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Epidote-amphibole and accessory phase mineral chemistry as a vector to low-sulphide platinum group element mineralization, Sudbury: laser ablation ICP-MS trace element study of hydrothermal alteration

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TABLE OF CONTENTS

Abstract **271**

Introduction **271**

Geological Setting of the Sudbury Hydrothermal System **272**

Sampling and Methodology **272**

Alteration Assemblage Samples 272

Results and Data Analysis **276**

Rare-Earth Element Characteristics of Epidote-Allanite, Amphibole and Titanite 277

Pathfinder Mineral Chemistry of Epidote-Allanite and Amphibole-Chlorite 277

Epidote-Group Minerals 277

Amphibole and Chlorite 279

Discussion **282**

Significance of Host-Rock Normalized Mineral Chemistry 282

Possible Controls on the Trace Element Distribution in Epidote 283

Element Partitioning among Minerals 283

Implications for Exploration **283**

Acknowledgements **284**

References **284**

Figures

Figure 1. Location map of the barren and mineralized hydrothermal alteration in the Sudbury structure and schematic section of the Sudbury study area 273

Figure 2. Photographs of pre-, syn-, and post-mineralization epidote in the Sudbury structure 274

Figure 3. Photographs of barren and mineralized alteration zones with amphibole in veins, amygdules, and replacement zones in the footwall and hanging wall of the Sudbury Igneous Complex 275

Figure 4. Plots of rare earth element distribution patterns in pre-sulphide epidote, amphibole, titanite, and sulphide-silicate assemblages 278

Figure 5. Rare earth element plots of epidote-, amphibole-, titanite-, and allanite-bearing alteration assemblages 280

Figure 6. Absolute, and host-rock normalized concentration plots of epidote from multiple hydrothermal assemblages 281

Figure 7. Plots of Sn versus Ni, the key pathfinder elements in amphibole from barren and mineralized assemblages using absolute concentrations and host-rock normalized values 282

Tables

Table 1. Summary of alteration styles and minerals analyzed in barren and mineralized environments 276

Table 2. Summary of systematic element partitioning among coexisting minerals in footwall alteration zones 283

Epidote-amphibole and accessory phase mineral chemistry as a vector to low-sulphide platinum group element mineralization, Sudbury: laser ablation ICP-MS trace element study of hydrothermal alteration

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ABSTRACT

In Sudbury, one of the world's largest Ni-Cu-Co mineral districts, geophysical methods have been successfully employed for detecting traditional contact and offset types of Ni-Cu-PGE ore for over a century. Recent discoveries of low- to no-sulphide, high-PGE tenor orebodies, defined in 2005 in the footwall environment to the Sudbury Igneous Complex (SIC), caused a shift in exploration focus to the detection of these precious metal-rich resources. These high-grade orebodies are hosted in randomly distributed impact-derived breccia (Sudbury breccia) entirely within Archean and Proterozoic country rocks and comprise two footwall styles: a) high-sulphide vein-style Cu-PGE ores (i.e. Strathcona, McCreedy East 153 chalcopyrite veins) with a widely recognized magmatic-hydrothermal origin and b) low-sulphide disseminations, blebs and stringers with high PGE tenor and dominated by silicate assemblages of hydrothermal origin. This second, low- to no-sulphide, high-PGE footwall ore-style is a challenge to detect in the field with traditional geophysical methods used for magmatic deposits due to the absence of chalcopyrite or sulphide minerals, resulting in a need for development of non-conventional exploration techniques.

Proper classification is important for guiding future exploration for the low-sulphide metal-rich deposits in the footwall to the Sudbury Igneous Complex. Key hydrothermal alteration assemblages with distinct trace element signatures may aid the development of discriminant mineral chemistry diagrams to yield criteria that help find these high-grade PGE hydrothermal footwall ores. The aim of this study was to establish typical element-associations and behaviours for the paragenetically different hydrothermal assemblages produced during the diverse post-impact magmatic-hydrothermal history of the footwall and hanging-wall units of the Sudbury structure to detect a unique signature for alteration related to the high-tenor PGE mineralization. Factors affecting the trace element distribution patterns in epidote, amphibole, titanite, and allanite are examined, including the element partitioning between coeval minerals, the crystal structural control, and the effect of country rocks on the fluid-rock interaction, and detection of pathfinder elements. As and Zn in epidote and amphibole are host-rock dependant. The pathfinder elements Ni, Pb, Sn, and Co in epidote and amphibole are the most reliable elements to distinctly fingerprint the PGE mineralizing alteration in the footwall. However, mineral-pair partitioning of elements between epidote-amphibole-titanite and allanite indicate that single mineral phases or elements should not be used.

