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Black shale as an environmental hazard: a review of black shales in Canada

Ingrid Reichenbach

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Black Shale as an Environmental Hazard: A Review of Black Shales in Canada

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FOREWORD

In 1990, under a Memorandum of Understanding between the Geological Survey of Canada (GSC) and the Geological Survey of Prague (GSP), an agreement was made to undertake studies related to environmental geochemistry. One topic that warranted investigation was that of 'black shale as a natural hazard'. The complex assemblage of chemical elements that black shales commonly host has a significant bearing on the environment, and ultimately on the quality of human health.

The first step for the GSC was to assemble the information that was already available. It became apparent that such information is widely scattered through the literature, and that there was a requirement for synthesis as well as compilation. Consequently, a contract was let for a consultant (Ingrid Reichenbach) to undertake this task and provide some recommendations for further research. Her report, submitted in 1992, has brought together into one volume a valuable database on black shales in Canada, and has outlined the aqueous geochemistry of those elements commonly enriched in, and readily mobilized from, black shales. This report will provide the foundation for future studies on the environmental problems that may be related to the natural occurrence of black shales and to the problems that may arise from their disruption.

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ABSTRACT

Black shales are known to be important reservoirs of carbon, sulphur and heavy metals. As a result, they are potentially both mineral and energy resources, and environmental hazards. This report comprises the compilation of a database on black shales in Canada. The database includes: 1) a bibliography of over 200 entries, 2) a bedrock compilation map of black shale deposits in Canada (by province), 3) a tabulation of salient features of black shale deposits in Canada, and 4) general data on the speciation, mobility and toxicity of trace metals/metalloids present in black shales (i.e., Ag, As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, U, V, and Zn). In addition to the database, this report includes several case studies of environmental impacts attributed to black shales, for example, acid drainage at Halifax Airport (Halifax, Nova Scotia) and selenium contamination of soil and water (San Joaquin Valley, California).

The term black shale includes a wide variety of sediments and sedimentary rocks. The definition proposed by members of the U.S. Working Group of the IGCP Project 254 for a "black shale" is "a dark-coloured (grey or black), fine-grained (silt sized or finer), laminated sedimentary rock that generally is argillaceous and contains appreciable carbon (>0.5 wt. %)." Their proposed definition of a "metalliferous black shale" is " a black shale that is enriched in any given metal by a factor of 2X ... relative to the U.S. Geological Survey Standard SDO-1". Their definitions were used rather loosely in compiling this database because geochemical data was rarely available.

Black shales, ranging in age from Archean to Cretaceous, occur throughout Canada. They have been mapped in varying degrees of detail, sometimes occurring on maps as separate units, but most often included with other rock types within a larger map unit. A compilation map of black shale deposits in Canada is contained in this report, and was compiled from readily available federal and provincial geological maps, theses, and scientific papers and reports.

This report concludes with several recommendations for further study. Perhaps one of the most important is the need for further research on chemical speciation studies of those trace elements most likely to impact the environment adversely such as mercury, arsenic, and selenium (based on factors such as mobility and toxicity).

1. INTRODUCTION

1.1 BACKGROUND

Black shales are known to be important reservoirs of carbon, sulphur and heavy metals. As a result, they are potentially both mineral and energy resources, and environmental hazards. The importance of such shales prompted the formation of the International Geological Correlation Program (IGCP) Project 254, Metalliferous Black Shales and Related Ore Deposits, in 1987. More recently, collaborative research on "Black Shale as an Environmental Hazard" was begun as a joint project among the Geological Survey of Canada, the Czechoslovakian Geological Survey, and the British Geological Survey. This report was prepared for the Geological Survey of Canada as part of the "Black Shale as an Environmental Hazard" Project.

1.2 SCOPE

This report comprises a review of databases on black shales in Canada. It includes:

1) a bibliography of over 200 entries, including: a comprehensive selection of references on black shale deposits in Canada; overview and frequently referenced papers on the origin and geochemistry of black shales worldwide; and references on the aqueous geochemistry of the trace metals/metalloids of environmental concern that are present in black shale;

2) a bedrock compilation map of Canada - by province - delineating major black shale deposits, with emphasis on those occurring in populated areas;

3) a tabulation of salient features of black shales present in Canada; and

4) general data on the speciation, mobility and toxicity of trace metals/metalloids present in black shales.

In addition to the above, this report includes several case studies of environmental impacts attributed to black shales and concludes with recommendations for further studies.

2. WHAT IS A BLACK SHALE?

2.1 DEFINITION

> "A great variety of rocks are designated as black shales. Their composition(s) and origins differ greatly. For instance, they can be bituminous, phosphatic, carbonate-free or -rich, high or low in trace metals, sulfidic to a point of even being considered ore, and sometimes surprisingly low in carbon when compared to the average shale. With respect to (the) environment of deposition, a black shale can be of freshwater, brackish, marine or hypersaline origin, in other words, black shales can virtually be found in all aquatic habitats. They may contain abundant macro- and microfossils, or may be fossil-free. Black shales may be laid down in the shallow epicontinental sea, along continental margins, or in deep oceans and lakes. They can be formed in situ, or be allochthonous in nature. Their organic matter can be mature or immature...'Why do we group such a diverse group of sediments together which obviously only share one property, namely that of being black?'
>
> The answer is: all black shales are linked directly or indirectly to high organic activity and the cycling of biogeochemical elements, most notably carbon, nitrogen, phosphorous, sulphur, oxygen plus heavy metals such as iron, molybdenum, vanadium, and uranium" (Degens et al., 1986, as quoted in Huyck, 1990).

Because the term black shale includes such a wide variety of sediments and sedimentary rocks, it is difficult to find a concise, yet inclusive definition. The definition proposed by members of the U.S. Working Group of the IGCP Project 254 for a "black shale" is "a dark-coloured (grey or black), fine-grained (silt sized or finer), laminated sedimentary rock that generally is argillaceous and contains appreciable carbon (>0.5 wt.%)." Their proposed definition of a "metalliferous black shale" is "a black shale that is enriched in any given metal by a factor of 2X (except for beryllium, cobalt, molybdenum, and uranium, for which 1X is sufficient) relative to the U.S. Geological Survey Standard SDO-1" (Huyck, 1990).

For the purposes of compiling this database on black shales in Canada, the above definition applies as far as "a dark-coloured..., fine-grained...sedimentary rock that generally is argillaceous". However, this part of the definition alone encompasses too wide a range of sedimentary rocks, since data are only sometimes available on the texture, and rarely on the geochemistry, of black shales in Canada. Consequently, these qualifying characteristics cannot always be used, and in lieu of all the necessary data, deposits are included in the database if they are consistently referred to as black shale in the scientific literature.

2.2 ORIGIN

The origin of black shales is far from clearly understood, and several models have been proposed for their formation (Berry and Wilde, 1978; Demaison and Moore, 1980; Arthur et al., 1984; Robertson, 1984; Levanthal, 1987; Coveney et al., 1991; Wignall, 1991). Most call

upon the interplay of three main variables to preserve relatively high concentrations of organic matter: 1) increasing the supply of organic matter, 2) increasing the rate of sedimentation, and 3) decreasing the oxygen content of the bottom water.

Organic matter is supplied to the sediments from primary biological productivity in the surface waters or from terrigenous organic matter derived from land plants. Areas of increased primary productivity occur as the result of upwelling of deep nutrient-rich waters. Increased supplies of terrigenous organic matter are constrained by fluvial discharge and by the climate and vegetation of the drainage area.

High sedimentation rates aid in the preservation of organic matter by burying it more rapidly and removing it from zones of bioturbation, oxic decomposition, and sulphate reduction. Although organic-carbon contents and accumulation rates may be higher in high-sedimentation-rate sequences, the organic matter itself may be somewhat more poorly preserved than that deposited under anoxic conditions (Arthur et al., 1984).

One of two situations leads to oxygen depletion in natural waters - deficient oxygen supply or excessive oxygen demand (see Demaison and Moore, 1980). Oxygen concentrations of less than 0.2 - 0.5 ml/l inhibit the activity of benthic metazoans. Eventually, bioturbation ceases, leaving anaerobic bacteria as the only effective reworkers of organic matter. The lack of bioturbation acts as a limiting factor to diffusion of oxidants into the sediment and results in laminated and organic-rich sediments.

The above processes account for several characteristics of black shale, such as their finely laminated or non-bioturbated texture, sparse fauna, high organic carbon content, and dark colour (due to high org-C content).

2.3 MINERALOGY AND GEOCHEMISTRY

Shales contain a wide range of constituents including clay minerals, quartz, feldspar, carbonates, iron oxide, sulphur minerals, and organic materials (Potter et al., 1980). The types and proportions of constituents present is a function of provenance, depositional environment, geologic age and diagenetic history.

Pyrite is the common sulphur mineral present in black shales. It is of particular importance to this study because many of the trace elements of environmental concern occur in the sulphide fraction (Tardy, 1975). The amount of pyrite that may form is limited by the rates of supply of decomposable organic matter, dissolved sulphate, and reactive iron detrital minerals. Under euxinic marine conditions, a plentiful supply of both organic matter and hydrogen sulphide brings about the formation of high concentrations of pyrite, which are limited only by the availability of reactive iron-minerals (Berner, 1983).

One of the classic studies on the geochemistry of black shale is that of Vine and Tourtelot (1970). Statistical methods were used to determine the composition of the "average" black shale and to provide a definition for "metal-rich" black shale for 21 minor elements (see Table 3.3.2). More recently, the IGCP 254 U.S. Working Group recommended using the USGS reference sample SDO-1 (see Table 3.3.2) as an average black shale against which to define metal-rich black shale (Kane et al., 1990; Huyck, 1990). In general, one or more of the following metals will be enriched in a metal-rich black shale relative to an average black shale: Ag, As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, U, V, and Zn. The availability of metals in solutions that have come into contact with organic matter throughout its history is probably the most significant factor in determining the suite of enriched metals present in black shale (Vine and Tourtelot, 1970). Further discussion of the complex process of enrichment in black shale is beyond the scope of this report.

Several studies have examined the association of minor elements with major rock constituents in black shale. Many of the trace metals are associated with the organic fraction including Ag, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, U, V, and Zn (Bell, 1978; Breit et al., ; Cameron and Jonasson, 1972; Desborough and Poole, 1983; Demaison and Moore, 1980; Tardy, 1975; Swanson, 1961; Vine and Tourtelot, 1970). As, Co, Cr, Cu, Hg, Mo, Ni, Se, V, and Zn are also concentrated in the sulphide fraction (Cameron and Jonasson, 1972; Desborough and Poole, 1983; Tardy, 1975); V, Cr, and Zn in the phosphate fraction (Tardy, 1975); and Zn and Cd in the sphalerite fraction (Desborough and Poole, 1983).

2.4 PHYSICAL PROPERTIES

There is little information and understanding regarding the physical properties of shales compared to that available on other sedimentary rocks. This is due to inherent problems associated with their fine grain size, and also because they are usually regarded as source rocks and seals rather than reservoir rocks. Therefore, they have not been afforded the same degree of interest as conventional reservoir rocks such as carbonates and sandstones.

Some recent research includes: discussion of the origin of shale fabric (Bennett et al., 1991; Moon and Hurst, 1984; Robertson, 1984); porosity, permeability and grain density data on cores of Devonian shales in the Appalachian Basin (Davies et al., 1991); and research on the microstructure of shales undertaken to evaluate them as potential nuclear waste repositories (Lee et al., 1991).

Results from research on shales generally document that they have a fine grain size, small pore size, and low values of porosity and permeability. Permeabilities range from 10^{-16} to 10^{-12} cm^2 and porosities range from 0-10% (Freeze and Cherry, 1979). Shales are a diverse and highly variable type of rock, therefore, these values can vary significantly, particularly if the rock is highly fractured.

3. BLACK SHALES IN CANADA

3.1 LOCATION

Black shales, ranging in age from Archean to Cretaceous, occur throughout Canada. They have been mapped in varying degrees of detail, sometimes occurring on maps as separate units, but most often included with other rock types within a larger map unit. The provincial sketch maps on the following pages (Figures 3.1.1 to 3.1.12) show locations of black shale deposits as compiled from readily available federal and provincial geological maps, theses, and scientific papers and reports. Taken together, they comprise a compilation map of black shale deposits for all of Canada.

Because the overall focus of this project is on the potential environmental impact of black shale, particularly on the human population, more emphasis was placed on black shale deposits in populated areas. Table 3.2.1 summarizes population centres across Canada in the vicinity of black shale deposits. Some black shales are not included on the compilation maps because they occur in remote, unpopulated parts of Canada. Alternatively, black shales may not appear if they are not reported in readily available scientific literature.

