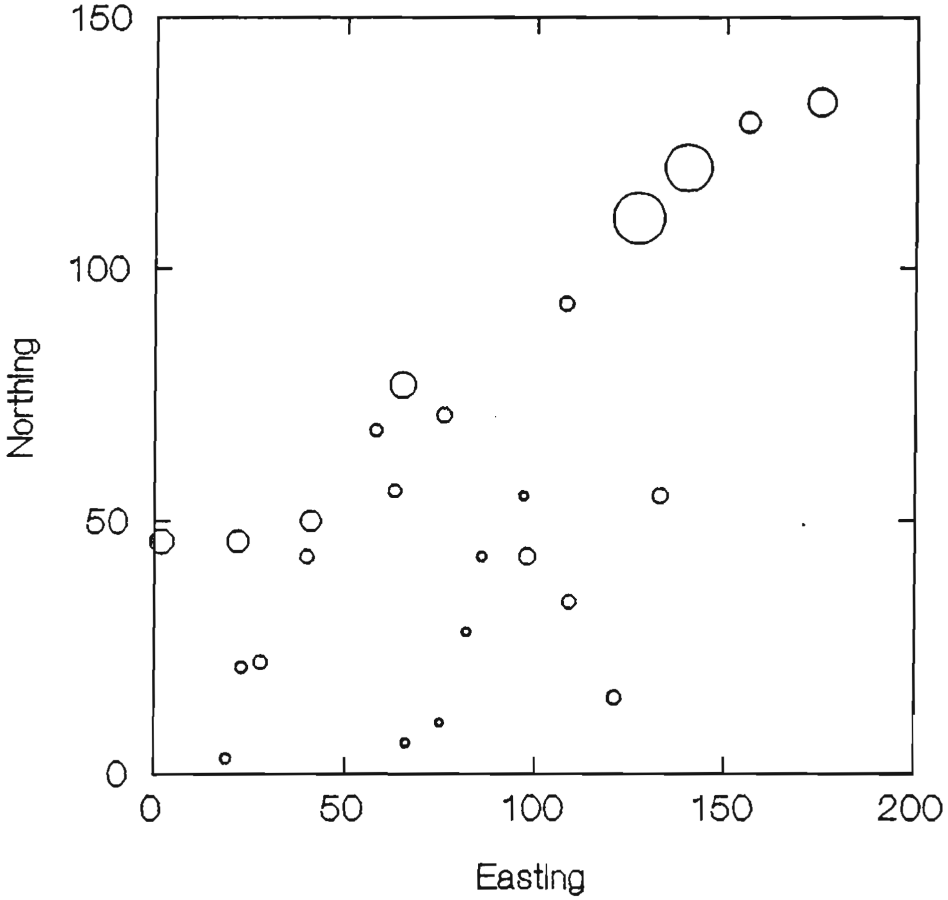


Figure 5. *Norwegian test data, symbol map with circles scaled in proportion to Fe content (see Fig. 3 for drainage pattern).*

should be the group of 6 values occurring between 2.5% and 4% Fe. These data form a small discrete group and may be important to the interpretation. Their presence is hidden in the box-plot, whereas cumulative probability plots permit every data point to be viewed in the context of those surrounding it. Because the data do not fall on a straight line they are not normally distributed; it appears that no single distribution exists. One interpretation is that a complex background situation occurs below 2.5% Fe where there is possibly more than one background population; there are 2 obvious outliers which may be related to the precipitation of fresh Fe hydroxides in the stream bed; and there is the intermediate group of 6 samples which could be related to either the known Zn-Cd-Cu mineralization or fresh hydroxides, or both. The spatial distribution of the Fe data, Figure 5, is depicted by circular symbols whose diameter is proportional to Fe concentration. From Figure 5 it can be seen that the provisional interpretation with a threshold of 2.5% is feasible, the highest Fe occurs in the northeastern area of Fe hydroxide precipitation, and intermediate Fe levels occur on the mineralized tributary.

The data for Zn are presented in Figure 6 on an arithmetic scale and in Figure 7 on a logarithmic scale. The arithmetic box-plot reveals 4 extreme outliers, and the asymmetry of the box indicates a positively skewed distribution; in such cases as this a logarithmic display is worth investigating. The logarithmic plot (Fig. 7) reduces the impact of the outliers and reveals only 3 extreme values. However, the logarithmic cumulative probability plot provides needed scale expansion at lower Zn levels where interest lies around potential threshold values and is far more interesting. The 4 extreme outliers are separated from the bulk of the data by a group of 6 other individuals. Two potential thresholds values are 150 and 70 ppm.

Tukey box-plots and cumulative probability plots serve two different purposes. The box-plot provides a quick graphical summary of the data, like a histogram or stem-and-leaf plot (Systat, 1990); whereas, a cumulative probability plots provides detailed information on the statistical distribution of the data. Possibly the best replacement for the histogram is the box-and-whisker plot (Garrett, 1988); in these, the box remains the same, but the whiskers extend to the 5th and 95th percentiles and minimum and maximum values are represented by asterisks. These plots simply describe the data the way they are with no concern for

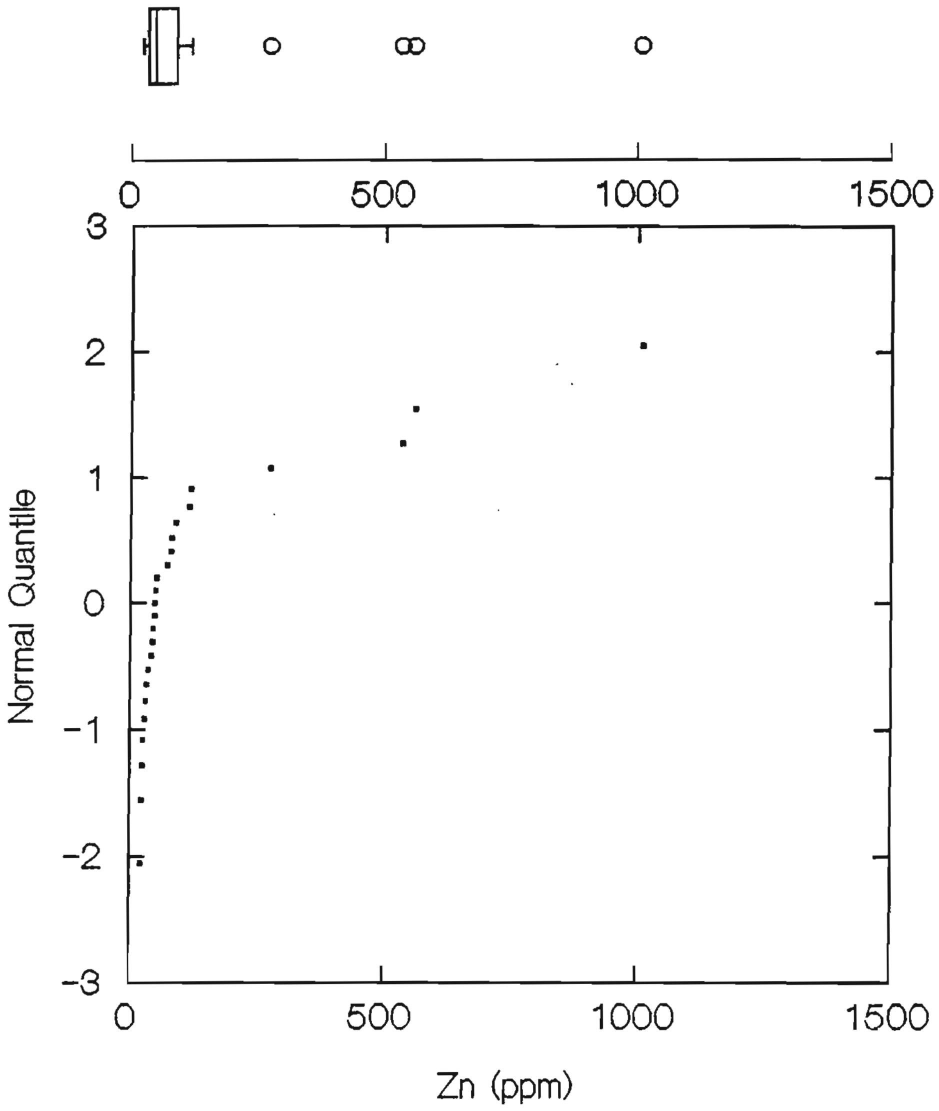


Figure 6. *Norwegian test data, Tukey box-plot and cumulative probability plot for Zn.*

extreme value detection, which can be better achieved using a cumulative probability plot. Unfortunately, Systat, with which this presentation has been illustrated, can not display box-and-whisker plots. Both kinds of box displays may be modified so that a "notch" indicating the 95% confidence bounds around the median replace the median bar (Garrett, 1988; Systat, 1990). These "notched" displays are particularly useful when data for an element have been subdivided by rock-type or geochemical landscape and they are plotted side-by-side. When two "notches" do not overlap there is good evidence for stating that the medians