INTRODUCTION

World-class Ni deposits, mined for over 125 years in the camp, are hosted within igneous rocks along and near the basal contact of the Sudbury Igneous Complex (SIC) and its offset dyke structures. The last fifteen years witnessed the evolution of exploration, which was initially focussed on locating Ni-Cu ores in igneous-hosted, contact and offset magmatic-dominant environments, shift towards searching for PGE-rich deposits within impact, shock-derived breccia, the so-called Sudbury breccia, in magmatic-hydrothermal and hydrothermal footwall environments. The two "footwall-styles" of mineralization (1) sharp-walled, high-sulphide vein and (2) disseminated, blebby and stringer, low-sulphide ore (Farrow et al., 2005) have different metal associations, alteration assemblages, and most significantly timing and processes of formation.

The aim of this study was to establish typical element-associations and behaviours for the paragenetically different hydrothermal assemblages produced during the diverse post-impact magmatic-hydrothermal

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history of the footwall and hanging-wall units along the North and East Ranges of the Sudbury structure to potentially detect a unique signature for alteration related to the high-tenor PGE mineralization. Recognizing and classifying the footprint of low- (to no-) sulphide PGE mineralization involved discriminating the mineral chemistry of the pre-, syn- and post-impact (1850 Ma) hydrothermal alteration assemblages. The goals of this study were to (1) characterize the mineral chemical signatures of epidote-allanite, amphibole, and titanite formed by multiple hydrothermal events in different settings, processes, and fluid sources, in order to discriminate PGE-mineralized from barren zones; (2) determine the robustness of the epidote trace-element signature with an enlarged dataset from orebodies and showings across the North Range; and (3) illustrate the factors affecting epidote-amphibole, epidote-titanite, and amphibole-titanite mineral pair compositions to provide effective diagrams for use in detecting PGE-endowed orebodies.

GEOLOGICAL SETTING OF THE SUDBURY HYDROTHERMAL SYSTEM

The Sudbury structure is the product of a comet (Pope et al., 2004; Petrus et al., 2014) that impacted the Archean and Proterozoic crust 1850 Ma ago (Krogh et al., 1984) and whose most prominent feature, the SIC controls the distribution of Ni-Cu-PGE ores in the Sudbury mining camp (Fig. 1). The originally flat-lying, ~150–200 km diameter x 3 km thick igneous body (SIC) was tectonically deformed, folded into a doubly plunging syncline, and eroded into its present much smaller shape. Following the impact, a large hydrothermal system was generated (Ames et al., 1998) that was heated by the cooling SIC and impacted crust and resulted in fluid/volatile circulation through the breccia and structures, both above and below the SIC (Farrow and Watkinson, 1992; Li and Naldrett, 1994; Hanley and Mungall, 2003; Hanley et al., 2004; Ames et al., 2006) (Fig. 1b).