3.2 CHARACTERISTICS

The salient features of the black shale deposits compiled in Section 3.1 are tabulated in Table 3.2.1. The characteristics listed are modified from a data form developed for IGCP 254 (see Huyck, 1990). One modification is the addition of data on the lithology of the member, formation or group containing the black shale of interest because the black shale units are rarely formally named, or mapped, separately from surrounding beds. However, data on the fabric, colour, mineralogy, TOC, organic type, maturity, paleontology, bioturbation and depositional environment refer specifically to the black shale unit. The thickness refers to that of the formal mapped unit.

Another modification of the IGCP form is the inclusion of the age of the black shales, in addition to known (or hypothesized) correlations as taken from the scientific literature. This will help to place individual black shales within a broader, regional framework.

3.3 GEOCHEMISTRY

Tables 3.3.1 and 3.3.2 are a compilation from the scientific literature of average trace element analyses and average major element analyses for black shales in Canada. Many more black shales have been sampled and analyzed than this compilation suggests. For example, Goodfellow (pers.com.) has collected over 6000 samples of Paleozoic black shales from the Selwyn Basin, Richardson Trough, Blackstone Trough and Matepedia Trough and analyzed for

40-50 major and trace elements; however, the data have not yet been compiled and tabulated for publication. Similarly, van Staal (pers.com.) has collected and analyzed numerous black shales from New Brunswick; again, the data are not yet ready for publication. There are likely many other examples of unpublished geochemical data sets on black shales. Therefore, the compilation of analytical data in Tables 3.3.1 and 3.3.2 has the potential to be greatly expanded.

For comparative purposes, Table 3.3.2 includes analyses for average black shale (Vine and Tourtelot, 1970), metal-rich black shale (Vine and Tourtelot, 1970), USGS SDO-1 standard (Kane et al., 1990) and metalliferous black shale - defined relative to USGS SDO-1 (Huyck, 1990). Unfortunately, none of the black shales from Canada have been analyzed for as complete a suite of trace elements as the reference analyses. Based on the available data, they do not appear to be metal-rich, with the exception of the Kettle Point Formation and the Road River Formation. The Marcellus Formation does not appear enriched, which may be a result of sampling bias (Johnson et al., 1989).

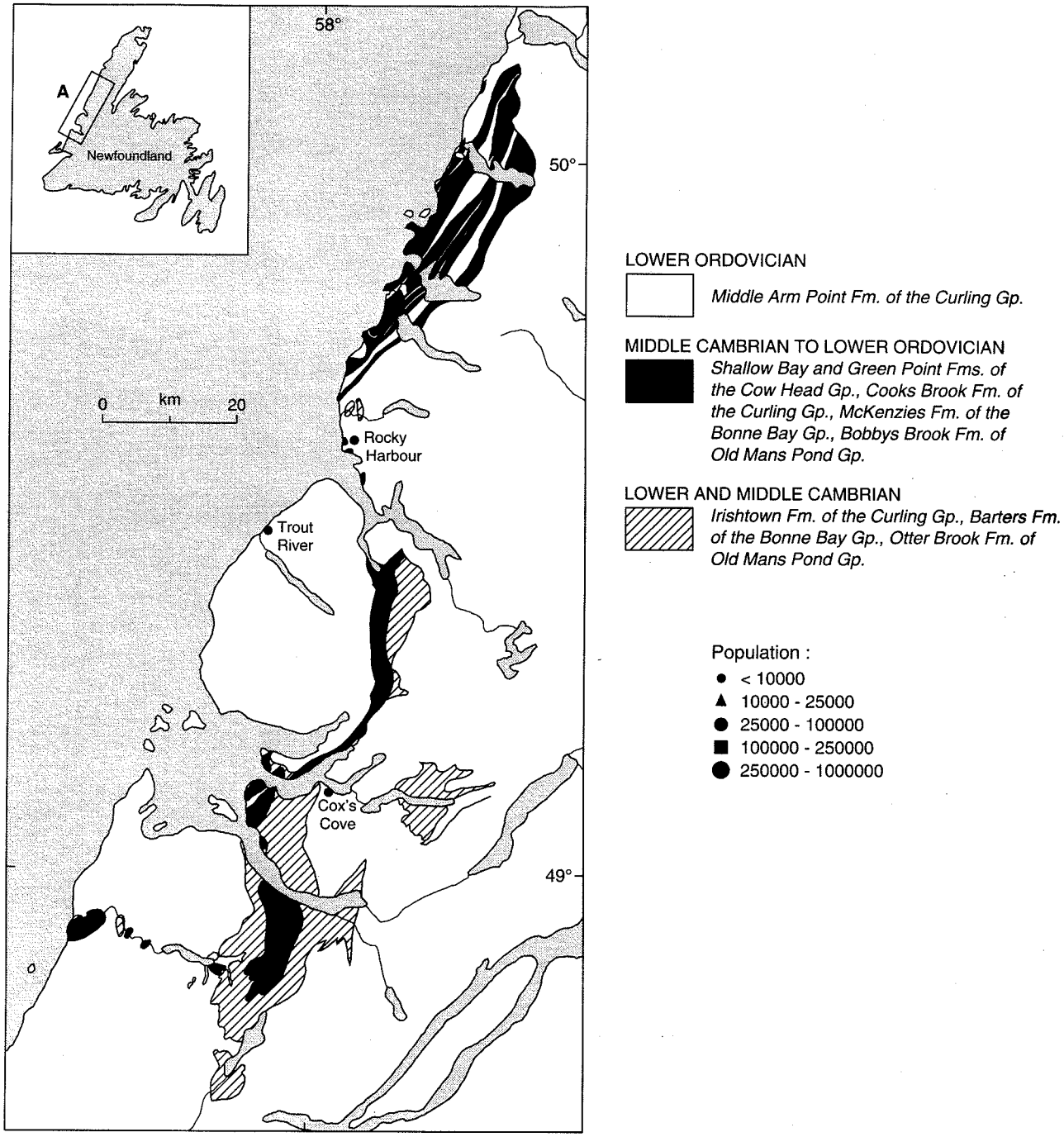

Figure 3.1.1 Distribution of the Curling and Cow Head Groups, Newfoundland (after Williams and Cawood, 1987).

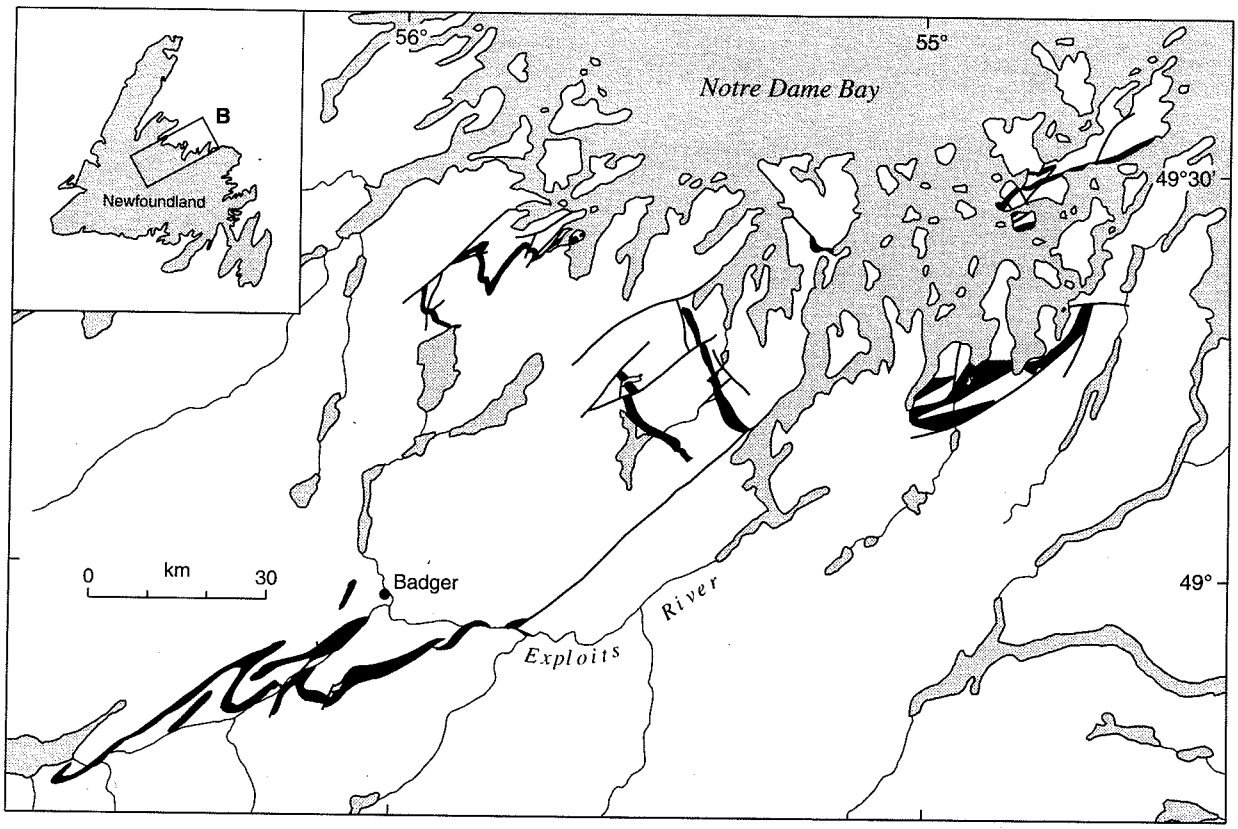

Figure 3.1.2 Distribution of the Shoal Arm Formation, Harbour Shale, and Dark Hole Formation, Newfoundland (after Kean, Dean and Strong, 1981).

MIDDLE ORDOVICIAN

Shoal Arm Fm., Lawrence Harbour Shale, Dark Hole Fm. (includes Rogers Cove Shale)

Population :

- < 10000
- 10000 - 25000
- 25000 - 100000
- 100000 - 250000
- 250000 - 1000000

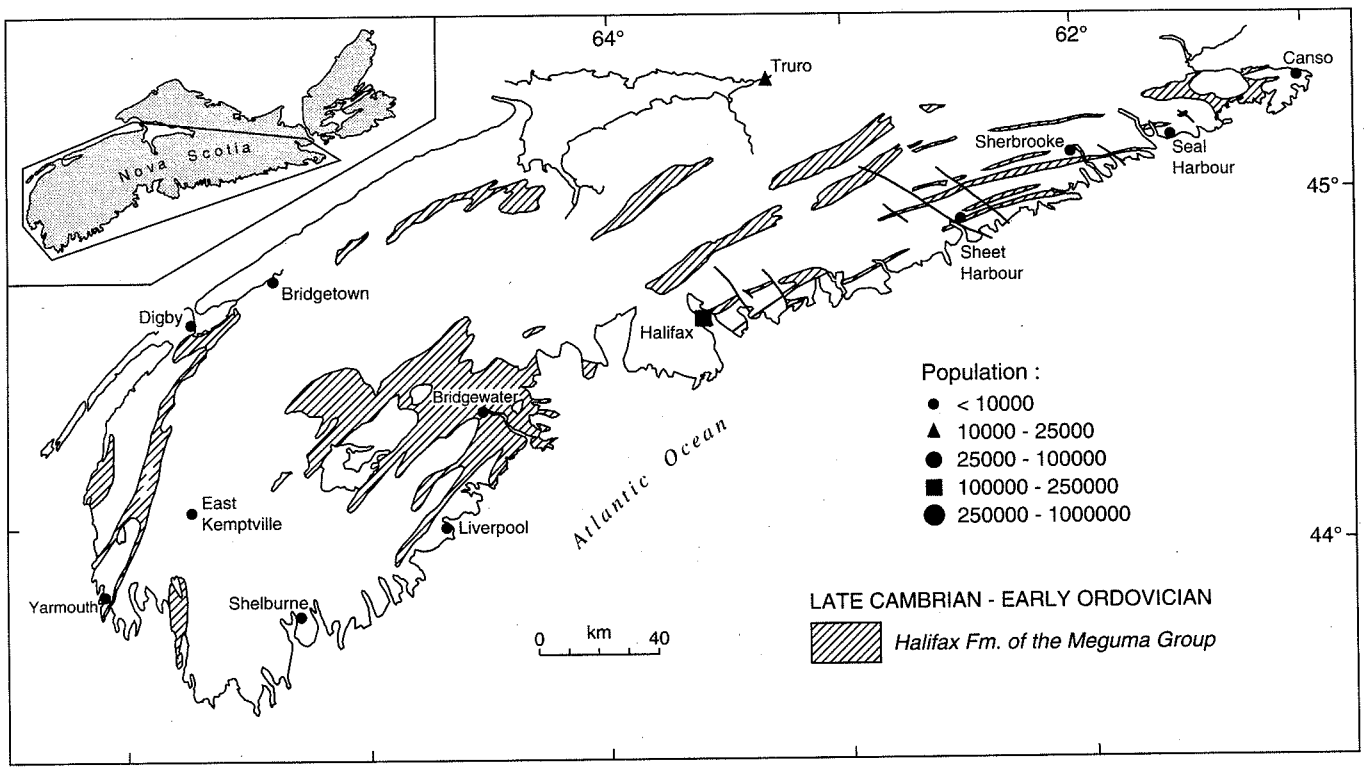

Figure 3.1.3 Distribution of the Halifax Formation, Nova Scotia (after Keppie, 1979).