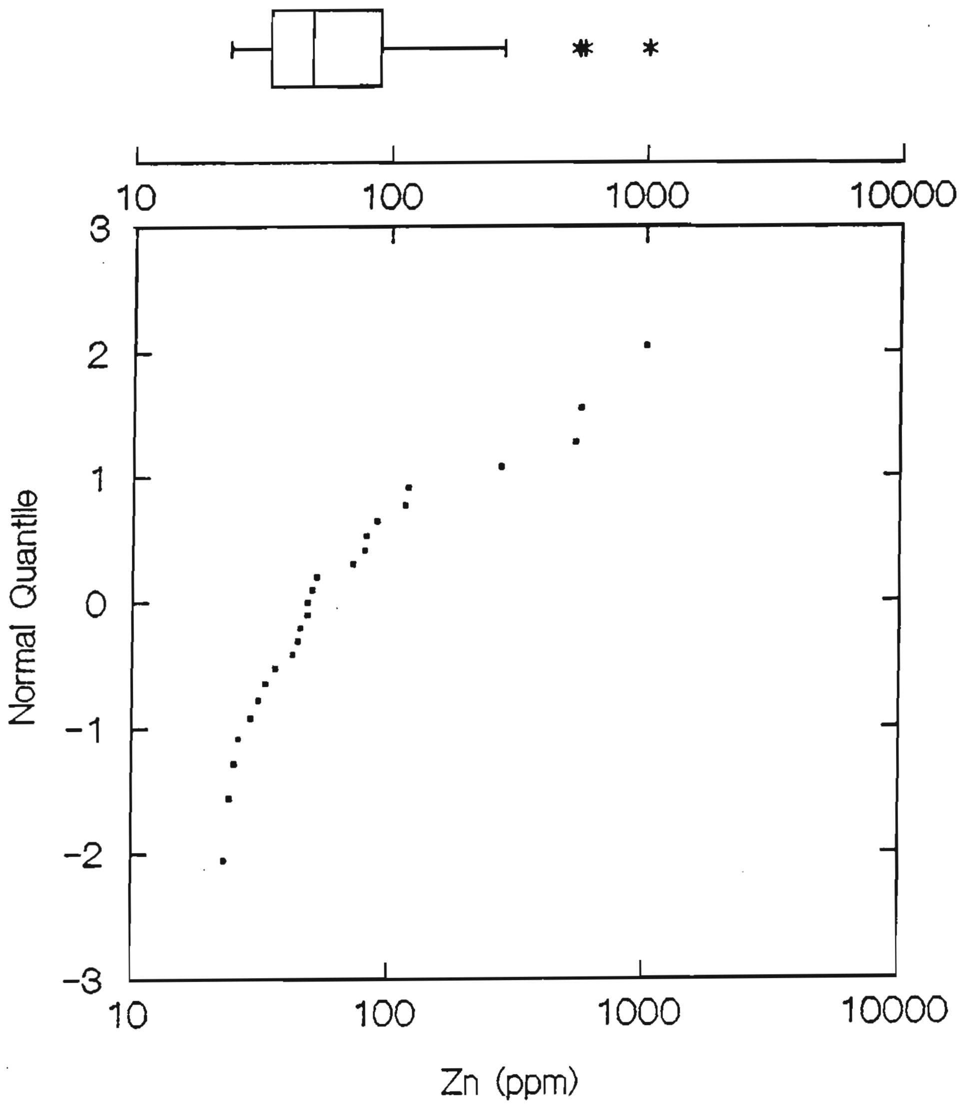


Figure 7. *Norwegian test data, Tukey box-plot and cumulative probability plot for Zn with logarithmic scaling.*

(average backgrounds) of the respective data-sets are significantly different at the 95% confidence level.

To assist an interpretation it is useful to have a list of the data sorted into descending order, Table 1. In addition to the sample number and Zn value the rank has been placed in the table, largest value 25 and lowest value 1, and the fractile computed. The fractile is equal to the "rank minus a half, divided by N" and for large data-sets is essentially the

```
                         ID$           ZN     ZN_RANK     ZN_FRACT

CASE    1               # 15     1010.000      25.000        0.980
CASE    2               # 16      560.000      24.000        0.940
CASE    3               # 13      535.000      23.000        0.900
CASE    4               # 23      274.000      22.000        0.860
CASE    5               # 22      118.000      21.000        0.820
CASE    6               # 12      115.000      20.000        0.780
CASE    7               #  9       89.000      19.000        0.740
CASE    8               # 24       81.000      18.000        0.700
CASE    9               # 25       80.000      17.000        0.660
CASE   10               # 10       72.000      16.000        0.620
CASE   11               #  5       52.000      15.000        0.580
CASE   12               #  4       50.000      14.000        0.540
CASE   13               # 14       48.000      12.500        0.480
CASE   14               # 17       48.000      12.500        0.480
CASE   15               # 21       45.000      11.000        0.420
CASE   16               # 18       44.000      10.000        0.380
CASE   17               #  3       42.000       9.000        0.340
CASE   18               # 19       36.000       8.000        0.300
CASE   19               # 20       33.000       7.000        0.260
CASE   20               # 11       31.000       6.000        0.220
CASE   21               #  6       29.000       5.000        0.180
CASE   22               #  7       26.000       4.000        0.140
CASE   23               #  2       25.000       3.000        0.100
CASE   24               #  1       24.000       2.000        0.060
CASE   25               #  8       23.000       1.000        0.020
```

Table 1. *Norwegian test data, Zn data with ranks and fractiles listed in descending order.*

percentile divided by 100. Fractiles are used in preparing cumulative probability plots, either by hand (see Hoffman, 1986) or by computer software - in which case the user does not see them displayed. They can also be used to estimate the percentiles of a data-set; for example, the 75th percentile lies between ranks 19 and 20, i.e., 89 and 115 ppm. The corresponding fractiles are 0.74 and 0.78, thus the 75th percentile is estimated at a quarter of the interval above 89 ppm, i.e., 95.5 ppm.

In conjunction with the stream network and sample numbers from Figure 3 it can be seen that the 4 highest values above a tentative threshold of 125 ppm Zn are associated with both the Zn-Cd-Cu mineralization (#13, #15, #16) and the precipitation of Fe hydroxides (#23). The lower threshold of 70 ppm pulls in 2 samples from the main stream (#9, #12) that reflect the mineralization, but also 4 additional samples influenced by Fe hydroxide precipitates. The situation is therefore one where it is difficult to discriminate between two non-background processes on the basis of a single element. What is clear is that 70 ppm is a reasonable value for an "outer limit of background variation". The spatial distribution of the Zn data is presented in Figure 8, where symbol diameter is proportional to log Zn. The dispersion train from the Zn-Cd-Cu mineralization is evident, but so is the fact that other samples, whose chemistry is influenced by Fe hydroxide precipitation, exhibit Zn levels of the same order of magnitude.

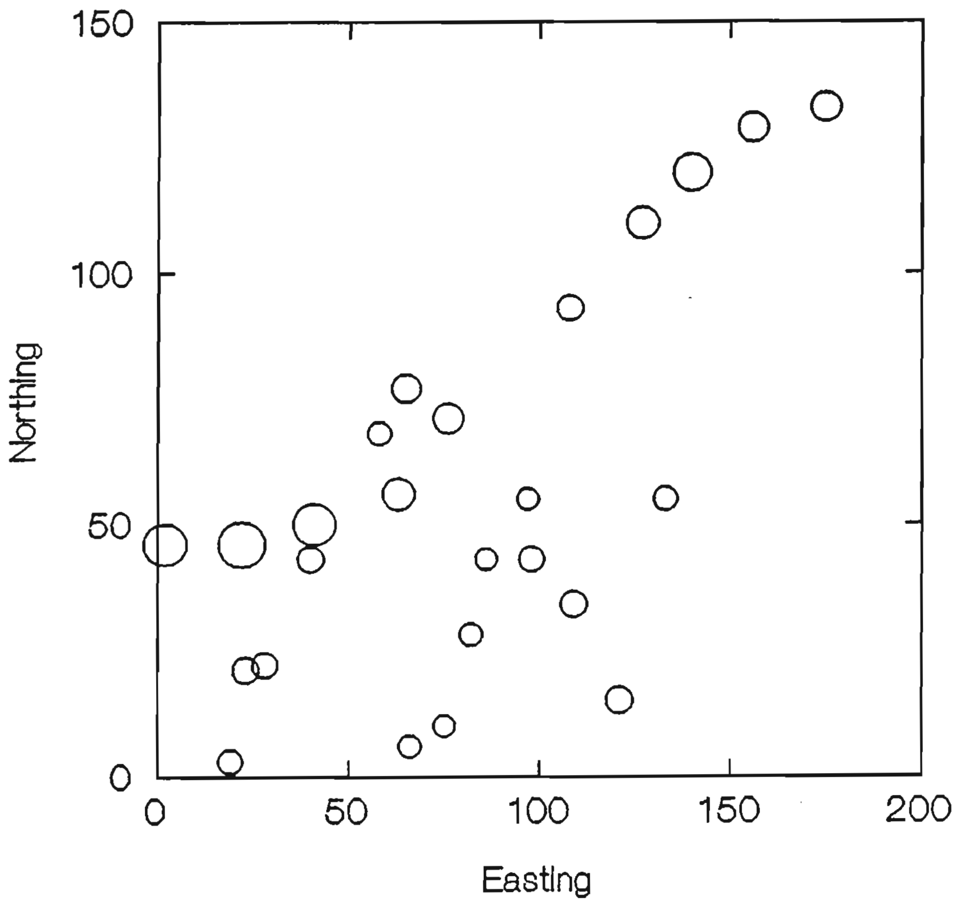


Figure 8. *Norwegian test data, symbol map with circles scaled in proportion to Log Zn content (see Fig. 3 for drainage pattern).*