Impact-generated hydrothermal systems may circulate many types of fluids and gases in the impact craters above, below, and within the melt sheet (e.g. Sudbury), at the central uplift (e.g. Manson, Chicxulub) and along impact-derived and pre-existing crustal structures (e.g. Chicxulub, Haughton) (McCarville and Crossey, 1996; Osinski et al., 2001; Naumov, 2002; Abramov and Kring, 2004; Ames et al., 2004). Groundwater, deep crustal fluids, seawater, if present in the target area, and basement fluids commonly recharge an impact site after the initial impact stage, when both target materials and the bolide are volatilized, the crust is melted, and then faulted and the impact site is cooled to the geothermal gradient over a protracted time period. The circulation of mixed fluids and volatiles is strongly dependent on host-rock permeability and the duration of the impact-generated hydrothermal system, which in turn is controlled by crater size, i.e., with little to no alteration in small craters (Melosh, 1989; Abramov and Kring, 2004). Fluids may utilize permeable pathways, such as shallow and deep-seated fault structures in large-scale (~200 km) modified craters, as well as impact-derived breccias developed around the transient crater in the target rocks (pseudotachylite/cataclasite; e.g. Sudbury breccia). Evidence for the Sudbury impact-induced hydrothermal system is based on field observation, mineralogical mapping, fluid inclusion, stable and radiogenic isotopic evidence for fluid and volatile flow, below, within and above the SIC (Farrow and Watkinson, 1992; Ames et al., 1998; Farrow and Watkinson, 1999; Hanley et al., 2005, 2011; Ames and Farrow, 2007; Campos-Alvarez et al., 2010; Tuba et al., 2014; Kerr et al., 2015). Fluids and volatile sources identified in the Sudbury crater include (1) groundwater and deep brines; (2) orthomagmatic volatiles released from impact generated melts; (3) Proterozoic seawater; and (4) an exotic footwall hydrocarbon-bearing fluid (Farrow and Watkinson, 1992, 1999; Ames et al., 1998; Molnar et al., 2001; Hanley et. al., 2005, 2011; Ames et al., 2006; Kerr et al., 2014) (Fig. 1b).

Hydrothermal assemblages with albite-K-feldspar, epidote, amphibole, chlorite, quartz, titanite, or scapolite are present above, below, and within the SIC. Non-aqueous fluid constituents, such as CO_2 and more recently, hydrocarbons are known components of the Sudbury hydrothermal system, as evidenced above the SIC by large (60 x 1 km) semi-conformable calcite alteration zones in the upper part of the Onaping Formation (Ames et al., 1998, 2006), calcite-quartz and actinolite-epidote below the SIC in the footwall PGE / Cu-PGE mineralized zones (Farrow and Watkinson, 1992; MacMillan, 2014), and the recognition of hydrocarbons in fluid inclusions in the ores and pre-impact target rocks (Bunch et al., 1999; Hanley et al., 2005; Mungall et al., 2007; Wright et al., 2010; Kerr et al., 2015).

SAMPLING AND METHODOLOGY

Alteration Assemblage Samples

Eight alteration types from the footwall and hanging wall of the SIC were identified across the North and East ranges of the Sudbury structure and are described in general paragenetic order relative to the main Cu-sulphide mineralizing stage for the footwall types (Ames et al., 1998, 2006; Tuba et al., 2010, 2014), (Figs. 2, 3, Table 1). Alteration assemblages with epidote (Fig. 2) and/or amphibole (Fig. 3) that are pre-sulphide mineralization (i.e. chalcopyrite-PGM veins) and generally barren are found as miarolitic cavities in "footwall granophyre" (Fig. 2a), pervasive epidote-