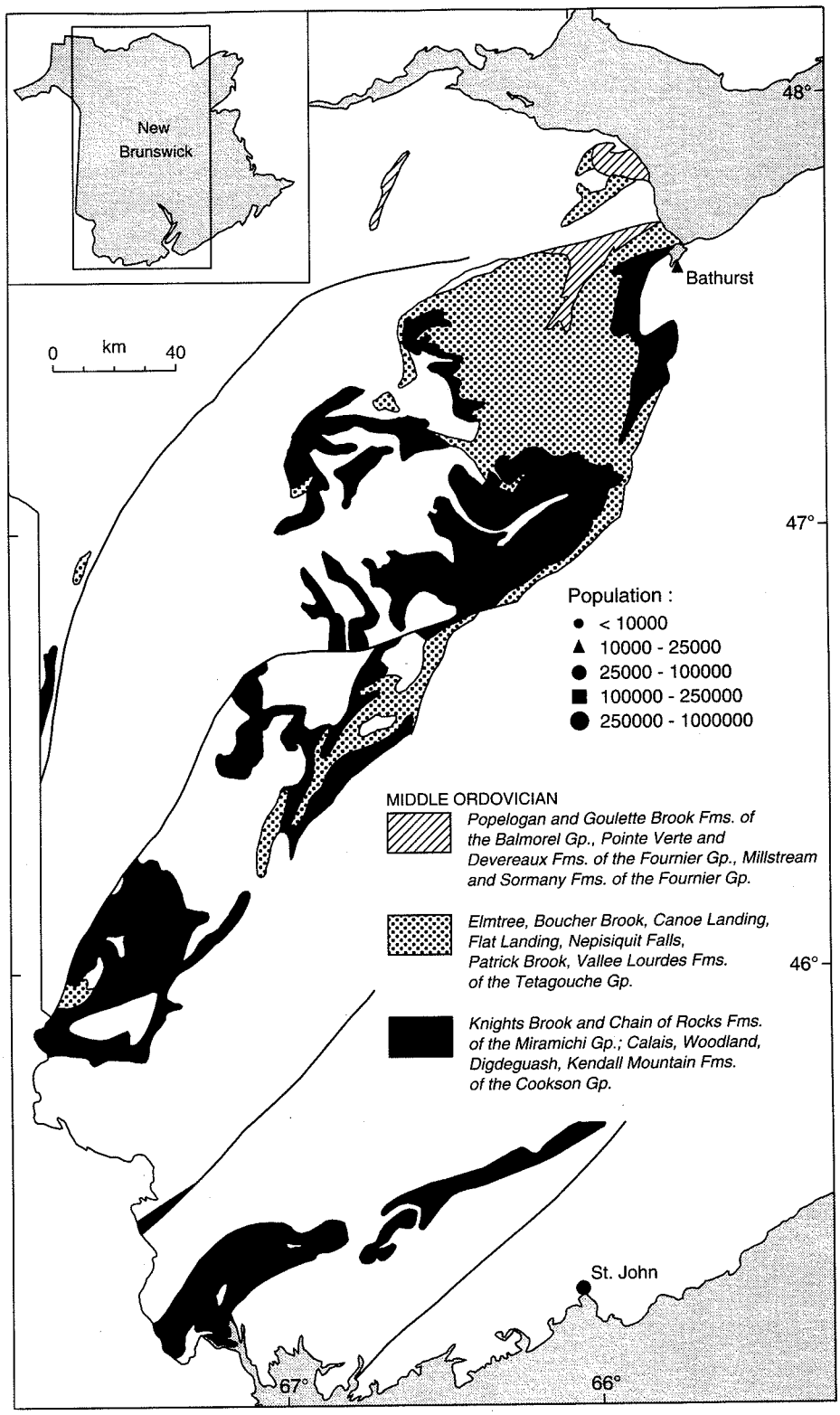

Figure 3.1.4 Distribution of black shale bearing formations, New Brunswick (after van Staal and Fyffe, 1991).

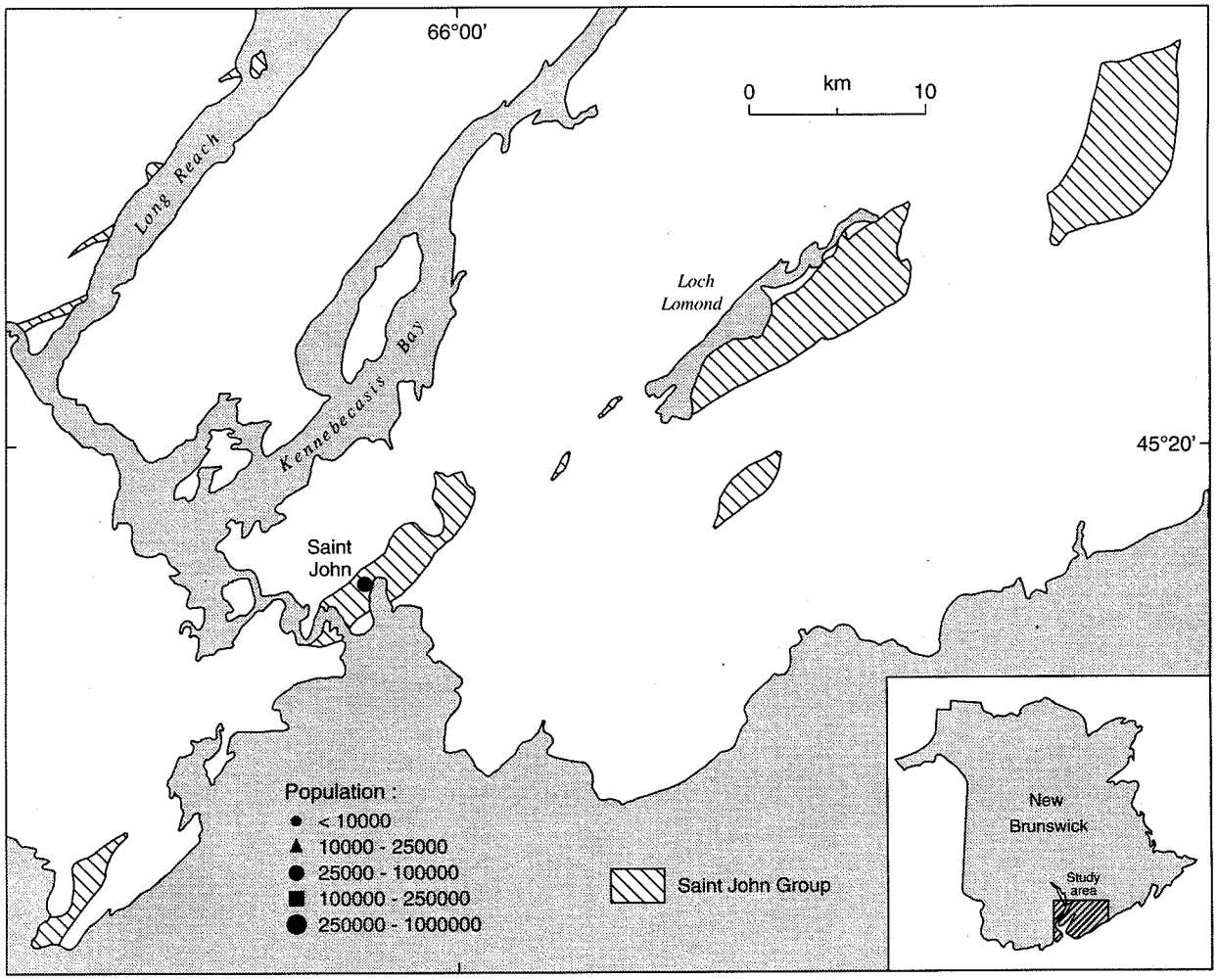

Figure 3.1.5 Distribution of the Saint John Group, New Brunswick (after Tanoli, 1987).

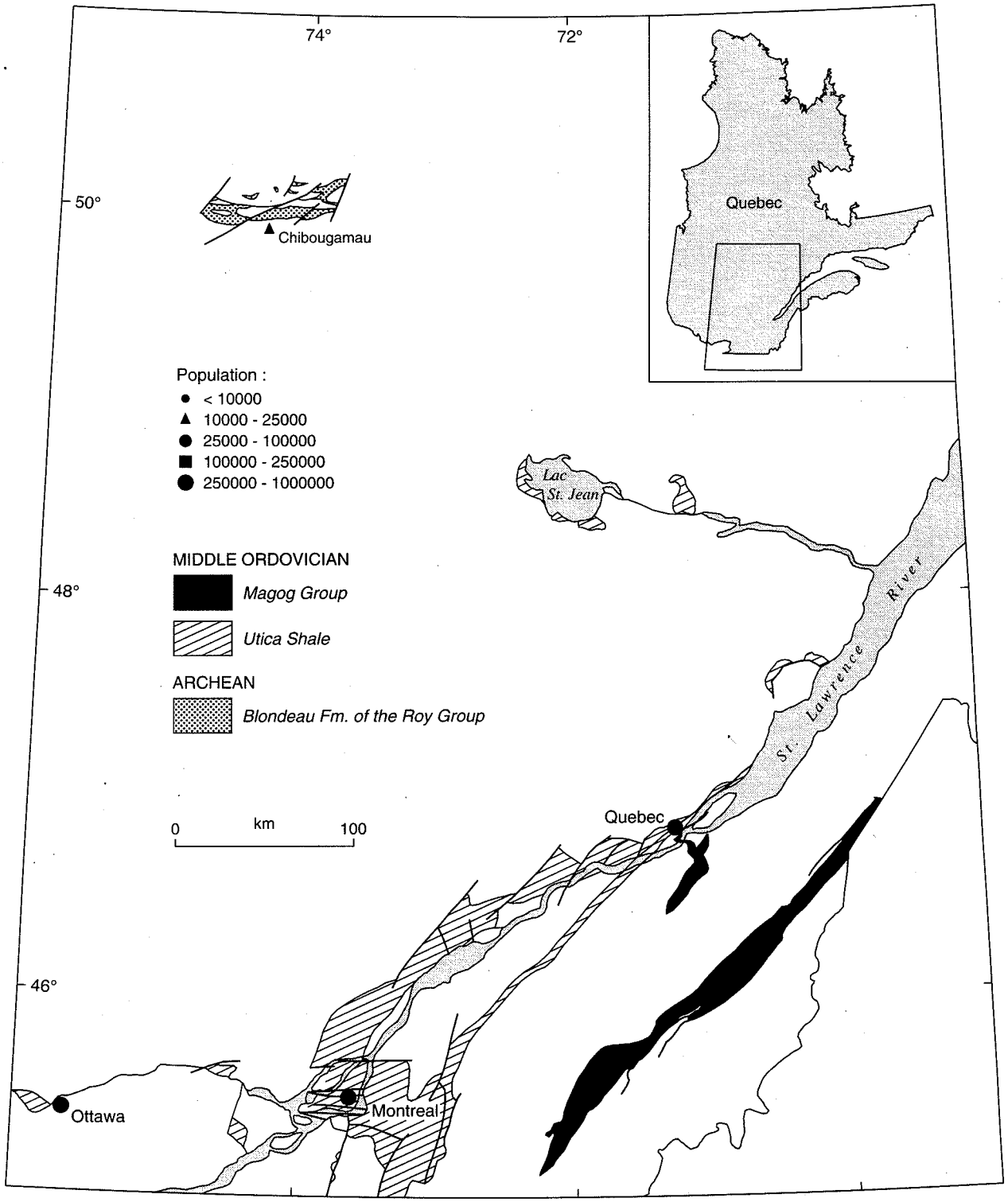

Figure 3.1.6 Distribution of the Magog and Utica Groups (after Avramtchev, 1985) and the Blondeau Formation, Quebec (after Tait, 1987).