It might be tempting simply to reject all elevated Zn samples with high Fe from a list of those potentially related to mineralization. Great care has to be taken with such a rule. Very many mineral deposits contain significant amounts of Fe and Mn in ore or gangue minerals, and these will be dispersed away from the deposits with the ore elements. In further "filtering" a list, data for other elements that could occur in a mineral deposit should be reviewed, e.g., Cd, Hg, Sb, As, Te. If any of these occur with the Fe or Mn associated "anomaly" perhaps the source is in fact mineralization, and not co-precipitation in a background environment.

In surveys where many data have been collected from both the background and anomalous populations, more sophisticated aids can be used in selecting thresholds. Work by Sinclair (1976) and Stanley (1987) describe both pencil-and-paper and computer-based procedures for determining the summary statistics (mean and std. deviations) and relative proportions of background and anomalous populations. With this information in hand, thresholds may be selected and possible misclassification effects investigated. For example, if the threshold is set too low an unacceptable number of anomalous false alarms will be identified; if the threshold is set too high, some true anomalies will escape detection.

Estimation of Threshold - No Target Information Available

Firstly, "mean plus two standard deviations" will not be discussed as it is a totally discredited procedure in the computing environment of the 1990s. Its birth in the 1950s and 1960s was a result of computational necessity, not choice (Garrett, 1989b). With today's computers far simpler and better procedures are available.

Much of the misconception about threshold arises from the use of the term threshold in cases where there is no known mineralization on which to base its sensible selection. The term "inspection level" would be far preferable.

Given data-sets in which there are no obvious outliers, i.e., potential anomalies, as revealed by plotting cumulative probability plots it is still wise to check some proportion of the highest or lowest values, depending upon whether accumulation or depletion (alteration) are of interest. Usually some figure between 2% and 10% is common, depending on the data-set size. If a computer package is available that displays percentiles the matter is simple, the 2% and 5% figures correspond to the 98th and 95th percentiles of the data, and the data may be screened on the appropriate value. If such a package is not available the percentiles can be determined from a table of fractiles as demonstrated earlier with Table 1, and the top required percentage of samples can be identified directly from the sorted list.

Geochemists sometimes use rules-of-thumb, such as "4 times background" to establish an inspection level. The computation of a mean background makes assumptions as to underlying statistical distributions, for which sufficient information is often not available. Means are also influenced by high or low value outliers; to reduce the impact of high value outliers geometric means are often used, but in doing so an assumption of lognormality is made that is often not warranted. It is far better to use the median of the data, it is resistant, i.e., unperturbed, by up to almost 50 % outliers or below detection limit values.

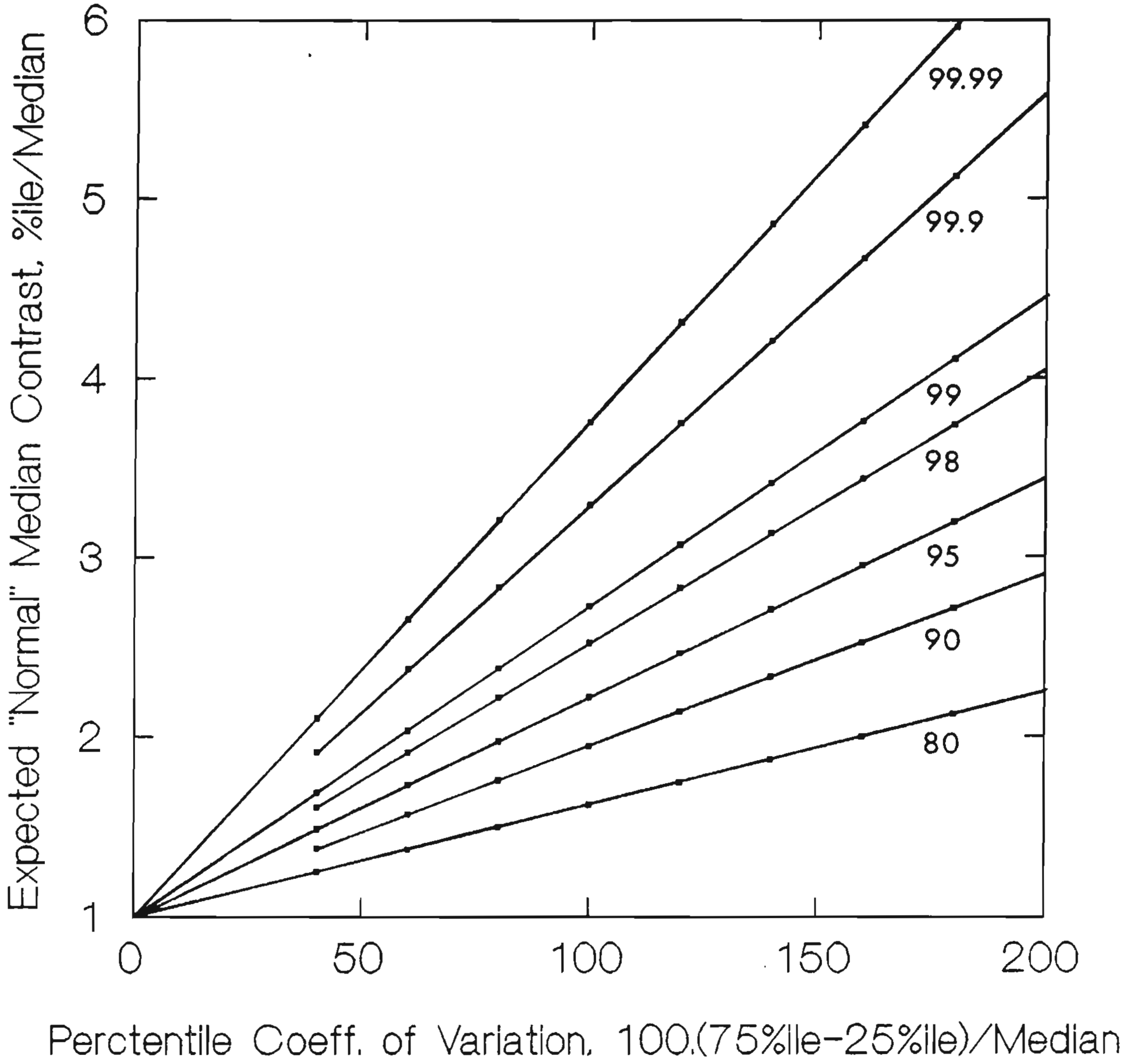


Figure 9. *Plot of Normal median contrasts for differing percentile coefficients of variation.*

Geochemical data are characterized by two properties, level and relief. A simple rule, such as, "greater than 4 times background" does not adequately consider factors affecting relief. A convenient way to measure relief when working with percentiles is to use the inter-quartile range (IQR). The IQR is the difference between the 3rd and 1st quartiles (75th and 25th percentiles), and is very close to the Hspread of Tukey's box-plot. In a normal distribution the standard deviation of a data-set may be estimated by multiplying the IQR by 0.7413. To aid in detecting outliers it is possible to compute for a given IQR that has been standardized like a coefficient of variation, i.e., 100.IQR/Median vs. 100.(Std. Dev.)/Mean, how many times the median a particular percentile should be in the case of a normal distribution (Fig. 9). Thus given a percentile coefficient of variation of 100% the value of the 99th percentile should be 2.7 times the median. If the 99th percentile is less than this it is unlikely that the value is an outlier in terms of the central 50% of the data. If, however, the value was 4 times the median it is higher than would be expected in terms of the central 50% of the data and may merit further attention. As can be seen from Figure 9, almost any data from a single distribution that is 5 or 6 times the median is worthy of further attention.

Plotting Geochemical Maps

Geochemical maps are essential to the interpretation task, but they pose some interesting problems. Firstly, for detailed interpretation, maps with the analytical result plotted at/by the sample site are essential. These, in conjunction with geology and other pertinent maps, and cumulative probability plots are the basis of good single element interpretive practice. They present the spatial and statistical relationships of the survey to the geochemist who then integrates or synthesizes this information so that the relevant exploration decisions can be made. Ideally, all the geoscience maps should be at the same scale; however, in the absence of large format plotting devices this is not always possible.