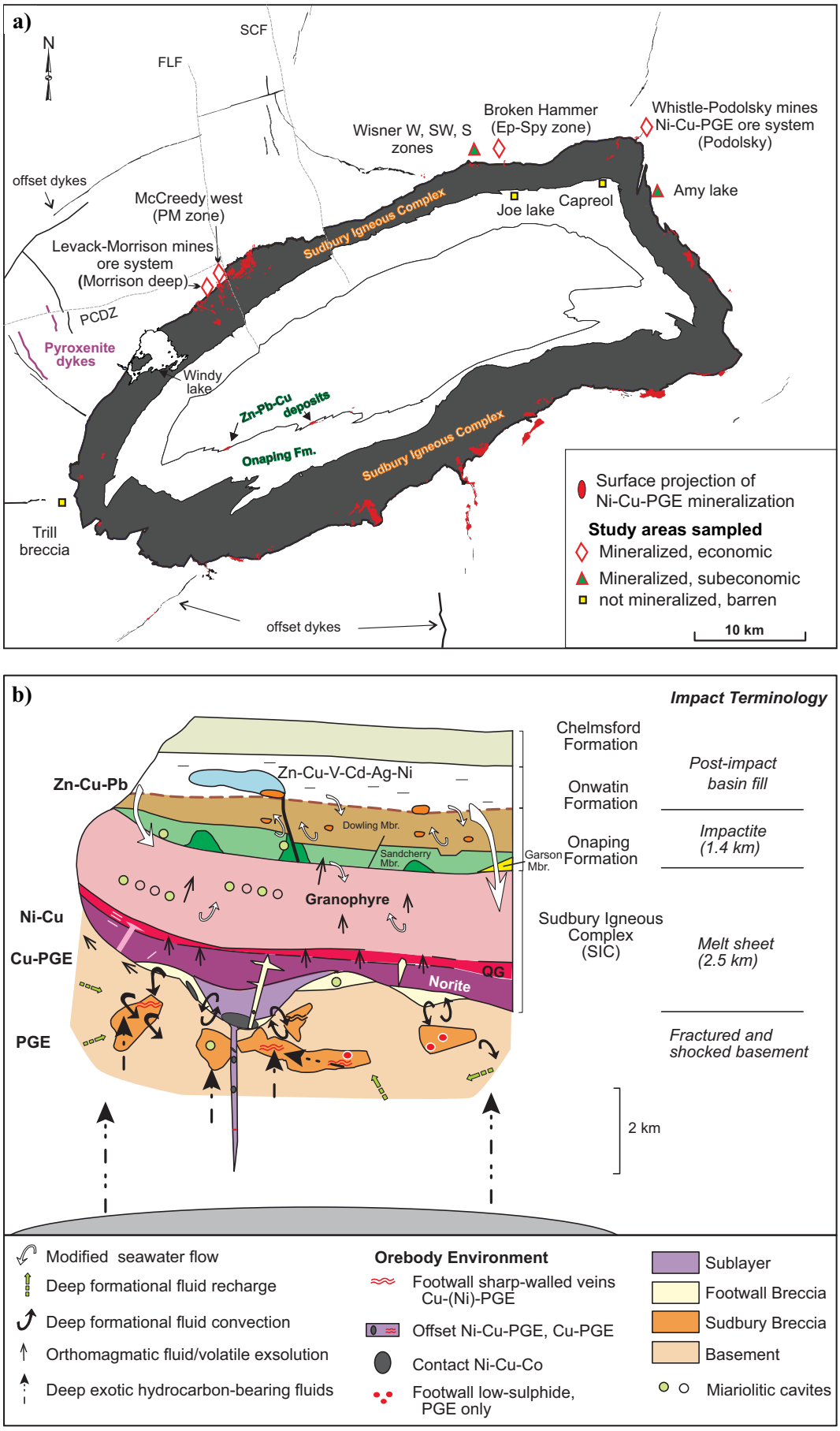


Figure 1. a) Location map of the barren and mineralized hydrothermal alteration studied in the Sudbury structure. **b)** Schematic section of the Sudbury hydrothermal system showing the relative stratigraphic location of ore types, fluid sources, and fluid/volatile flow (after Ames and Farrow, 2007). Abbreviations:
Ep = epiidote;
FLF = Flack Lake fault;
Fm = Formation;
PCDZ = Pumphouse Creek deformation zone;
SCF = Sandcherry Creek fault;
Spy = sperrylite.