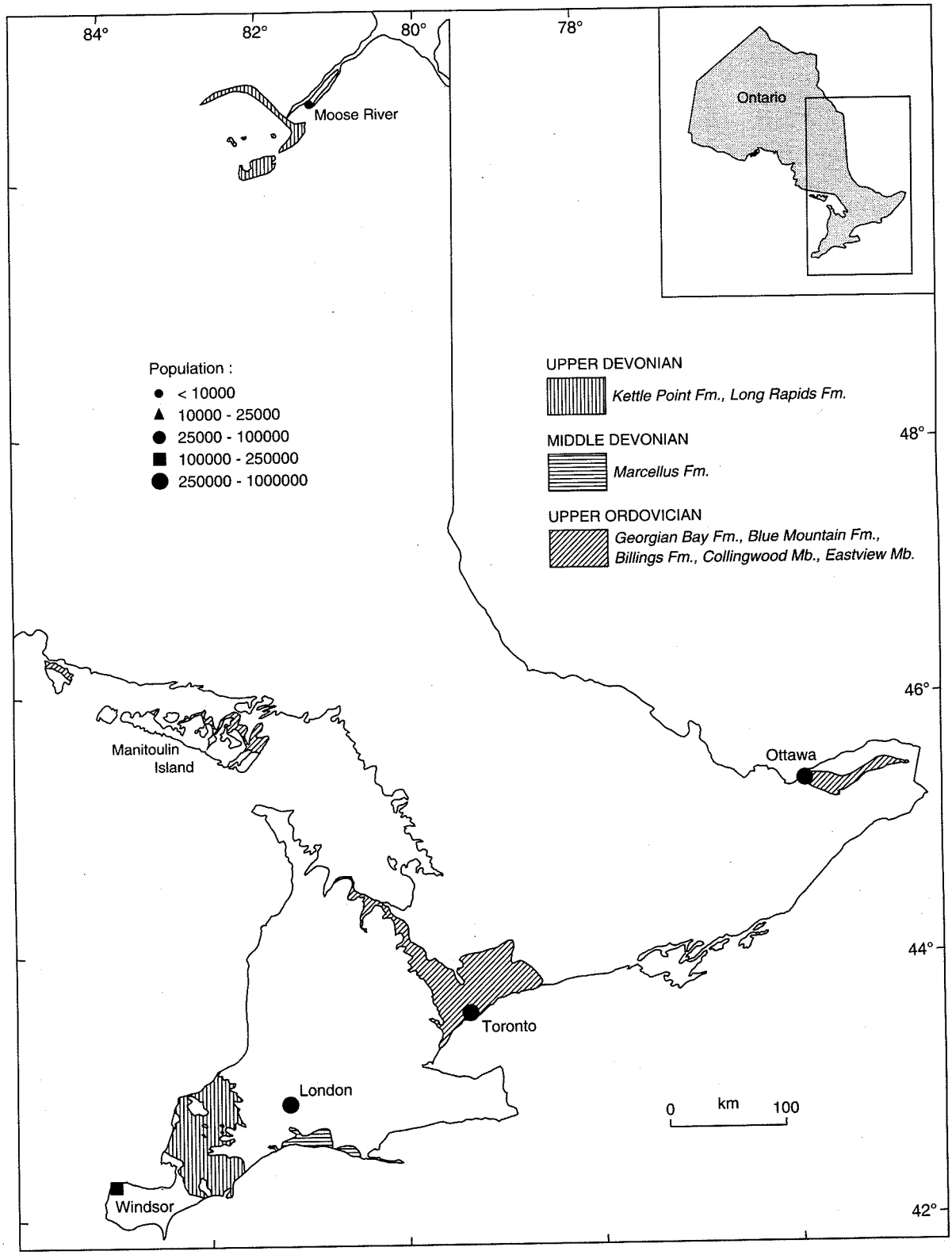

Figure 3.1.7 Distribution of the Kettle Point, Long Rapids, Marcellus, and Billings Formations and the Collingwood Member, Ontario (Ontario Geological Survey, 1991).

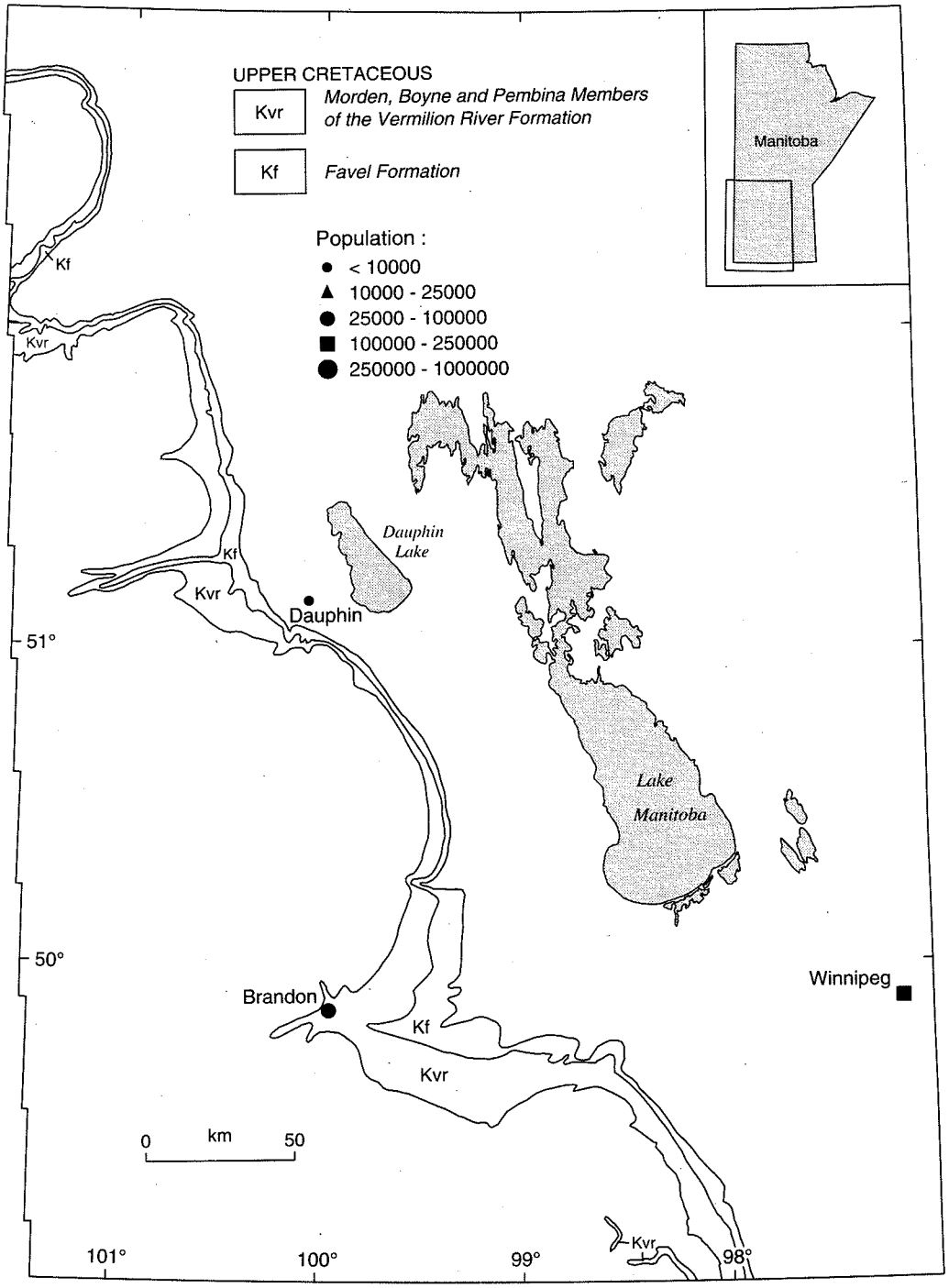

Figure 3.1.8 Distribution of the Boyne Member and Favel Formation, Manitoba (after Manitoba Geological Services Branch, 1979).

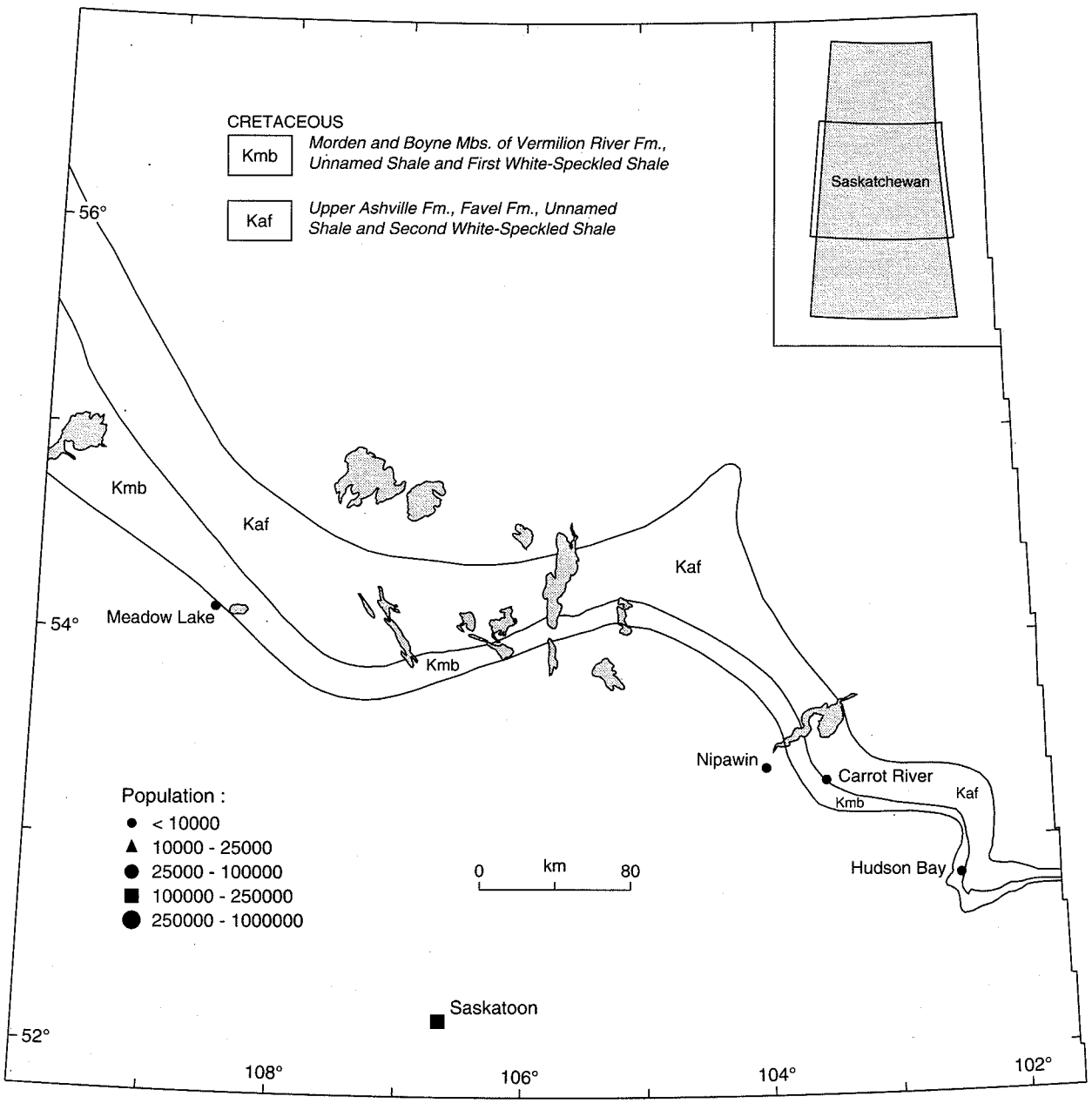

Figure 3.1.9 Distribution of the Boyne Member and Favel Formation, Saskatchewan (Byers et al., 1981).