At a management or decision-making level, maps with a greater graphical impact are desirable. The value maps have all the information, but it is not in a readily communicable form. For this purpose, some type of symbol map (e.g., Fig. 8) helps rapidly convey the required information. A wide number of symbols and glyphs, e.g., "trees", are available in different software packages. One point to remember is that the eye responds to area or "blackness" non-linearly. Therefore, in some instances a square root transform of the linear measure, e.g., symbol diameter, may help improve the graphic impact of a display.

Contour maps have always held an allure to the geochemist. However, contouring involves interpolating values between the known sample sites, and to do this a computer program uses one of many possible algorithms. A single algorithm is capable of producing dissimilar looking maps by simply varying the parameters, e.g., weighting function, grid size, number of nearest neighbours, etc., within a single algorithm (Howarth, 1983a). So, how does one know which algorithm and parameters are the most appropriate? Some would argue that geostatistical procedures are the answer, e.g., kriging; however, even their use involves some degree of subjective decision-making. Moreover, whilst kriging may work well over small areas in a single spatial domain, it may not work so well in a larger area where there are several domains with different spatial properties.

It is important to remember in the cases of stream and lake sediment and water surveys that the computer program assumes that the data point coordinate is at the centre of the area the value represents. This is not the geochemical reality, in such cases a pear is a good analogy, the sample is collected where the stalk exits the pear, but the data represents the geochemistry of the area of the pear "up-dispersion". As a rule-of-thumb, this spatial distortion becomes less objectionable when data are contoured at scales some 4 to 5 times larger than the original survey scale. For example in regional surveys, compiling 1:50,000 scale work at 1:250,000, and 1:250,000 scale work at 1:1 million.

When using a computer contouring package and selecting a particular contouring procedure (algorithm) it is essential to carefully study the map and determine its suitability in relation to the distribution of the data. What does the procedure do where there are large data gaps? If it interpolates geochemically significant "highs" or "lows" it may not be the best choice. Does it allow the user to select uneven contour intervals? A study of the cumulative probability plot for an element may suggest certain natural data break points as contour intervals. A good geochemical contouring package will permit the user to exploit these.

When a geochemist contours data by hand the procedure is unlike that undertaken by the blunt computer software instrument. The activity is not really contouring, sensu stricto, at all. The geochemist integrates such things as hill slope, catchment basin geometry and underlying geology into decisions as to where to put the pencil line. The procedure is more akin to "process clustering"; the geochemist outlines areas, and gradations between them, where different processes, as reflected by the geochemical responses, are dominant. Although it can be argued that hand-drawn maps are subjective and may be prone to undesirable and unrepeatable bias, they are often more valuable for reflecting the interpretive input of the geochemist. If the computer is used to simply plot the values it may well be a worthwhile investment of the geochemist's time to contour the data by hand. The manual procedure forces the geochemist to think about the data and the processes that have brought about its distribution, this is the very heart of interpretation, a task not fulfilled by a computer contoured map.

Lognormality in Exploration Geochemistry and Data Disaggregation

Much has been written about lognormality and the necessity of log-transforming data before carrying out statistical computations in exploration geochemistry. Thirty years of systematic regional geochemistry around the world has begun to shed some light on this topic.

More often than not, logarithmic cumulative probability plots for large geochemical data-sets plot as a straight line. However, this does not necessarily mean that the data are drawn from a lognormal population whose existence is due to a single lognormal geological process. Experience has shown that when these large data-sets are broken into smaller groups on the basis of parent bedrock types and geochemical landscapes, they exhibit distributions that are more normal than lognormal. What is being observed in the large data-sets is the result of mixing many normal and skewed distributions. In some cases the skewed distributions may be related to a mineralizing process and be lognormal. In others, especially those where geochemical dispersion is in the form of mineral grains, Poisson processes are important and these are skewed intermediately between normal and lognormal distributions.

Thus, transforming exploration geochemical data because they are "lognormally distributed" is incorrect. However, there are very good statistical reasons to log transform geochemical data prior to certain statistical analyses, such as homogeneity of variance and the fact that the data are from a percent or ppm closed number system (Garrett, 1989c).

For these reasons it is better not to log transform data during simple statistical procedures other than for reasons of scaling and data presentation, or to conform to the way geochemists think in ratios, i.e., "times" as in "4 times background", rather than additively. A far better procedure is to disaggregate the larger data-sets so that they correspond more closely to individual bedrock or geochemical landscape populations. This means more work as there are more subsets to study, however, the interpretation is simplified as "apples" and "oranges" are not mixed. There has been a tendency in the past to retain geochemical survey data together as a single set during interpretation; this in the author's experience is counter-productive.

A benefit of data disaggregation is that simple aids such as the expected "normal" median contrasts of Figure 9 become more effective, cumulative probability plots become easier to interpret, and the traditional coefficient of variation (CV) is a useful index of mineral potential. Experience in Canada's Uranium Reconnaissance Program showed that when CVs were less than 70% there was virtually no geochemical indication of mineral potential (Garrett et al., 1980); between 70% and 100% interesting geochemical anomalies were likely present; and in excess of 100% interesting geochemical anomalies were always present. This rule-of-thumb provided a quick way of deciding which element-geochemical landscape pairs were likely to be the most productive and worthy of detailed interpretational effort.

To disaggregate data, criteria are needed for separating groups. These largely come from field notes, which should contain such items as dominant source/underlying geology, soil or till colour, etc. There is no avoiding the value of well chosen and pertinent field notes that help elevate mindless "dirt bagging" to sensible exploration geochemistry.

Two Elements at a Time

It is well known in exploration geochemistry that trace element levels may be influenced by the amount of a major component in the sample material. Perhaps three of the best known examples are Fe and Mn hydroxides, and organic carbon; the co-precipitation and adsorption effects these may have play an important role in lake and stream sediment, and soil geochemistry.

The Norwegian test data-set used previously provides an example of one simple procedure that can aid interpretation. Figure 10 is a plot of log transformed Zn, Log_Zn, vs. Fe. Several features are of immediate note: a background population with Fe <2.5% and Zn <70 ppm; a group of 3 highest Zn low Fe (3%) samples; a group of high Zn high Fe (6%) samples; and two groups of higher Zn samples, one with lower Fe (1.7%) than the other (3%). The background data lie on a trend of increasing Zn with Fe. If this trend is extended the high Zn relative to Fe samples would fall above the trend, and the lower Zn relative to Fe samples would fall below the trend. These two groups of samples are those related to the Zn-Cd-Cu mineralization (above) and to Fe hydroxide precipitation (below).

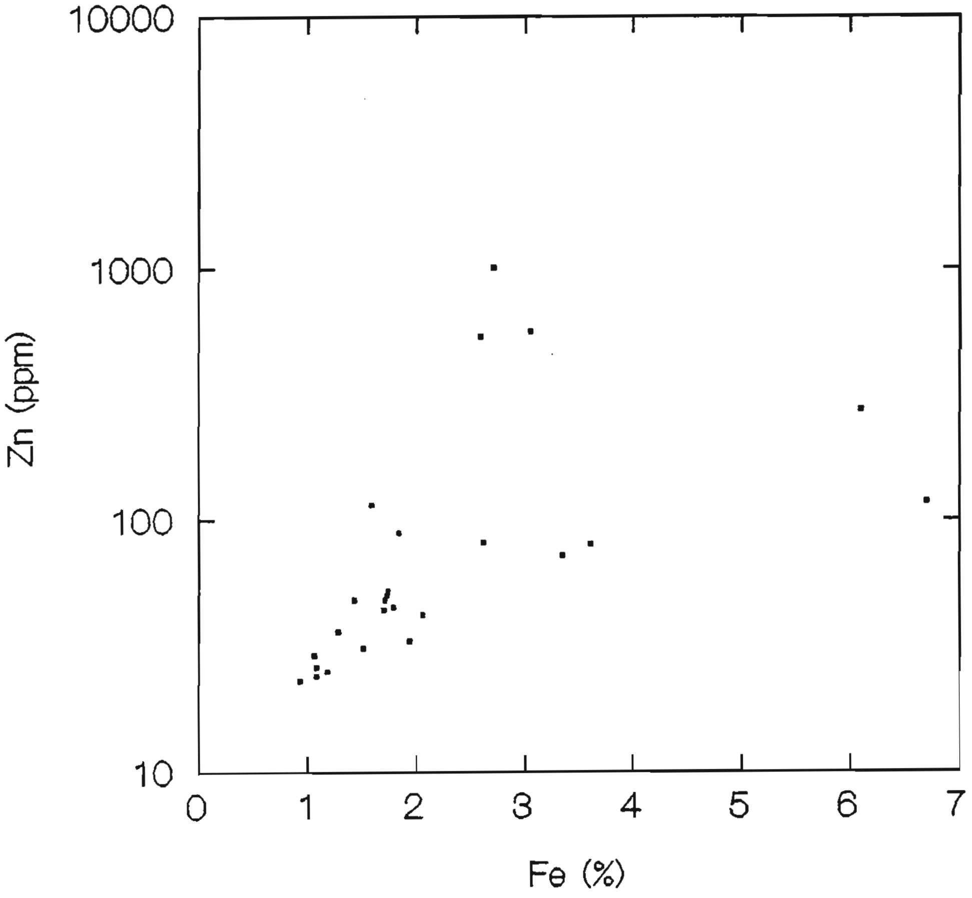


Figure 10. *Norwegian test data, plot of logarithmically scaled Zn vs. Fe (N=25).*