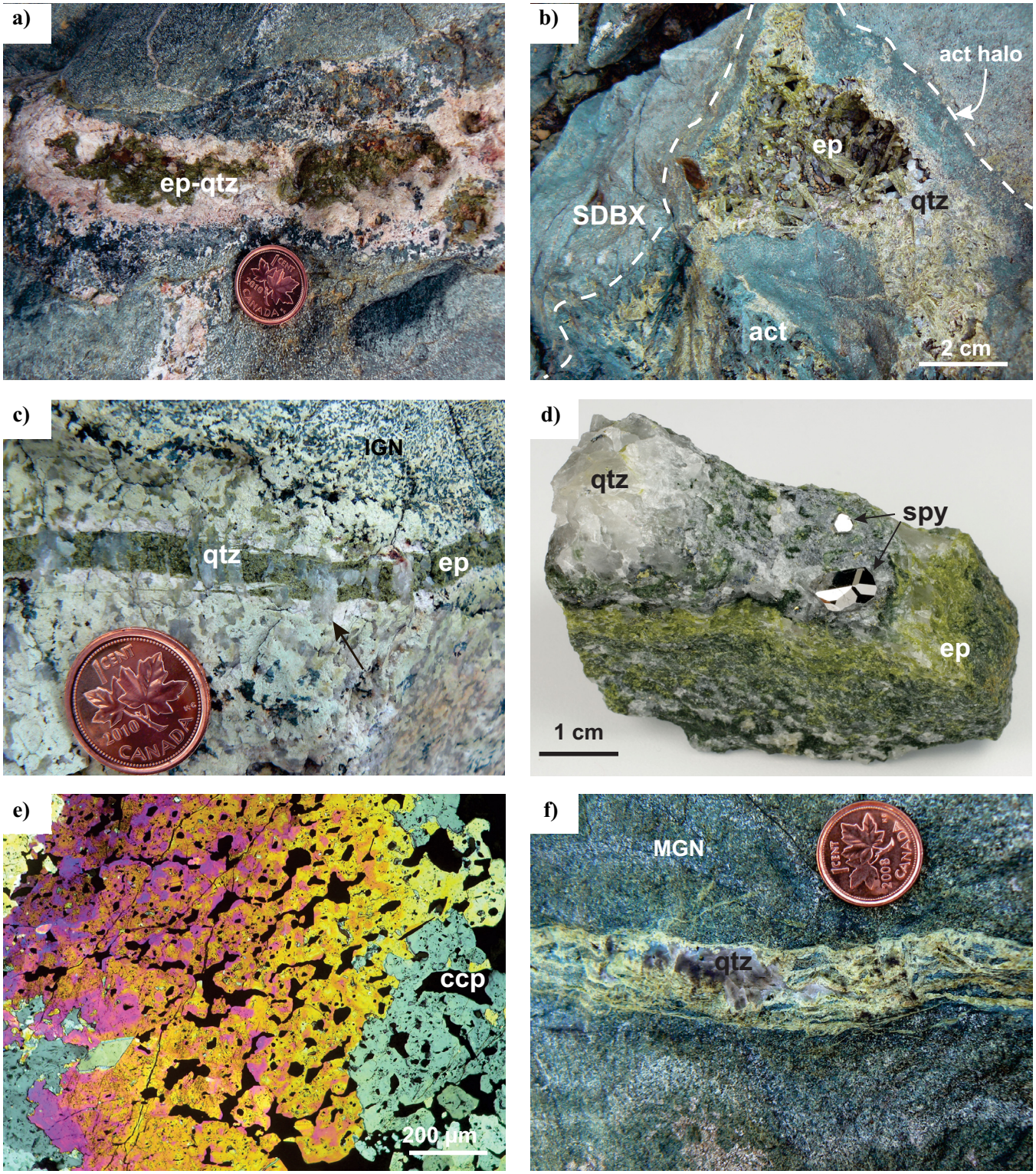


Figure 2. Examples of pre-, syn-, and post-mineralization epidote in the Sudbury structure. **a)** Miarolitic cavity in footwall granophyre, filled by epidote and quartz. Coin is 2 cm. **b)** Pre-sulphide, high-PGE, coarse prismatic epidote-quartz-actinolite open-space filling assemblage in Sudbury Breccia. Note the fine-grained amphibole halo. **c)** Extensional epidote-quartz vein cross-cuts intermediate gneiss with an overgrowth of rock-forming quartz into the vein cavity (arrow). This is a typical feature of barren extensional epidote-quartz veins. **d)** Hand sample of quartz-epidote-euhedral sperrylite ($PtAs_2$) assemblage from the margin of the Broken Hammer bulk sample pit. Note the bonanza platinum mineralization and absence of sulphide minerals. **e)** Poikilitic intergrowth of epidote and chalcopyrite, the characteristic textural feature of footwall high- and low-S mineralization. **f)** Example of a late, post-Sudbury shear-type epidote-quartz vein within mafic gneiss. Abbreviations: act = actinolite; ccp = chalcopyrite; ep = epidote; IGN = indiate gneiss; MGN = mafic gneiss; qtz = quartz; SDBX = Sudbury Breccia; spy = sperylitte.