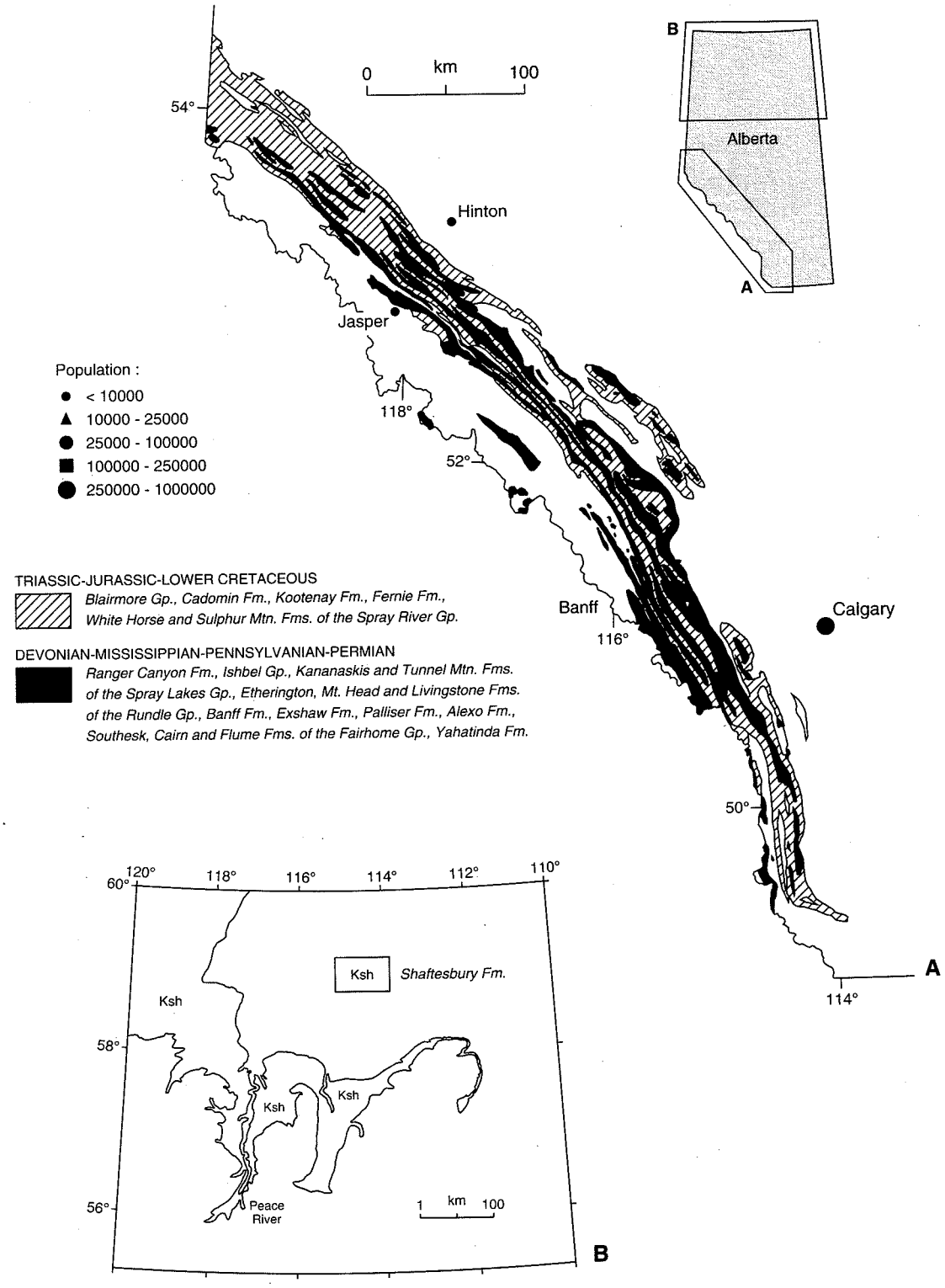

Figure 3.1.10 a) Distribution of the Fernie and Exshaw Formations, Alberta;
b) Distribution of the Shaftesbury Formation, Alberta (after Jackson, 1975).

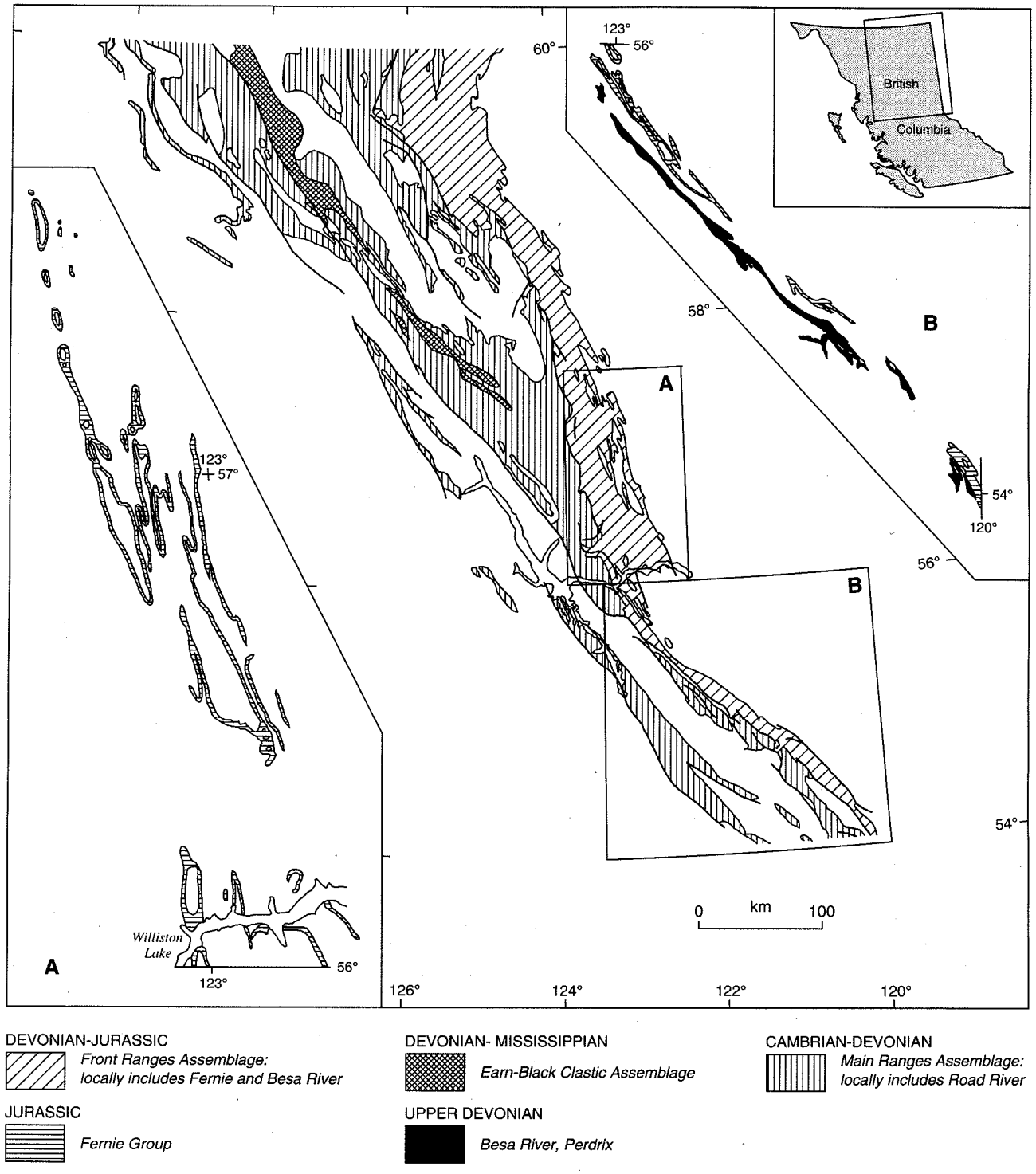

Figure 3.1.11 a) Distribution of assemblages containing the Fernie and Besa River Formations and the Earn and Road River Groups, British Columbia (after Tipper et al., 1981);

b) Distribution of the Fernie and Besa River Formations, British Columbia (above 56° after Stott, 1982; below 56° after Tipper, 1974).

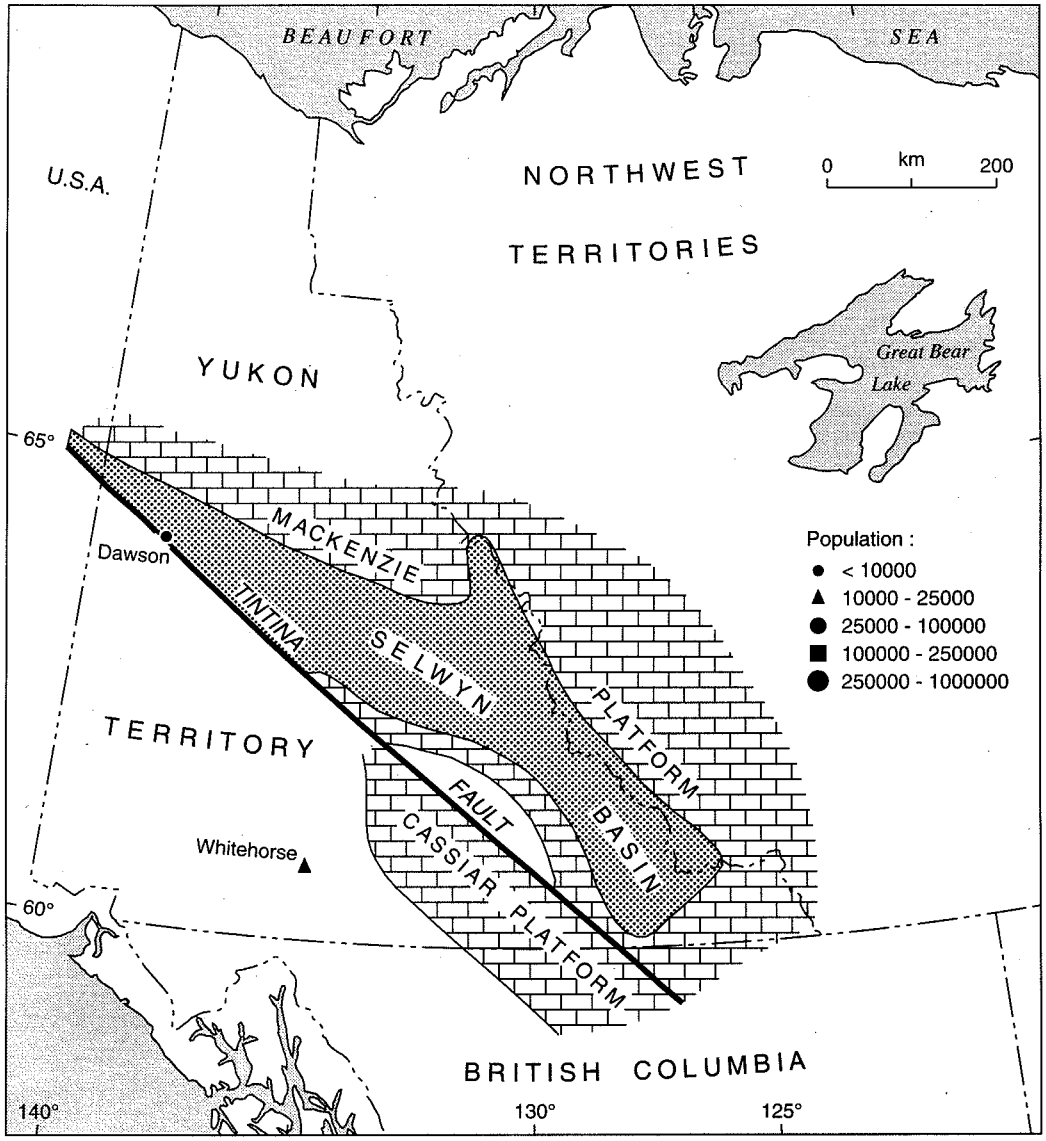

Figure 3.1.12 Distribution of Selwyn Basin stratigraphy, including the Mount Mye and Vangorda Formations and the Road River and Earn Groups, Yukon and Northwest Territories (after Jennings and Jilson, 1983).

Table 3.1.1 Population centres across Canada in the vicinity of black shale deposits.

Location	Population Range	Black Shale Deposits
Newfoundland		
Rocky Harbour	< 10 000	Curling and Cow Head Gps
Cox's Cove	< 10 000	Curling and Cow Head Gps
Trout River	< 10 000	Curling and Cow Head Gps
Badger	< 10 000	Shoal Arm Fm, Lawrence Harbour Shale, Dark Hole Fm
Nova Scoatia		
Halifax	100 000-250 000	Halifax Fm
Bridgewater	25 000-100 000	Halifax Fm
Liverpool	25 000-100 000	Halifax Fm
Yarmouth	25 000-100 000	Halifax Fm
Digby	25 000-100 000	Halifax Fm
Canso	25 000-100 000	Halifax Fm
Seal Harbour	25 000-100 000	Halifax Fm
Sherbrooke	25 000-100 000	Halifax Fm
Sheet Harbour	25 000-100 000	Halifax Fm
New Brunswick		
Bathurst	10 000-25 000	Tetagouche, Miramichi, Fournier and Balmorel Gps
St. John	25 000-100 000	St. John Gp
Quebec		
Quebec	250 000-1 000 000	Utica Shale, Magog Gp.
Montreal	250 000-1 000 000	Utica Shale
Chibougamau	10 000-25 000	Blondeau Fm
Ontario		
Ottawa	250 000-1 000 000	Billings Fm
Toronto	250 000-1 000 000	Collingwood Mb
London	250 000-1 000 000	Marcellus Fm
Manitoba		
Dauphin	< 10 000	Boyne Mb, Favel Fm
Brandon	25 000-100 000	Boyne Mb, Favel Fm
Saskatchewan		
Meadow Lake	< 10 000	Boyne Mb, Favel Fm
Nipawin	< 10 000	Boyne Mb, Favel Fm
Carrot River	< 10 000	Boyne Mb, Favel Fm
Hudson Bay	< 10 000	Boyne Mb, Favel Fm
Prince Albert	25 000-100 000	Boyne Mb, Favel Fm
Alberta		
Banff	< 10 000	Fernie and Exshaw Fms
Jasper	< 10 000	Fernie and Exshaw Fms
Hinton	< 10 000	Fernie and Exshaw Fms