A standard approach to such a problem is to fit a regression line to the data and study the Zn residuals, the differences between the actual values and values computed on the basis of Fe content, instead of the raw Zn data. In building a regression model the assumption of homogeneity of variance requires that the Zn data be logarithmically transformed. The model is usually thought of as one of the background geochemical relationship, but even so it is often erroneously computed using all the data (Table 2). In this case the model accounts for 30.4% of the Log_Zn variability (squared multiple r). The non-background outliers can severely distort the background model and should be removed. This is accomplished by fitting the model to only the Fe <2.5% and Zn <70 ppm data, Figure 11 and Table 3. One result of this outlier removal is that the new background-only model explains 58.5% of the Log_Zn variability, indicating a solid elemental inter-relationship. The background model:

```
DEP VAR:   LOG_ZN        N:         25  MULTIPLE R: 0.551  SQUARED MULTIPLE R: 0.304
ADJUSTED SQUARED MULTIPLE R:   .273      STANDARD ERROR OF ESTIMATE:            0.386

VARIABLE       COEFFICIENT     STD ERROR      STD COEF TOLERANCE      T    P(2 TAIL)

CONSTANT             1.448         0.145         0.000  .             9.972      0.000
FE                   0.173         0.055         0.551  .100E+01      3.166      0.004


                         ANALYSIS OF VARIANCE

SOURCE        SUM-OF-SQUARES   DF  MEAN-SQUARE      F-RATIO        P

REGRESSION             1.493    1        1.493       10.023        0.004
RESIDUAL               3.427   23        0.149


TOTAL OBSERVATIONS:      25


                       ZN          CU          PB          FE          MN

  N OF CASES               25          25          25          25          25
  MINIMUM              23.000       7.000       4.000       0.930     260.000
  MAXIMUM            1010.000     590.000      27.000       6.700    5920.000
  MEAN                139.600      73.600       9.720       2.255     871.200
  STANDARD DEV        231.223     156.352       4.766       1.444    1107.404
  SKEWNESS(G1)          2.685       2.524       2.092       1.942       4.027
  C.V.                  1.656       2.124       0.490       0.640       1.271
  MEDIAN               48.000      17.000       9.000       1.740     590.000
```

Table 2. *Norwegian test data, regression of Log Zn on Fe and summary statistics (N=25).*

$$\text{Log\_Zn} = 1.448 + 0.173\text{Fe}$$

can be used to compute the residuals described above for the whole data-set.

```
DEP VAR:   LOG_ZN       N:        15  MULTIPLE R: 0.765  SQUARED MULTIPLE R: 0.585
ADJUSTED SQUARED MULTIPLE R:    .553     STANDARD ERROR OF ESTIMATE:          0.085

VARIABLE       COEFFICIENT    STD ERROR     STD COEF TOLERANCE     T   P(2 TAIL)

CONSTANT             1.151        0.096        0.000  .           11.951     0.000
FE                   0.271        0.063        0.765  .100E+01     4.277     0.001


                       ANALYSIS OF VARIANCE

SOURCE        SUM-OF-SQUARES   DF  MEAN-SQUARE      F-RATIO        P

REGRESSION           0.132      1        0.132       18.292       0.001
RESIDUAL             0.094     13        0.007


TOTAL OBSERVATIONS:        15


                       ZN          CU          PB          FE          MN

  N OF CASES               15          15          15          15          15
  MINIMUM              23.000       7.000       4.000       0.930     260.000
  MAXIMUM              52.000      27.000      16.000       2.060     910.000
  MEAN                 37.067      12.600       8.667       1.481     515.333
  STANDARD DEV         10.423       5.755       3.063       0.359     185.159
  SKEWNESS(G1)          0.008       1.138       0.743      -0.052       0.406
  C.V.                  0.281       0.457       0.353       0.243       0.359
  MEDIAN               36.000      11.000       8.000       1.510     510.000
```

Table 3. *Norwegian test data, regression of Log Zn on Fe and summary statistics for the core background data subset (N=15).*

This has the effect of exaggerating the residuals for the outliers, making them more obvious. The residuals are standardized by dividing them by the estimation standard error:

$$\text{L\_Zn\_SR} = [\ \text{Log\_Zn} - (1.448 + 0.173\text{Fe})\ ] / 0.386$$

The cumulative probability plot of the standardized residuals is presented in Figure 12. The background population lies in the centre along a reasonably straight line, which indicates that the residuals in this region are close to normally distributed, and that the regression is an acceptable model of the background Log Zn vs. Fe relationship. The anomalous samples lie as two groups of 5, above and below the background data core, in two exaggerated tails, reflecting their different nature from background.

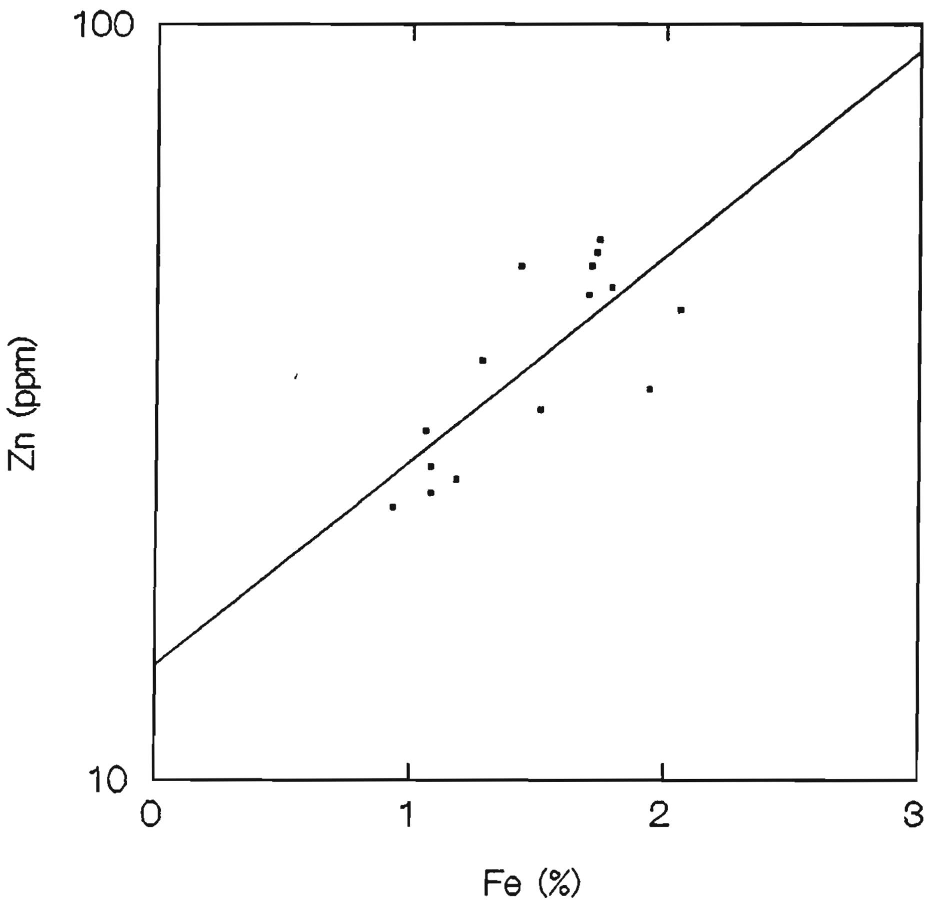


Figure 11. *Norwegian test data, plot of logarithmically scaled Zn vs. Fe for the core background data subset (N=15) with the regression line from Table 3 over-plotted.*

Finally the standardized residuals are plotted as a map in Figure 13. The five-station dispersion train from the Zn-Cd-Cu mineralization shows up as the largest circles (scaled by standardized residual value), and the high Zn due to Fe hydroxide co-precipitation samples plot as average-sized or smaller circles.

This simple regression procedure is successful because the known information on background and potentially anomalous samples has been integrated into the statistical analysis. The lesson here is that all the appropriate available geochemical information must be used in developing statistical models if they are to truly reflect the geochemical reality and be of any real value in aiding the interpretion task of the geochemist.