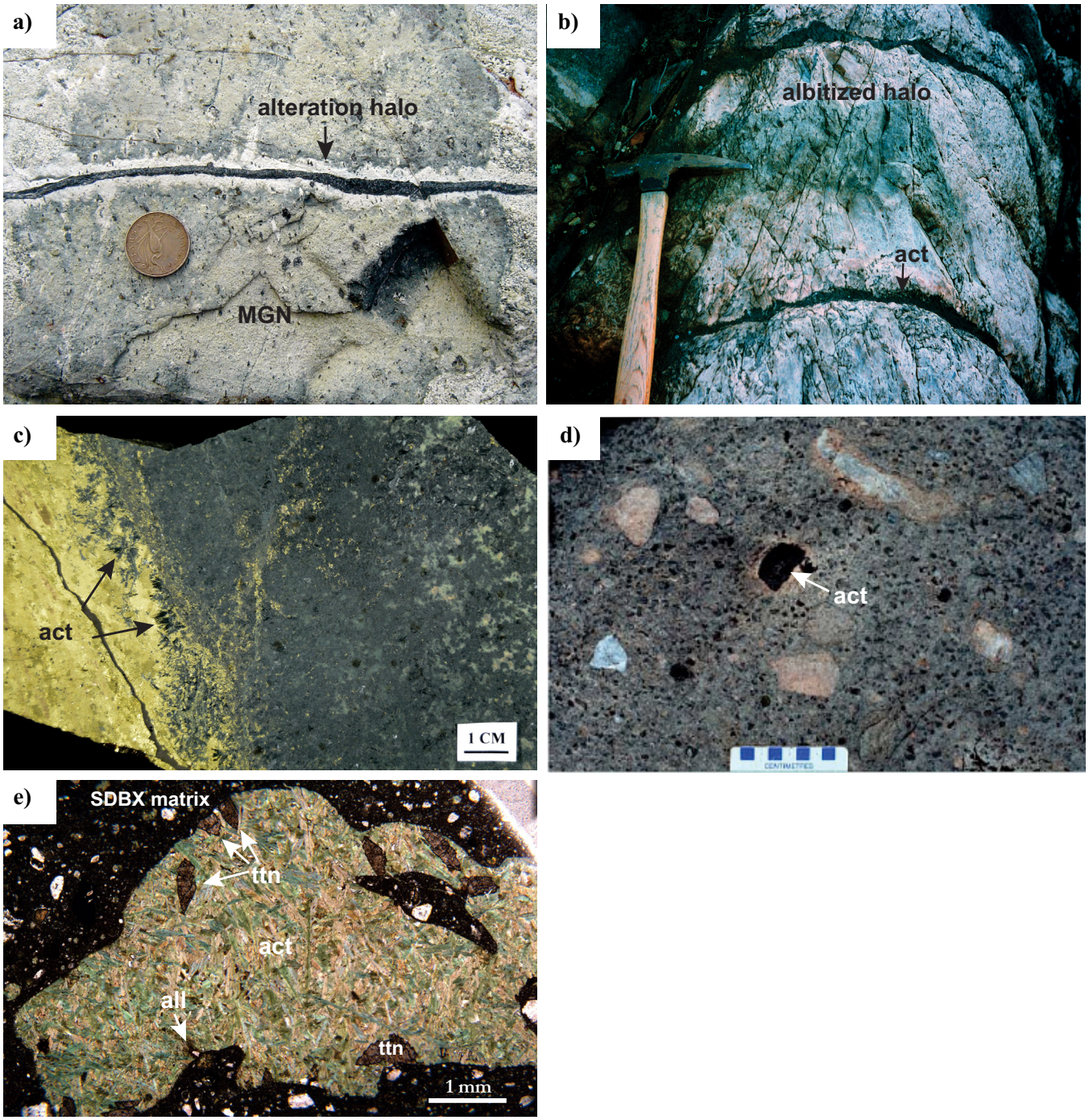


Figure 3. Diverse barren and mineralized alteration zones with amphibole in veins, amygdules, and replacement zones in the footwall and hanging wall of the Sudbury Igneous Complex. **a)** Amphibole vein in mafic gneiss, Amy Lake area. Note the white alteration halo of recrystallized feldspar, similar to that of the pre-sulphide pervasive and vein assemblages. **b)** Amphibole veins above the SIC in the Onaping Formation. Close-up of 1–2 cm actinolite veins and 12–18 cm alteration haloes within in a 3 m diameter zone with pervasive albite-quartz alteration haloes in close proximity to a fluidal breccia sill-dyke complex, Rockcut Lake, Capreol. **c)** Coarse amphibole (arrows) at the margin of a sharp-walled chalcopyrite-PGE vein and gabbro, Podolsky mine. **d)** Intense albitization in hanging-wall andesite breccia, Sandcherry member, Onaping Formation, with actinolite-filled amygdule (arrow). The altered equant-shard unit contains partially albitized (pink hue) quartzite fragments, matrix, and shards. Shards are actinolite-rich. Actinolite occurs in patches rimmed by albite and vice versa, Joe Lake area. **e)** Photomicrograph of amygdules filled with coarse amphibole (actinolite), titanite, and trace allanite hosted in Sudbury breccia, Trill area. Abbreviations: act = actinolite; all = allanite; MGN = mafic gneiss; SDBX = Sudbury Breccia; ttn = titanite.

Table 1. Summary of alteration styles and minerals analyzed in barren and mineralized environments.

Alteration type	Epidote	Allanite	Amphibole	Titanite	Mineralization style
Miarolitic cavities	coarse prismatic	in epidote core	coarse euhedral	euhedral	barren
Pervasive epidote-amphibole alteration, pre-sulphide mineralization	coarse prismatic	in epidote core	coarse euhedral, fibrous in halo		barren; occasionally high PGE
Epidote vein, pre-sulphide mineralization	coarse prismatic		fibrous in halo	euhedral	barren