Table 3.2.1 Characteristics of Black Shales in Canada

Name	Age	Location[1]	Lithology[2]	Thickness	Fabric[3]
Emma Fiord Fm	L. Carb	ARC	SLST/SH/SST	345m	thin-med bedded
Fernie Fm	Jur	AB/BC	SH/SST	69-537m	platy
Besa River Fm	M. Dev-Miss	BC/NWT/YK	SH/SLST/SST/LST	300-2255m	Lam
Earn Gp	M. Dev-Miss	BC/YK/NWT	SH/LST/CH/SST	<1300m	Lam/fiss
Exshaw Fm	Dev-Miss	AB/BC/NWT	SH/SLST/LST	7-50m	Fiss/lam
Road River Gp	Ord-L. Dev	BC/YK/NWT	SH/LST/CH/VOLC	<3000m	lam/cl
Boyne/Favel Fms	U. Cret	SK/MN	SH	<60m	lam/fiss
Shaftesbury Fm	L. Cret	AB	SH	<17m	lam
Kettle Point Fm	U. Dev	ON	MDST/SLST	<60m	fiss/lam
Long Rapids Fm	U. Dev	ON	SH/MDST/CARB	<85m	fiss/lam
Marcellus Fm	M. Dev	ON	SH/LST	1-12m	fiss
Collingwood Mb	U. Ord	ON	MRL/LST	<12m	lam/fiss
Utica Gp	M. Ord	QUE	SH/LST	<300m	?
Beauceville Fm	M. Ord	QUE	SH/VOLC	?	?
Blondeau Fm	Late Arch	QUE	SH/VOLC	<1000m	lam
Boucher Brook Fm	M.U. Ord	NB	WK/SH/VOLC	<3000m	lam/Shst
Elmtree Fm	U. Ord	NB	SH/SLST/WK/VOLC	?	?
Hayden Lake Fm	M. Ord	NB	SH/VOLC	<500m	?
Pointe Verte Fm	M. Ord	NB	SL/GRWK/LST	?	def
Millstream Fm	M. Ord	NB	SH/WK/ARK/LST	?	?
Popelogan Fm	M. Ord	NB	SH/CH	?	?
Bright Eye Brook Fm	L. Ord	NB	SH	?	?
Knights Brook Fm	L. Ord	NB	SH/SST	?	?
Cookson Gp	Ord	NB	SL/WK/SST	<1300m	?
Reversing Falls Fm	Camb-Ord	NB	SH	?	fiss
Silver Falls Fm	Camb-Ord	NB	SH/SST/LST	<80m	lam
Halifax Fm	L. Ord	NS	SL/SLST/LST	1000-8500m	lam
Shoal Arm/Dark Hole/ Lawrence Harbour Gps	N. Ord	NF	SH/CH	10-200m	lam/def
Cow Head/Curling Gps	M. Camb-U. Dev.	NF	SH/CON/LST	400m each	lam

1. BC: British Columbia; AB: Alberta; SK: Saskatchewan; MN: Manitoba; ON: Ontario; YK: Yukon; NF: Newfoundland; NS: Nova Scotia; QUE: Quebec; NB: New Brunswick; NWT: North West Territories; ARC: Arctic

2. ARK: Arkose; SLST: Siltstone; SH: Shale; SST: Sandstone; LST: Limestone; MDST: Mudstone; CON: Conglomerate; VOLC: Volcanics; SL: Slate; GRWK: Greywacke; CARB: Carbonate; MRL: Marlstone

3. Lam: Laminated; Fiss: Fissile; Cl: Cleaved; Def: Deformed; Shst: Schistose; CH: Chert; WK: Wacke

Name	Color	Mineralogy	TOC[4]	Org. Type[5]	Maturity	Biota	Depositional Environment[6]	References
Emma Fiord Fm	dk gry/blk	qtz-fdsp-calc-clay	3-46	ker	imm-mat	yes	lacustrine	49
Fernie Fm	gry/blk	qtz-ill-kao-pyr	1.37-4.95	?	?	no	anox/deep water	202, 203, 206
Besa River Fm	gry/blk	qtz-ill-pyr-chl-carb	2.0-6.0	?	?	yes	marine/dys	9, 123, 167, 181, 199, 214, 215
Earn Gp	bl-gry/blk	qtz-fdsp-clay-pyr-barite	0.3-7.3	?	?	?	marine/dys	1,74,80,81,96,102,134,135,141
Exshaw Fm	blk	qtz-carb-clay-pyr	0.6-4.7	?	?	?	anox/marine/<300m	32, 58, 88, 137, 182
Road River Gp	dk gry/blk	pyr	3.5-9.5	?	?	?	marine/trans	1, 8, 35, 68, 76, 80, 96, 102, 134, 135, 141
Boyne/Favel Fms	dk gry/dk bn	clay-calc-qtz-pyr-gyp-fdsp	1.0-11.0	ker	imm	yes	epeiric	59, 71, 113, 131, 143, 200
Shaftesbury Fm	?	clay-fdsp	0.47-5.56	bit	?	no	anox/shw mar	116
Kettle Point Fm	dk gry/blk	qtz-ill-pyr-fdsp-chl	5.0-16.0	ker/bit	imm-mat	yes	anox/marine	4, 11, 42, 133, 187, 188, 221
Long Rapids Fm	dk gry/blk	?	av. 4.3	?	?	yes	trans/marine/anox	19, 190, 216
Marcellus Fm	bl-gry/blk	?	1.0-10.6	ker	imm-mat	?	anox	11, 27, 105
Collingwood Mb	blk-bn	calc-qtz-ill-chl-pyr-phosph	0.9-11.2	bit/ker	mature	?	shw mar/dys/regress	11, 39, 40, 139, 189
Utica Gp	blk	calc-dol-clay-pyr	av. 7.0	?	?	?	?	92, 184
Beauceville Fm	blk	pyr (2-10%)	?	?	?	?	anox/forearc basin	45, 101, 198
Blondeau Fm	blk	clay-qtz-fdsp-sulfide	av. 1.7	bit	supermat	no	pro/<200m	3, 34, 149, 209
Boucher Brook Fm	dk gry/blk	qtz+?	?	?	?	?	back-arc/deep marine	154, 157, 180, 183, 197, 222, 223, 224
Elmtree Fm	dk gry/blk	?	?	?	?	?	?	154, 157, 180, 183, 197, 222, 223, 224
Hayden Lake Fm	red/grn/blk	?	?	?	?	?	?	154, 157, 180, 183, 197, 222, 223, 224
Pointe Verte Fm	blk/red	?	?	?	?	?	?	180, 222
Millstream Fm	blk	?	?	?	?	?	?	180, 222
Popelogan Fm	blk	?	?	?	?	?	?	168, 222
Bright Eye Brook Fm	blk	?	?	?	?	?	?	180, 222
Knights Brook Fm	dk gry/blk	graphite	?	?	?	?	?	180, 222
Cookson Gp	blk	?	?	?	?	?	?	180, 222
Reversing Falls Fm	blk	?	?	?	?	no	deep marine/anox	211, 236
Silver Falls Fm	blk	?	?	?	?	no	deep/dys	211, 236
Halifax Fm	blk/gry	qtz-fdsp-pyr-mang	?	?	?	no	prograding/anox	127, 158, 191, 192, 204, 238
Shoal Arm/Dark Hole/ Lawrence Harbour Gps	blk/red/grn	pyr-mang	?	?	?	yes	?	51
Cow Head/Curling Gps	blk/grn/red	clay-dol-qtz-fdsp-pyr	2.0-4.0	?	imm-mat	yes	anox/deep marine	22, 43, 232

4. Total Organic Carbon

5. Ker: kerogen
   Bit: Bituminous

6. anox: anoxic
   dys: dysaerobic
   trans: transgressive
   shw: shallow
   pro: prograding
   regress: regressive

Table 3.3.1 Major element geochemistry (wt%) of some black shale deposits in Canada and the United States.

REF.*	Si02	Al203	Fe203	Ca0	Mg0	Na20	K20	P205	Ti02	Mn0	S
3	49.28	12.27	9.34	1.05	1.54	0.38	3.35	0.11	0.71	0.042	5.35
5	48.5	7.2	3.88	4.92	1.21	0.30	2.67		0.36		
6	60.7	9.9	2.8	6.0	1.9		4.5		0.45		
7	59.19	13.91	5.64	1.29	1.76	0.66	3.73	0.08	0.70	0.03	3.47
8a	39.7	14.6	3.61	17.4	1.97	0.20	3.44	0.06	0.47	0.05	0.4
8b	45.8	16.5	4.49	9.0	2.31	0.2	4.31	0.07	0.58	0.03	1.17
8c	39.17	13.08	4.42	17.14	1.99	0.14	3.47	0.11	0.49	0.04	2.4
9	63.83	14.69	5.31	2.96	2.00	3.10	2.20	0.24	0.65	0.09	1.10
13	37.8	5.0	2.06	22.5	3.7	0.22	1.7	0.42	0.33	0.03	0.61

* References

3. USGS SDO-1 standard (Kane et al., 1990).
5. Average Exshaw Shale, n=42 (Duke, 1983).
6. Average Exshaw Shale (black), n=32 (Havard, 1967).
7. Average Kettle Point Fm, n=52 (Armstrong, 1986).
8. Average Marcellus Fm: a) organic-poor shale & b) organic-rich shale (Johnson et al., 1989); c) chip samples, including enclosing strata? (Brown, 1985).
9. Blondeau Fm, n=49 (Carignan et al.,1984).
13. Average Road River Gp (shale), n=9 (Goodfellow et al., 1980.

Blank

No folio

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Table 3.3.2 Trace element geochemistry of some black shale deposits in Canada and the United States.

REF.*	Ag ppm	As ppm	Au ppb	B ppm	Ba ppm	Bi ppm	Cd ppm	Ce ppm	Cl ppm	Co ppm	Cr ppm	Cs ppm	Cu ppm
1	1			50	300					10	100		70
2	7			200	1000					30	700		200
3	0.131	68.5	2.8	128	397	5	5	79.3	116	46.8	66.4	6.9	60.2
4	0.262	1.4	5.6	256	694	10	10	158.6	232	46.8	132.8	13.8	120.4
5		21			325				470	20.6	55.3	4.1	72
6					940								19
7a		82.3											80
7b		190											75.5
8c					299					9.8			118
9a			5.6							17	101.4		14.5
9b										23.51			75.5
10		22.9	9.3							9.3	107.7	3.6	
11		7.5			719					19.1			
12	0.4	22		23	76	0.4	4			11	18		50
13	0.34	5.2			6073		4.3	222		5.4	16.2		23
14		18	0.81		500					9	100		38

REF.*	Eu ppm	Ga ppm	Ge ppm	Hf ppm	Hg ppm	La ppm	Mo ppm	Nb ppm	Ni ppm	Pb ppm	Rb ppm	Sb ppm	Sc ppm
1		20				30	10		50	20			10
2		50				70	200		300	100			30
3	1.6	16.8	1.3	4.7	2.2	38.5	134	11.4	99.5	27.9	126	4.45	13.2
4	3.2	33.6	2.6	9.4	4.4	77	134	22.8	199	55.8	252	8.9	26.4
5		12.3		2.3			27.6		107	26	78	3.56	9.11
6									874		130		
7a							82.7		138.3	48.4			
7b							202		282	133.6			
8c		23.2						19.6	19.9	30.1	142.6		
9a													
9b									56	13			

10	0.8			3.3		27.7						2.6	14.2
11												0.89	
12			0.1				34		68	15		3.5	
13					0.05		6		15	8.8		1.8	
14							60		55	6		3.5	

REF.*	Se ppm	Sm ppm	Sr ppm	Ta ppm	Th ppm	U ppm	V ppm	W ppm	Y ppm	Yb ppm	Zn ppm	Zr ppm
1			200			2	150		30		<300	70
2			1500			30	1000		70		1500	
3	4.9	7.7	75.1	1.1	10.5	48.8	160	3.3	40.6	3.4	64.1	
4	9.8	9.8	150.2	2.2	21	48.8	320	6.6	81.2	6.8	128.2	330
5			222	0.65	9.2	15.6	227				102	
6			123			20					186	
7a						32.4	375.4				244.6	
7b						56.16	1440				934.8	
8c			254.6				83.8		45.7		70.3	100.2
9a											122.7	
9b											441.6	
10		4.9			7.9	3.6				2.3		
11				0.58		3.76	151					
12	11.7		170		5		121	<1			189	
13			706			2.7	198				116	96
14			42				430				185	

*** REFERENCES**

1. Black shale mean value (Vine & Tourtelot, 1970).
2. Metal-rich black shale (Vine & Tourtelot, 1970).
3. USGS SDO-1 standard (Kane et al., 1990).
4. USGS SDO-1 "metalliferous" (Huyck, 1989).
5. Average Exshaw Shale, n=42 (Duke, 1983).
6. Average Exshaw Shale (black), n=32) (Havard, 1967).
7. a) Average Kettle Point Fm, n=45 & b) Average Kettle Point Fm, Lithotype A: black mudstone, n=5 (Armstrong, 1986).
8. Average Marcellus Fm: a) organic-poor shale & b) organic-rich shale (Johnson et al., 1989); c) chip samples, including enclosing strata? (Brown, 1985).
9. Blondeau Fm: a) (Tait, 1987); b) n=49 (Carignan et al., 1984).
10. Magog Gp (shale/mudstone), n=115 (Godue, 1988).
11. Average Levis Shale, n=12 (Berry et al., 1986).
12. Average White Specks, n=56 (Dunn, 1990) - partial extraction (aqua regia)
13. Average Road River Gp (shale), n=9 (Goodfellow et al., 1980).
14. Average Lower Earn Gp (Hulbert et al., 1992).