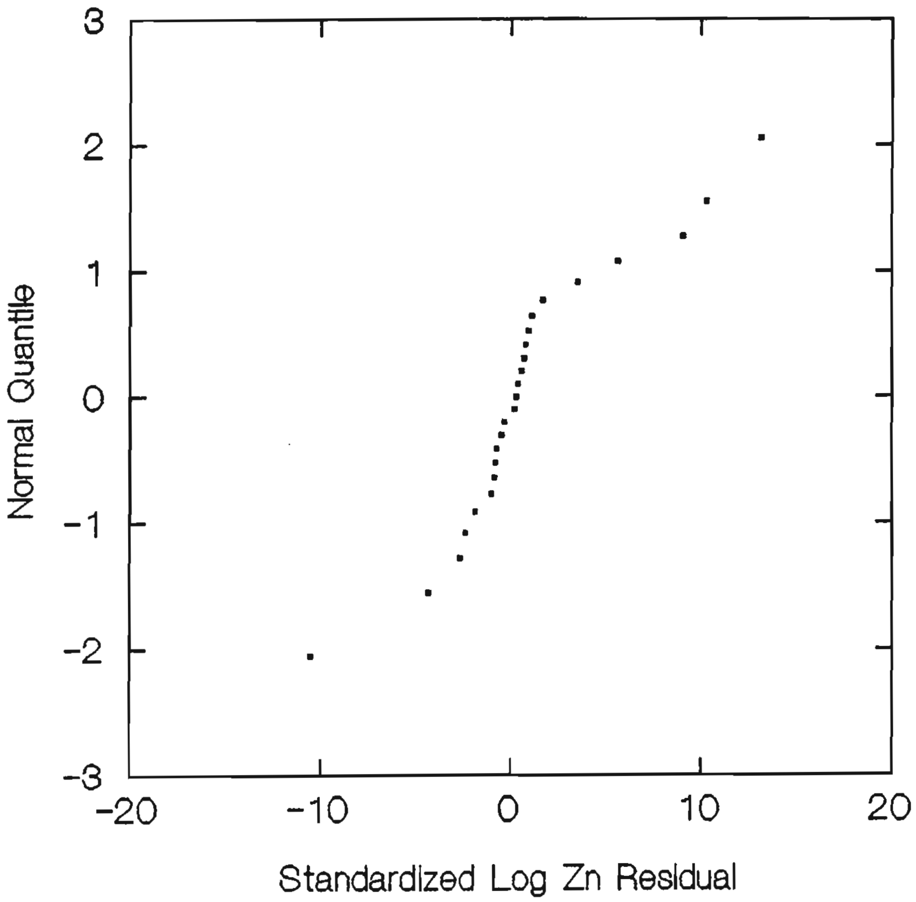


Figure 12. *Norwegian test data, cumulative probability plot of the standardized Log Zn regression residuals for the total data-set (N=25) on the core background data subset (N=15).*

Many Elements at a Time

Today's multi-element geochemistry often gives access to whole suites of data for the ore and pathfinder elements characteristic of a particular deposit type. Geochemists have often used sophisticated multivariate statistical analysis procedures to work with such data-sets. However, the application of these is not without serious problems due to the presence of the very anomalous samples in the data-set that are being sought distorting the linear statistical models (Garrett, 1989a).

A simple but effective way of combining elemental suites into a single number or index for map plotting is weighted sums (Garrett et al., 1980; Appendix B). What is more, the geochemist remains firmly in control of the elements included in the weighted sums

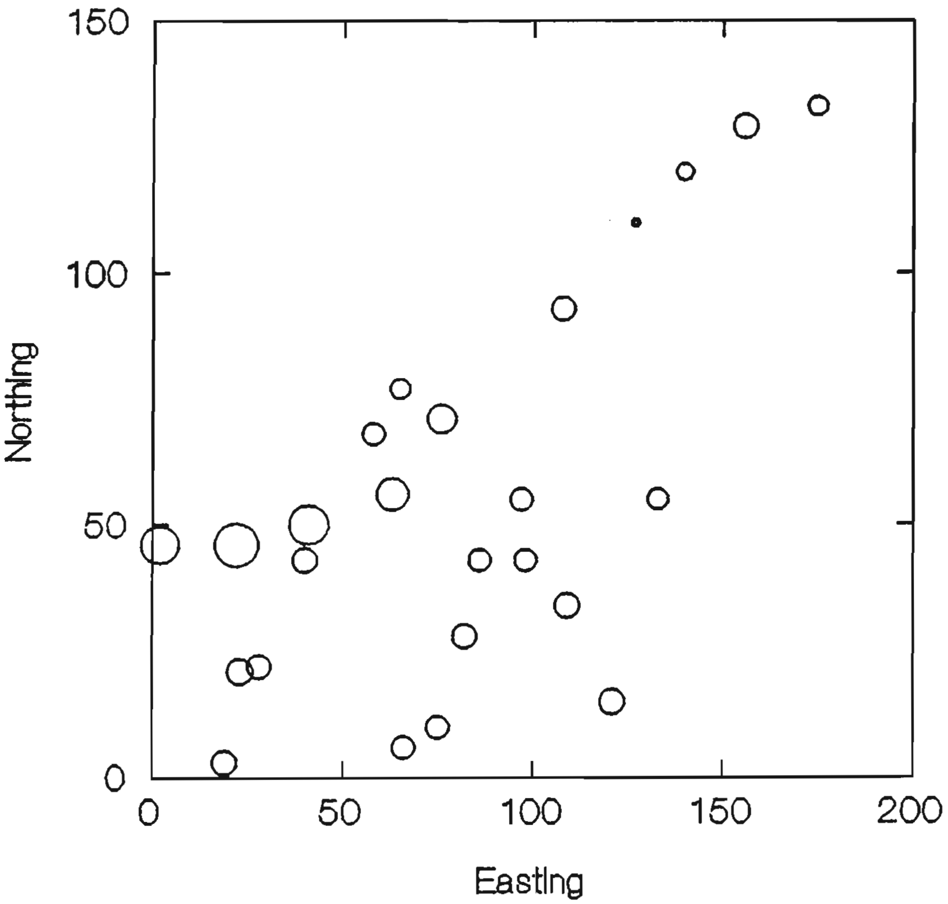


Figure 13. *Norwegian test data, symbol map with circles scaled in proportion to the standardized Log Zn regression residual (see Fig. 3 for drainage pattern).*

model and their relative contributions. In effect, weighted sums are "geochemist-controlled" factor scores, where the factor loadings (weights) are based on the geochemist's knowledge of geochemistry and metallogeny.

Using the Norwegian data example Cu, Zn and Cd can be combined into a single weighted sum. Firstly, the relative importance of the elements has to be defined; as Cu is less effected by Fe hydroxide precipitation than Zn and Cd it will be given an importance of 2 relative to importances of 1 for Zn and Cd. Weights need not necessarily be positive, so the Fe hydroxide effect can be reduced by also giving Fe a relative importance of 1 but making the weight negative. Expressing the relative importances as weights that sum to 1, weights of 0.4 for Cu, and 0.2 for Zn, Cd and Fe are obtained. These weights then have to be re-expressed so that the sum of their squares is equal to 1. This is achieved by dividing each weight by the square root of the sum of the squares of the 4 weights, i.e., 0.529, by which we obtain Cu - 0.756, and Zn, Cd and Fe - 0.378.

The weights are applied to the variables after they have been standardized with respect to their geochemical backgrounds. Strictly speaking this standardization should use the means and standard deviations. However, experience has shown that weighted sums can be made more effective by using estimates of these statistical parameters that are resistant to the very outliers and patterns that are the objects of interest. This is easily accomplished by using the median for the mean, and estimating the standard deviation as 0.7413 times the interquartile range (Hspread). Again, if there are obvious outliers it is best to remove these before determining the median and interquartile range. This is particularly important for small data-sets; if more than 25% outliers, potential anomalies, exist they may distort the estimates of the 1st or 3rd quartile if they all occur low or high respectively.

In order to demonstrate the effectiveness of this procedure the initial removal of obvious outliers has been omitted, resulting in the following table (statistics by Systat, 1990):

	Cu	Zn	Cd	Fe
Relative Importance	2	1	1	1
Weight	0.4	0.2	0.2	0.2
Normalized Weight	0.756	0.378	0.378	-0.378
Median	17	48	0.6	1.74
Upper Hinge	32	89	1.0	2.62
Lower Hinge	10	33	0.4	1.43
Hspread (approx. IQR)	22	56	0.6	1.19
Est. Std. Dev.	16.3	41.5	0.445	0.882

The cumulative probability plot of the weighted sum (Figure 14) shows the exaggerated high value tail resulting from the procedure. The spatial distribution is presented in Figure 15. The samples on the mineralized tributary are clearly the most "anomalous", and the two down dispersion samples from the main stream are discernable above background. The worst Fe hydroxide associated false anomaly is still recognizable - but at a high background rather than anomalous level.