Amphibole amygdules		euhedral -Trill	acicular -Trill coarse euhedral -Onaping	coarse euhedral (Trill only)	barren
1. Broken Hammer epidote-quartz-sperrylite assemblage	coarse prismatic				high PGE
2. Footwall mineralization, extensional silicate vein	coarse prismatic (in epidote-quartz veins)		acicular euhedral (in amphibole veins)	euhedral (in amphibole veins)	occasionally high PGE; barren
3. Footwall mineralization, sulphide-silicate assemblage	poikilitic		euhedral		high- and low-sulphide, high-PGE
Post-Sudbury shear-type veins	fine- to medium-grained euhedral				barren

amphibole (Fig. 2c), epidote-quartz veins (Fig. 2b), and amygdules in Sudbury breccia (Fig. 3a). The epidote-quartz-sperrylite ($PtAs_2$) bonanza ore at Broken Hammer (Ames et al., 2014), (Fig. 2d) is pre-sulphide mineralization and early in the mineralizing sequence, followed by extensional silicate veins (Fig. 2b) that are cut by high-sulphide chalcopyrite-rich sharp-walled veins that may contain marginal amphibole (Fig. 2c) or poikilitic epidote (Fig. 3e). Late "post-Sudbury", shear-type epidote-quartz veins are the youngest alteration assemblage studied in the footwall environment. Amphibole veins with albitized margins are present in the footwall and hanging wall, as are amphibole-filled amygdules whose paragenetic sequence is unknown (Fig. 3a,b,d,e).

To properly classify and fingerprint alteration assemblages indicative of Sudbury footwall (Cu)-PGE mineralization, an extensive suite of 62 samples and four alteration minerals representing a diversity of post-impact alteration assemblages were analysed in situ by LA-ICP-MS and electron microprobe. Trace element data of 54 elements were collected from epidote, allanite, amphibole, and titanite to establish typical element-associations and classification criteria, with special emphasis on alteration assemblages associated with PGE mineralization, to test the robustness of the PGE-ore geochemical fingerprint identified earlier from a smaller dataset (Tuba et al., 2014).