4. AQUEOUS GEOCHEMISTRY

4.1 TRACE ELEMENTS

The focus of this section is on the aquatic behaviour of metals and metalloids present in black shale that are of environmental concern due to their potential toxicity to aquatic life or humans. The elements discussed in the following sections include: Sb, As, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, Se, U and V. These trace elements may be introduced to the hydrosphere by natural processes, such as weathering and mineral dissolution, or by anthropogenic activities, such as quarrying of shale. The latter activity can result in the release of metals, because relatively impermeable shale is broken up and exposed to water and oxygen.

Whether a particular trace element goes into solution depends on the mineral in which the element occurs. For example, the trace elements may be present in chemically resistant minerals such as apatite, or in sulphides, which weather rapidly in oxygenated water.

4.1.1 Antimony

Antimony is commonly found in the +3 and +5 oxidation states. Sb(lll) complexes with inorganic and organic acids to produce antimonial salts. Trivalent complexes include antimony trioxide and antimony trichloride. Little is known about the aqueous geochemistry of Sb(V) (CCREM, 1987).

Under moderately oxidizing conditions, antimony is found as a hydrated trioxide. As a result of the relative stability of the antimonites and antimonates in the redox range of surface water, most of the antimony is probably transported in solution. The extent to which sorption processes reduce the concentrations of antimony in solution is unknown, although antimony does have an affinity for clay and mineral surfaces. Coprecipitation with hydrous iron, manganese and aluminum may also occur. In reducing environments, stibine (SbH_3) may be formed, but will be readily transformed to the oxide Sb_2O_3 in aerobic water.

There are few studies on the bioaccumulation of antimony in the aquatic environment. The biomethylation of antimony has not been demonstrated; it is, however, thought to occur because the elements surrounding antimony in the periodic table are subject to methylation (Parris and Brinckman, 1976).

4.1.2 Arsenic

Arsenic exists in the +5, +3, 0, and -3 oxidation states in aquatic systems. The metal is extremely rare and As(-lll) is found only at extremely low Eh values (Moore and Ramamoorthy, 1984). As(V) is the stable form in aerobic water. As(lll) is the predominant form under anaerobic conditions. Arsenic may form a wide range of inorganic and organic compounds with a large number of elements.

Adsorption and coprecipitation are major factors in controlling aqueous arsenic concentrations. Phases that may coprecipitate with, or adsorb arsenic include hydrous oxides and hydroxides of iron, aluminum, manganese, metal sulphides, clay minerals and organic matter (Pierce and Moore, 1980; Wagemann, 1978). Laboratory studies of arsenic adsorption on ferric oxyhydroxide indicate that higher pH solutions have a lower adsorption capacity relative to more acidic solutions. Because ferric oxyhydroxide is nearly always found in oxidized sedimentary environments, this lowered adsorption capacity at elevated pH values is consistent with a tendency for slightly alkaline, non-thermal groundwater to have elevated arsenic concentrations. Under most conditions, coprecipitation or sorption of arsenic with hydrous iron oxides is probably the predominant process in the removal of dissolved arsenic from the water column.

Inorganic forms of arsenic prevail in most natural waters; however, both As(lll) and As(V) form stable bonds with carbon, resulting in numerous organo-arsenical compounds (Lemmo et al., 1983). The deadly poisonous organic derivative, dimethyl arsine, is converted from inorganic arsenic by methanobacteria which are normally present in anaerobic sediments of the aquatic environment (Luh et al., 1973). Like many other toxic metals, arsenic can be biologically concentrated through food chains.

4.1.3 Cadmium

The form and fate of cadmium in water are complicated. They depend upon its chemical speciation, which is determined by water pH and hardness, as well as the presence of ligands and coexisting metal cations (Moore and Ramamoorthy, 1984). In natural surface waters, cadmium occurs principally as free Cd(ll) ions, cadmium chloride and cadmium carbonate. Cadmium solubility decreases as water pH increases above pH 9.0 because of the formation of cadmium hydroxide (Moore and Ramamoorthy, 1984). Redox potential is believed to have little direct influence on cadmium speciation; however, under reducing conditions and in the presence of sulphur, insoluble cadmium sulphide is produced.

Sorption is probably the most important process for the removal of cadmium from the water column. For example, exchange of cadmium for calcium ions in carbonate; coprecipitation with hydrous iron, aluminum and manganese oxides; and, in waters of high organic content, adsorption of cadmium to humic substances and other organic complexing agents occurs.

Cadmium may be accumulated by a number of aquatic organisms. Bioaccumulation of cadmium is influenced by water hardness, temperature, pH, and presence of complexing agents. There are few recorded instances of cadmium poisoning in humans following consumption of contaminated fish or water; however, several epidemiological studies have demonstrated a causal relationship between exposure to cadmium and cancer incidence (Moore and Ramamoorthy, 1984).

4.1.4 Chromium

The two important oxidation states of chromium in natural waters are +3 and +6. Cr(Vl) predominates under oxidizing conditions while Cr(lll) predominates under more reducing conditions. Cr(lll) has a strong tendency to form stable complexes with negatively charged inorganic and organic species, or colloidal hydrous oxides in neutral solutions. It is essentially immobile in most groundwaters because of its low solubility above a pH of 4-5. Cr(Vl) is quite soluble, existing in solution as a complex anion. However, Cr(Vl) is easily reduced to Cr(lll) by Fe(ll), dissolved sulphides, and certain organic compounds. By contrast, Cr(lll) is oxidized rapidly by a large excess of MnO_2 and slowly by oxygen under natural conditions (Moore and Ramamoorthy, 1984).

Cr(lll) adsorption by soils and clays is generally very high, with adsorption increasing with pH. At around a pH of 4, Cr(lll) is relatively immobile due to adsorption. Adsorption of Cr(Vl) by clays and soils is low to moderate in the pH ranges of natural groundwater. Adsorption of Cr(Vl) decreases with increasing pH. Little or no adsorption occurs above a pH of 8.8 (see Calder, 1988).

Chromium is bioaccumulated by aquatic organisms. Cr(Vl) is more toxic to animals and plants than Cr(lll) because of its ability to penetrate cell membranes (Moore and Ramamoorthy, 1984).

4.1.5 Cobalt

Cobalt exists in the -1, 0, +1, +2, +3 and +4 states; however, only Co(ll) and Co(lll) are common in aqueous solutions. The major dissolved species of cobalt in aerobic fresh water at pH 8.0 are Co(ll) and carbonate. Cobalt forms very stable complexes with such compounds as EDTA and NTA; the chelation of cobalt to such multidentate ligands strongly enhances its solubility and mobility in aqueous systems.

Cobalt may be removed from solution by adsorption to suspended particulates and sediment materials. In laboratory experiments, 90% of the cobalt was adsorbed by montmorillonite and illite (Kharkar et al., 1968). Adsorption to clay minerals is influenced by pH; it is low at low pH, but approaches 100% when the pH is between 7-10. In aerobic fresh water, calculations predict that adsorption to silica, ferric oxide and manganese oxide amount to less than 2% (Vuceta and Morgan, 1978). Organic compounds in water may cause desorption and solubilization of cobalt from inorganic fractions of sediment.

Some aquatic organisms may readily accumulate cobalt. Because concentration factors generally decrease with increasing trophic status, biomagnification is not considered to be significant.

4.1.6 Copper

Copper exists in the 0, +1, +2 and +3 oxidation states; the two most common are Cu(I) and Cu(II). Cu(I) is unstable in aerated solutions and will normally be oxidized to Cu(II). The dissolved phase may contain free ions as well as copper complexed to inorganic or organic ligands (Moore and Ramamoorthy, 1984). Copper is generally more soluble in acidic water, and precipitates as $Cu(OH)_2$ at pH values above 6.5. In the presence of excess cupric ion in alkaline waters, carbonates, hydroxides, oxides and sulphides will form colloidal suspensions or will precipitate out of solution.

Sorption and precipitation play major roles in determining the abiotic fate of copper in the aquatic environment. Copper has a high affinity for hydrous iron and manganese oxides, clays, carbonate minerals and organic matter. In reducing acidic environments, remobilization of sorbed or coprecipitated copper can occur.

Copper is highly toxic to aquatic plants, invertebrates and freshwater fish. It is readily accumulated by plants and animals; however, it is not thought to be biomagnified to any significant extent. Copper is not acutely toxic to humans (Moore and Ramamoorthy, 1984).

4.1.7 Lead

Lead exists in the 0, +1, +2 and +4 oxidation states; Pb(II) is the most common. Chemical speciation of lead compounds in water is complex, and depends upon several factors including the solubility of lead compounds, pH, dissolved oxygen and the presence of coexisting inorganic and organic compounds (Moore and Ramamoorthy, 1984). The sulphides, sulphates, oxides, carbonates and hydroxides of lead are almost insoluble (Hem and Durum, 1973). Lead solubility is very low in water containing lead, carbon dioxide and sulphur and in strongly reducing environments of low pH ($pH < 2$). Between pH 6-8, solubility of lead is a complex function of pH and dissolved CO_2. At constant pH, the solubility of lead decreases with increasing alkalinity. Below pH 6.5, the solubility of lead increases. In natural water, most of the lead in the dissolved phase may be complexed by organic ligands. In addition, a significant portion of lead is bound to colloids, either hydrous iron oxides or organic macromolecules depending on the composition of the water (Moore and Ramamoorthy, 1984).

Sorption is the dominant mechanism controlling the distribution of lead in the aquatic environment and is correlated to organic content and grain size. In the absence of soluble complexing species, lead is almost totally sorbed as precipitated species at $pH > 6$.

Biomethylation of Pb(II) has been observed only in laboratory anaerobic conditions (Moore and Ramamoorthy, 1984). Lead is bioaccumulated by aquatic organisms. Microcosm studies indicate that lead is not biomagnified (Lu et al., 1975). Many environmentally important lead compounds such as halides, sulphates, phosphates, and hydroxides are insoluble and thus are of relatively low toxicity in aquatic systems (Moore and Ramamoorthy, 1984).

4.1.8 Mercury

Mercury exists in the 0, +1 and +2 oxidation states. The chemical speciation depends on pH, redox potential, and nature and concentration of anions which form stable complexes with mercury (Moore and Ramamoorthy, 1984). In deionized water under moderate oxidizing conditions above pH 5, the predominant species present is elemental mercury. In natural waters containing micro- and macrosolutes which may be potential ligands for mercury, Hg(11) is expected to predominate at low redox potential (Ramamoorthy and Masssalski, 1979). Under mildly reducing conditions, mercury will be in the form of insoluble sulphide.

Mercury concentrations in aqueous solution are relatively small due to the tendency of mercury compounds to sorb onto sediments. Sediment binding capacity is related to organic content, and appears to be little affected by pH. In anaerobic sediments, mercury tends to combine with sulphur.

The chemical behaviour of mercury is complicated by the ability of microorganisms to convert inorganic mercury to mono- and dimethylmercury under both aerobic and anaerobic conditions. The organic compound formed is a function of the microbial flora, organic carbon and inorganic mercury concentrations, pH and temperature (Bisogni and Lawrence, 1975). Methylated mercury has a high affinity for biotic tissue and is readily taken up by organisms. Analyses of fish have shown that the mercury accumulated in their tissues is almost entirely in the form of methylmercury. Mercury bioconcentration factors for aquatic organisms are usually high (CCREM, 1987). Lower pH values generally increase mercury solubility, rate of methylation and rate of uptake. The microbial methylation of mercury is probably responsible for increasing the toxicity and geochemical mobility of mercury in aquatic systems.

4.1.9 Molybdenum

Molybdenum occurs in five oxidation states with Mo(lV) and Mo(Vl) predominating; it does not exist in nature in a pure metallic state (Jarrell et al., 1980). Dissolved molybdenum in water occurs mainly as molybdate $(MoO_4)^{2-}$ and bimolybdate $(HMoO_4)^{-}$. Adsorption and coprecipitation of the molybdate anion by hydrous oxides of iron and aluminum play primary roles in determining the aquatic fate of molybdenum.

Above pH 5, the influence of sorption decreases, and molybdenum in natural waters is essentially dissolved (Jarrell et al., 1980). As redox potential is lowered, the solubility of molybdenum increases. Molybdenum concentration and organic content are weakly correlated.