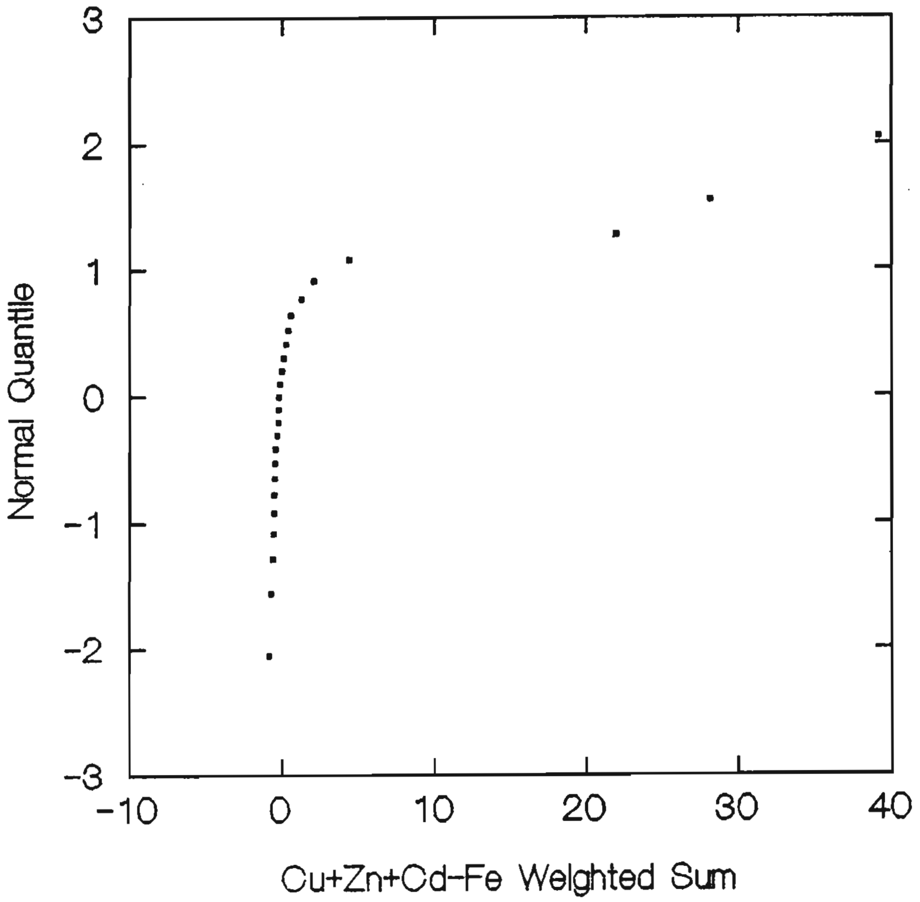


Figure 14. *Norwegian test data, cumulative probability plot for the Cu+Zn+Cd-Fe weighted sum.*

In comparison with principal components or factor analysis this procedure is simple and fully under the geochemist's control. It provides a very useful tool for combining multi-element analytical data into single values that relate directly to geochemical and metallogenic processes known to the interpreter.

A MAD Strategy

In the previous sections several tools have been presented to assist the geologist and geochemist in interpreting data. However, just having a tool-box is not enough; the question is, how to use the tools and put together an interpretation? Can a strategy for Management, Analysis and Display (MAD) be developed?

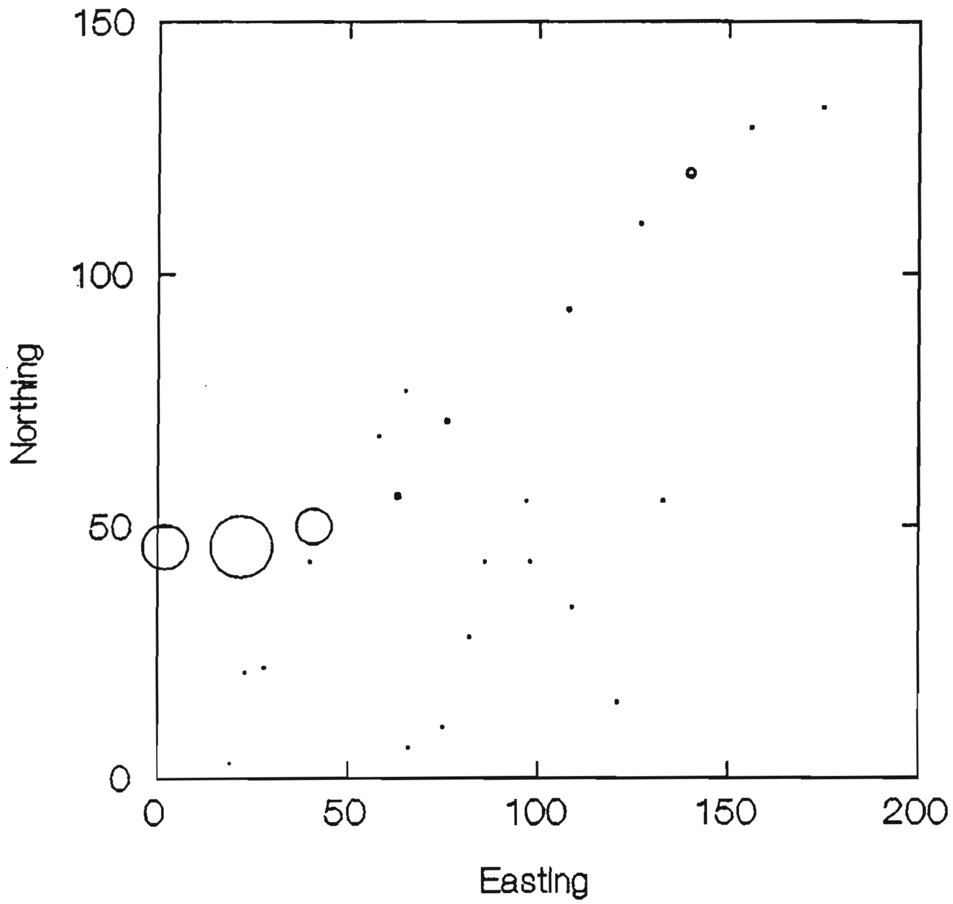


Figure 15. *Norwegian test data, symbol map with circles scaled in proportion to the Cu+Zn+Cd-Fe weighted sum.*

There is no escaping the requirement for quality control checking. One may be able to get away with poor practice for some time, but sooner or later a situation will arise that makes it impossible to take the required exploration decisions. The most common is probably a shift in analytical results between batches or years, and this is so easily detected by the inclusion of a relatively small number of Control Reference samples. Getting the expensively-acquired data into a machine processible form then permits its thorough inspection, and tends to ensure its preservation beyond the life of the survey.

The philosophy of interpretation presented is one of disaggregation. There is absolutely no geological reason to keep a survey data-set as a single entity during interpretation and statistical analysis. The task of establishing thresholds or inspection levels is made significantly easier if data are broken down into subsets that relate to separate geological or geochemical landscape entities. Although the same procedures will be repeated for each subset, interpretation is more efficient because the data are now drawn from single dominant populations. This facilitates the task of outlier and anomaly recognition, and detection of subtle anomalies that have been transported further from source or are related to less well-developed, or deeply buried, mineralization. The total sum of time spent on the different subsets will be less than the time spent on a large complex aggregate data-set for the same depth of interpretation.

There is a statistical, as well as geochemical, reason behind this approach. Reliable statistical estimates require large data-sets, yet extreme values, outliers and geochemical anomalies are rare events by definition, if not reality. Therefore, estimating the statistical parameters of the outliers is a difficult, if not impossible, task. Especially if the individuals in what appears to be a single group of outliers are in fact drawn from several anomalous poulations, each with different statistical parameters. Far better to build on strength, there are an abundance of background data; thus it is wiser to carefully define the limits of the background population(s) and then focus attention on those individuals that do not fit the background model(s). It is these outliers that will be the most interesting geochemical anomalies.

Disaggregation requires either that there are some geochemical data that facilitate splitting the initial data-set, or that appropriate field observations have been made to permit subdivision. Obviously, field observations are recorded in the field prior to analysis. The selection of parameters to record therefore requires thought and planning before the survey starts. There is far more to exploration geochemistry than just going off and putting "dirt in the bag". Surveys are undertaken to meet some objective, usually to aid in taking an exploration decision. If surveys are going to be effective, the various phenomena that may affect the background levels and dispersion processes need to be anticipated by the geologist or geochemist and field observations made that permit the recognition of these and the subsequent appropriate subdivision of the data.

The process of plotting maps, looking at the cumulative probability plots and subdividing the data into easily interpretable units is iterative. First geochemical value maps must be plotted and the probability plots inspected. After that, the decision to subdivide on a spatial, field data or geochemical data basis must be taken, followed by appropriate action and re-inspection of the several parts. Once a subset can be split off and the factors controlling its distribution identified, there is no need to keep it with the remaining data still to be interpreted, for its presence just confuses the situation. The interpretive task is to subdivide survey data into a number of subsets, each with a specific geochemical control; it can be likened to peeling an onion, and if done properly need not be a tearful exercise! During this exploratory data analysis, thresholds or inspection levels are established for each group that warrants its own separate treatment. The analysis may well show that separate levels are not necessary, however, this has to be proven or the more subtle anomalies related to more distant or deeply-buried mineralization will not be recognized. What can be more embarrassing than to write an area off, walk away from it, then a year later have another geochemist come in and find significant mineralization that was subtlely reflected in your earlier data - but you missed it.

During the interpretation for a particular element those remaining must not be ignored, even if they are not formally involved through computation. One of the great advantages of geochemistry is that it is possible to work with suites of elements that respond to ore-forming and other geochemical processes. A decision in a borderline situation can often be made with greater confidence after reviewing other elemental data to determine if the overall geochemical pattern or signature "matches" the suspected process.

In many cases it is useful to look at pairs of elements that have a geochemical relationship. However, care has to be taken not to knowingly mix data from different populations. For example, in an area of felsic and intermediate igneous rocks Zn levels would be expected to decrease as Pb increased in the transition from a dark-mineral rich rock to one containing K-feldspar phenocrysts. In the same area, base-metal sulphide occurrences could cause Zn and Pb levels both to rise. In this case there are two trends in the data, a background antipathetic trend related to rock-forming minerals and crystal chemistry, and a sympathetic association related to a sulphide mineral-forming process. With the exception of obvious high level Zn-Pb anomalies the result of superimposing the two data-sets is to mix antipathetic and sympathetic relationships on top of each other and come up with a hard-to-interpret shot-gun blast of points on a Zn-Pb plot. A useful tool in such cases may be to work with a ratio, Zn/Pb (other useful examples are Ni/Cu, Ni/Co and Cu/Zn), this may help focus attention on individuals that are "off the main trend" and can sometimes even be improved by plotting the ratio against one of the variables, e.g., Ni/Cu vs. Cu. All the time the outliers, the "different samples" are being sought that differ from the main mass of the data. These are the individuals that have to be explained, possibly in terms of mineral potential.

There is a role for regression modelling, but not as a routine procedure. Where there are good reasons for believing that the threshold or inspection level may be a function of another measured variable, e.g., Fe, Mn or organic carbon, a regression model is an elegant and effective approach. But care must be taken to ensure that the data are as "clean" as possible. The Zn-Pb example above is a case in point. If there are just a few sulphide-related samples hidden in the data-set and they do not badly distort the background regression model they will be found. But as the proportion of sulphide-related data increases the statistical model will deteriorate as the clear background data relationship is obscured, and the exercise will be a failure. Where good prior geochemical and metallogenic models exist the technique of weighted sums can help distil a multi-element phenomenon down to a single mappable value.

During this whole exercise two sets of maps are required. The key value map on which the interpretation is built up, and on which geochemical domains and landscapes are plotted; and many throw-away symbol type plots, often of ratios, residuals or weighted sums. The scanning of these "ideas" symbol maps helps decide which of the new numbers really aid the interpretation. One or more of these may play a critical role in a final report when they clearly define the areas of highest mineral potential.

To conclude, well planned statistical analysis driven by geochemical considerations can reveal useful facts about a data-set, and help identify that small proportion of the samples related to mineral occurrences.

Advanced Techniques

Many papers and books have been written on the application of computers and statistics to aiding the interpretation of exploration geochemical data, for example, Howarth and Martin, 1979; Garrett et al., 1980; Howarth, 1983b; Howarth and Garrett, 1986; Garrett, 1989c; and Agterberg and Bonham-Carter, 1990. These publications provide reviews and references for those wishing to pursue these matters further.

Much of the innovative work being carried out today is in three areas. Firstly, the application of Geographic Information Systems (GIS) to geochemical problems and the integration of exploration data. GISs are still expensive hardware and software purchases, however prices have dropped significantly in the last 10 years, and there is no reason to suspect that they will not continue to do so. Secondly, enormous amounts of multi-element data are being produced by the use of INAA and ICP-ES laboratory procedures. The thorough screening of these data, and the search for more subtle outliers and anomalies requires the use of multivariate statistical procedures. It is expected that current work in this field will eventually produce relatively easy-to-use software for general application in geochemical exploration. Lastly, but not least, the advent of cheap colour graphics devices is permitting colour maps and plots to be used effectively in conveying the interpretations developed through computer usage. Spatial filtering procedures are being used to help recognize locally "anomalous" situations that may be indicative of mineral potential.

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APPENDIX A

Plotting Control Lines for Duplicate Analysis Quality Control Charts

The precision at some concentration level c, P_c, is defined via the coefficient of variation, cv%, at the 2 standard deviation level as an approximation for the 95% confidence level, i.e.,

$$P_c = \pm 2 \, . \, 100.s_c/c$$

$$P_c = \pm \text{cv\%} \, . \, 2$$

where s_c is the standard deviation of n replicate analyses, x_i, at the average concentration c, i.e.,

$$s_c = \sqrt{(1/[n-1])\Sigma_{i=1}^{n}(x_i-c)^2}$$

Now let M_d be the median value of the difference between 2 analyses at the concentration c, then:

$$M_d = k_\alpha \, . \, 2^{0.5} \, . \, s_c$$

$$M_d = k_\alpha \, . \, 2^{0.5} \, . \, P_c.c/200$$

where k_α is the normal deviate for the α percentile of the half normal distribution.

Values of M_d for various P_c, where c is 100

α	k_α	±5%	±10%	±15%	±20%
50	0.6745	2.38	4.77	7.15	9.54
75	1.1504	4.07	8.13	12.2	16.3
90	1.6449	5.82	11.6	17.4	23.3
95	1.9600	6.93	13.9	20.8	27.7
99	2.5758	9.11	18.2	27.3	36.4

For any row of the table the entries are additive. Therefore, to obtain the value of M_d at ±25% add the row entries for ±10% and ±15%, or for M_d at ±30% multiply the row entry for ±15% by 2. For c equal to 10 divide the table entries by 10, and for c equal to 1000 multiply the entries by 10.

When using the control charts, if the line corresponding to α equal to the 95th percentile is plotted one would expect only 5% of the differences to be "above the line". If more than 5% fall above the line the precision of the analyses is worse than that for which the chart is plotted. Conversely, if less than 5% plot "above the line" the precision is better than expected.

APPENDIX B

Computation of Weighted Sums

Weighted sum variables have a mean of 0 and a standard deviation of 1, therefore they may be used like standard or normalized scores. They are in fact a multi-variable normal score that can be likened to a principal component or factor score from multivariate statistics. The major difference, however, is that the user chooses the weights, relative importances, for each variable according to some geochemical and/or metallogenic model.

Relative importances, r_j, are defined in ratio form, e.g., 2:1:3:1, for the m variables. The individual, j-th of m, importances are converted to weights that sum to 1, w_j, as follows:

$$w_j = r_j \cdot (\Sigma_{j=1}^{m} r_j)^{-1}$$

which for the example yields 0.286, 0.143, 0.428 and 0.143. A requirement of the weighted sums procedure is that the squares of the final weights, coefficients a_j, sum to 1. This is achieved by the following transformation:

$$a_j = w_j \cdot (\Sigma_{j=1}^{m} w_j^2)^{-\frac{1}{2}}$$

which for the example yields coefficients of 0.517, 0.259, 0.774 and 0.259.

Computation of the normal scores requires a mean, $\bar{x}_j$, and standard deviation, s_j, for each, j-th, of the m variables. These summary statistics should represent the background population within the data-set. Therefore, the use of robust estimators, $\bar{x}_j^*$ and s_j^*, that are resistant to the presence of the outliers, potential anomalies, being sought is recommended, e.g., weighted or trimmed statistics. A simple and practical procedure that has been found effective is to use the median as an estimator for the mean, and to estimate the standard deviation from the interquartile range (IQR), therefore:

$\bar{x}_j^* = M$, and

$s_j^* = 0.7413 \cdot IQR$

The interquartile range is the difference between the 3rd and 1st quartiles (75th and 25th percentiles), and is approximately equal to Hspread or the Midrange. For large data-sets the high resistance of the median and interquartile range to outliers, up to 50% and 25% outliers respectively, makes initial trimming, i.e., rejection of obvious and extreme outliers, unnecessary. However, the user should always check to see if better background estimators can be obtained by using trimming prior to determining the median and IQR.

The normal score for the j-th variable of the i-th case in the data-set, z_{ij}, may then be computed as follows:

$$z_{ij} = (x_{ij}-\bar{x}^*_j)/s^*_j$$

and the weighted sum for the i-th case in the data-set, ws_i, computed as:

$$ws_i = \Sigma^m_{j=1} a_j z_{ij}$$

GEOLOGICAL SURVEY OF CANADA
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