Molybdenum is not a serious environmental contaminant in terms of human health, but has potentially hazardous implications for ruminant animals by causing a copper deficiency (Doyle and Fletcher, 1977; Jarrell et al., 1980; Erdman, 1990).

4.1.10 Nickel

Nickel may occur in oxidation states ranging from -1 to +4 in aqueous systems; however, it occurs predominantly in the divalent state. Under anaerobic conditions and in the presence of sulphur, nickel will form insoluble sulphides. Under aerobic conditions below pH 9, nickel will form compounds with hydroxide, carbonate, sulphate and organic ligands. The concentration and speciation of nickel will depend on competing processes such as coagulation, precipitation, sorption, and complexation/chelation with dissolved organic and inorganic ligands (Moore and Ramamoorthy, 1984).

Nickel adsorbs to iron and manganese oxides and suspended organic matter, which is an important mode of nickel transport, and coprecipitates with iron and manganese oxides. It is considered highly mobile in aqueous systems, with sorption playing a relatively minor role in water below pH 6.

Nickel is bioaccumulated by some aquatic organisms. Studies with freshwater fauna indicate the absence of biomagnification through the food web. Nickel is essential at trace levels for human health. Acute toxicity arises from competitive interaction with five major essential elements: calcium, cobalt, copper, iron and zinc (Moore and Ramamoorthy, 1984).

4.1.11 Selenium

The oxidation state of selenium may be -2, 0, +4 or +6. Inorganic species are determined principally by the pH and Eh conditions, but competitive solubilities, complexation, and biological interactions play a part (Herring, 1991). Selenide will be present only under very reducing and alkaline conditions. Its mobility will be limited by the extremely low solubility of most selenide compounds. Under usual redox and pH conditions, selenite will be the stable form of selenium. Selenites may undergo significant sorption onto hydrous metal oxides and clay minerals, in the pH range of 3-8, causing immobilization of Se. Under acidic and reducing conditions, selenites are reduced to elemental Se, which is very insoluble in aqueous systems and generally resistant to oxidation or reduction. Alkaline and oxidizing conditions favour the formation and stability of the selenates which are the most mobile of the selenium species because they form soluble compounds. Previously, selenate was thought to be either unstable or not to form.

Selenium forms organic compounds. Microbial processes can produce reduced organoselenium species, such as dimethyl selenide, and the ubiquity of these compounds in the environment suggests these processes are an important part of the aqueous geochemistry and geochemical cycle of selenium (Cooke and Bruland, 1987).

Selenium is not toxic to plants, but it can easily become toxic to animals through excessive dietary intake (e.g. Boon, 1989). The particular species of selenium is critical. Elemental selenium is considered to be practically nontoxic. However, when converted into more biologically assimilable forms, selenium can readily concentrate in organisms in toxic quantities (Wilbur, 1980).

4.1.12 Uranium

Uranium may exist in the +3, +4, +5 and +6 states. U(Vl) is the most stable. Uranium does not occur naturally in elemental form. Generally, in oxidizing environments, U(Vl) predominates; U(lV) is present in reducing environments. The chemical speciation of uranium ions in aqueous solution is quite complex because of the many possibilities of complexing reactions with all ions. In aerobic waters, the most significant complexing agent for uranium is carbonate (Drever, 1982). The uranyl carbonate species are all quite stable in the typical ranges of redox potential found in natural waters. Sulphur complexes are also soluble, whereas potassium and phosphate complexes are quite insoluble.

Sorption to clay minerals such as kaolinite below pH 5 and sorption to hydrous ferric oxide at higher pH in aerobic waters will reduce the mobility of uranium (Giblin et al., 1981).

Uranium is not an essential element; however, it is found in most living tissues. It may be accumulated by numerous aquatic plants, lower organisms, invertebrates and fish. Because uranium concentrations decrease with increasing trophic status, biomagnification is not expected.

4.1.13 Vanadium

Vanadium may exist in the 0, +1, +2, +3, +4 and +5 oxidation states. It is highly mobile in neutral or alkaline environments. Its mobility decreases in oxidizing and acidic environments, whereas in reducing environments it is nearly immobile. Dissolved vanadium is usually in the pentavalent form. Although vanadium speciation has been studied extensively in marine systems, studies of vanadium speciation in freshwater systems are scarce (CCREM, 1987).

Little information is available on the bioaccumulation of vanadium by freshwater species. Trace quantities of vanadium have been found in freshwater and marine fish. Studies on the extent of vanadium bioaccumulation in aquatic ecosystems show little evidence for biomagnification (CCREM, 1987).

4.2 ACID DRAINAGE

As discussed in Section 2.3, many black shales are rich in pyrite, which is recognized as a major source of acid drainage (Drever, 1982; Stumm and Morgan, 1981). Acid waters cause environmental problems because most organisms are adapted to waters buffered by the carbonate system and cannot tolerate strong acidity. Furthermore, many toxic trace elements are mobilized only under strongly acidic conditions. It is clear from Section 4.1 that black shales have the potential to release toxic metals to both ground and surface water.

If black shale deposits are disturbed, pyrite is exposed to air and water and the following sequence occurs: the sulphide of the pyrite is oxidized to sulphate, which releases dissolved ferrous iron and acidity; the ferrous iron is then oxidized to ferric iron, which hydolyzes to insoluble ferric hydroxide, releasing more acidity (Stumm and Morgan, 1981). The acidity may initially be neutralized by the alkalinity in the ground water. If the acidity generated is greater than the initial alkalinity of the water, all the alkalinity will be consumed and an acid water will result.

Research suggests that the abiotic oxidation of sulphide is catalyzed by sulphide oxidizing bacteria. They thrive under acid conditions, so that once acidity is initiated, acid production becomes more rapid and the acidity problem increases (Drever, 1981).

In the absence of some disturbance such as quarrying, blasting, mining, road cutting, or excavating, acid waters are uncommon because dissolved oxygen in the groundwater is insufficient to produce acidity greater than the alkalinity of the groundwater. Therefore, acid drainage is probably only a potential environmental hazard of black shale that has been significantly disturbed.

4.3 DISCUSSION

For any calculations involving chemical equilibria, adsorption, mobility, bioavailability, bioaccumulation, or toxicity, it is necessary to know the speciation of a particular element. For example, chelated forms of heavy metals such as copper, cadmium, mercury, etc. are less toxic than the unbound ions (Moore and Ramamoorthy, 1984).

The solubility of phases containing the trace element of interest as a major constituent provides a general upper limit to the aqueous concentration of that element. Adsorption, by manganese and iron oxides in particular, is probably the most important process in maintaining the aqueous concentrations of trace elements at levels far below those predicted by equilibrium calculations (Drever, 1982).

5. CASE STUDIES

There are several documented cases of adverse environmental impacts related to black shale. The following synopses of a few cases discuss impacts such as: release of toxic metals to surface and ground water, acid drainage to surface and ground water, and elevated indoor and outdoor radon levels.

5.1 HALIFAX, NOVA SCOTIA

In 1982, a large quantity of mineralized slate bedrock of the Halifax Formation was excavated at the Halifax Airport. The bedrock was used as taxiway fill with the remainder placed in a disposal area. Acid drainage (pH 3) began discharging at both locations and a lime treatment facility was established to neutralize the runoff. Nonetheless, acid drainage continued discharging into the Salmon River watershed. This led to the initiation of an environmental impact study to determine the effects of acid drainage on the Salmon River aquatic system (Lund et al., 1987); the results follow.

Field observations of the bedrock revealed pyrite and arsenopyrite, with minor amounts of pyrrhotite, sphalerite and chalcopyrite. These minerals occur along quartz veins and cleavage planes and were exposed to weathering and leaching following blasting. They were the principal source of acid drainage at the airport and contain iron, arsenic, copper, zinc, nickel and aluminum.

Undisturbed bedrock groundwater is a calcium sulphate type water with high pH (7.7). Water in both the disturbed bedrock and the waste rock pile had a lowered pH: 3.25-3.75 for the former, and 2.4 for the latter. Chemical data indicated significant loadings of metals and acidity to receiving waters from the airport. The effect of acid drainage was observed up to 10 km downstream from the airport vicinity. The resulting water quality in the Salmon River watershed was considered toxic to fish, which will not survive in the longer run unless the acidity of the airport drainage is returned to background levels.

5.2 SOTKAMO, FINLAND

Early Proterozoic black shale formations occur in eastern Finland. They are rich in carbon, sulphur and metals and commonly contain 0.2 ppm mercury, on average. In the area of Lake Kolmisoppi, in Sotkamo, there is a Ni-Cu-Zn occurrence in black shales, which contains 1.7 ppm mercury, on average, up to a maximum of 7.5 ppm.

Pike in Lake Kolmisoppi exhibit anomalous mercury concentrations in relation to two other lakes studied in Sotkamo. As metalliferous black shale is one of the most readily weathered rocks in Finland, and mercury concentrations in the shale near Kolmisoppi are anomalous, the shale is strongly indicated as the source of the mercury in the fish (Loukola-Ruskeeniemi, 1990).

5.3 SAN JOAQUIN VALLEY, CALIFORNIA

In the San Joaquin Valley, California, subsurface agricultural drainage waters, resulting from the leaching of salinized soils, have been used in wildlife habitats. At one, Kesterton National Wildlife Refuge (KNWR), up to a 64% rate of deformity and death in embryos and hatchlings of wild aquatic birds was documented in 1983. The contamination of the ecosystem has developed from naturally occurring Se, in a form that is highly mobile in the environment and that is able to bioaccumulate in the food chain. Presser and Swain (1990) considered the Coast Ranges as a source of the Se contamination. Their conclusions follow.

Acidic (pH 4) seeps issue from weathered shales of the Moreno Formation in the Coast Ranges. Their solution chemistry indicates the oxidation of pyrite, yielding hydrous sodium and magnesium sulphate salts. The salts act as temporary geological sinks for selenate, which is incorporated in the space normally occupied by the sulphate anion. When coupled with a semi-arid to arid climate, fractional crystallization and evaporative concentration can occur creating a Se-enriched fluid. The oxidative alkaline conditions necessary to ensure the concentration of soluble selenate (see Section 4.11) are provided in the accompanying marine sandstones of the Panoche and Lodo Formations and the eugeosynclinal Franciscan assemblage. Runoff and mass wasting in the area provide the mechanisms which transport Se to the farmlands of the west-central San Joaquin Valley. Subsurface drainage from these soils consequently transports Se to refuge areas in amounts elevated enough to cause a threat to wildlife.

5.4 OHIO

Radon, a natural radioactive gas, can cause lung cancer in people who have been exposed to high levels over a long period of time. Radon gas is clearly associated with the geologic occurrence of uranium (Tanner, 1986). In Ohio, the black Ohio Shale of Upper Devonian age is the most enriched and widespread of the uranium-bearing bedrock formations. For this reason, Harrell et al. (1991) investigated the indoor radon hazards associated with its outcrops.

Study results showed that the amount of radon gas emanating from the Ohio Shale is a direct function of the uranium concentration in the shale. Where the average thickness of the sediment overburden exceeds 27 m, much of the radon in houses may be derived from Ohio Shale clasts in the glacial till. In other areas where the average overburden thickness is 6 m or less, the indoor radon levels appear to be directly controlled by emanations from the underlying Ohio Shale bedrock. Abundant vertical fractures in the bedrock may be greatly facilitating the upward migration of radon.

6. RECOMMENDATIONS

Based on the preceding information, recommendations for further study are the following:

1. Prioritize black shale deposits in Canada according to their potential to impact the environment in a manner harmful to humans and wildlife. Factors to consider include: proximity of the black shale to population centres, potable water sources, and surface waters; extent of fracturing in the black shale; pyrite content; disruption of the black shale by quarrying, road cutting, or excavating, in general; and, the fate of the black shale if disturbed (e.g. stockpiling, road bedding). One example of a "priority black shale" would be the Halifax Formation in Nova Scotia.

2. Prioritize those trace elements known to occur in black shales according to factors such as mobility and toxicity. Some "priority trace elements" would be mercury, selenium, and uranium, among others.

3. Compile geochemical data (published and unpublished, if available) on the priority black shales. If no data are available, collect unweathered rock samples, or utilize archival samples, and analyze for a complete suite of priority trace elements. Quantify pyrite content simultaneously. Re-evaluate the priority black shales based on their trace element and pyrite contents and eliminate those shales that do not pose an environmental threat due to potential toxic metal release or acid drainage.

4. Compile available ground water and surface water geochemical data upgradient and downgradient of both undisturbed and disturbed priority black shales; or, collect the appropriate water samples for analyses. Analyze for major ions and priority trace elements. Compare rock geochemistry with water geochemistry to evaluate the impact of the black shale on the aqueous system.

5. Initiate further research on chemical speciation studies of the priority trace elements. Perform leaching tests to elucidate the importance of different mineral phases (e.g. carbonate, sulphide, silicate, organic) on the leachability of the priority trace elements from black shale.

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