Background host-rock compositions were determined from representative least-altered host rocks that were collected distal to the altered sample in the same locality and were used to normalize the epidote mineral chemistry (Table A1 in Tuba and Ames, in press). Normalization of the mineral chemical data to bulk host-rock composition eliminates the chemical effects of fluid-rock alteration that were significant in a few of the alteration assemblages. The complete mineralogical and geochemical dataset, including detailed descriptions, the full mineral chemical databases, and methodologies used (electron microprobe and laser ablation ICP-MS of epidote, allanite, amphibole, and titanate) can be found in Tuba and Ames (2015).

Samples collected from North Range footwall environments include the Deep zone of the Morrison deposit, the PM zone of the McCreedy West deposit, the North zone of the Podolsky deposit, the epidote-quartz-sperrylite zone of the Broken Hammer deposit, all with economic low-sulphide PGE mineralization. Exploration trenches exposing sub-economic low-sulphide mineralization at Wisner West, Southwest and South zones in the North Range as well as Amy Lake-PGE zone in the East Range were also sampled (Fig. 1). Hydrothermal alteration is present in the SIC's footwall and hanging wall, with similar mineral assemblages but lacking PGE mineralization. These barren hydrothermally altered rocks were collected in the Trill and Windy Lake footwall environment and in the Joe and Rockcut Lake areas in the hanging-wall environment, along the North and East ranges (Ames and Gibson, 2004 a,b) (Fig. 1).

RESULTS AND DATA ANALYSIS

Epidote is a ubiquitous mineral in many barren and mineralized alteration assemblages along the Sudbury

North Range (Table 1, Fig. 1b). Epidote associated with Sudbury Cu-PGE and PGE deposits has similar major-element compositional ranges with $Fe^{3+}/(Fe^{3+}+Al)$ compositions, (X_{Fe}= 0.18–0.37) and average ratios (X_{Fe}=26, n=72 high-S, and n=41 low-S; Ames et al., 2015) that generally imply oxidizing conditions for low-sulphide PGE-rich mineralization. However, the major-element substitution is complicated as it can be also affected by temperature, fluid, and bulk-rock compositions, CO_2 fugacity, and pressure (Arnason et al., 1993). In addition, the rare-earth and trace-element compositions of the common minerals epidote and amphibole and accessory minerals allanite and titanite were characterized. The elements analysed in minerals were plotted on three diagrams and include (1) pathfinder elements — Co, Ni, Cu, Zn, As, Pd, Ag, Sn, Sb, Pt, Au, Pb, and Bi; (2) other elements — Mg, Sc, V, Cr, Mn, Rb, Sr, Y, Zr, Nb, Mo, Rh, Cd, Cs, Ba, Th, and U; and then (3) rare-earth elements (Figs. 4, 5). Elements close to the detection limit of the ICP-MS in both epidote and amphibole, included Ag, Sb, Pt, Au, Bi, Mo, Rh, Cd, and Cs, and others usually detected in very low concentrations regardless of the alteration type include Pd and Bi in epidote.

Rare-Earth Element Characteristics of Epidote-Allanite, Amphibole, and Titanite

The mineral trace-element data were normalized to the bulk rock geochemistry of the host rock for all data to minimize the influence of host rock (Tuba and Ames, 2015: Table A1). Trace element data show that certain rare-earth element (REE) patterns are more frequent in some alteration groups, although REE concentrations vary significantly within these groups and, in some cases, even within a sample (Fig. 4). The most useful feature of the host rock-normalized REE plots in the characterization of the alteration groups is the diagram topology, whereas other features (e.g. size of Eu anomaly, level of REE-enrichment of a single mineral) do not show systematic variations. Classification of the alteration groups based on mathematically expressed La:Lu (or other light REE:heavy REE) ratios was not possible as individual analyses in heterogeneous samples may scatter in a wide range; therefore the topology of REE plots defined by all analyses in a given sample (typically around 10 ablation spots) was studied. A REE pattern was considered characteristic if it appeared in about 90% of the samples within an alteration group. The presence or absence of the three REE-bearing minerals epidote, titanite, and allanite strongly affects the patterns of individual minerals in the various alteration assemblages (Fig. 5) (Tuba and Ames, 2015).

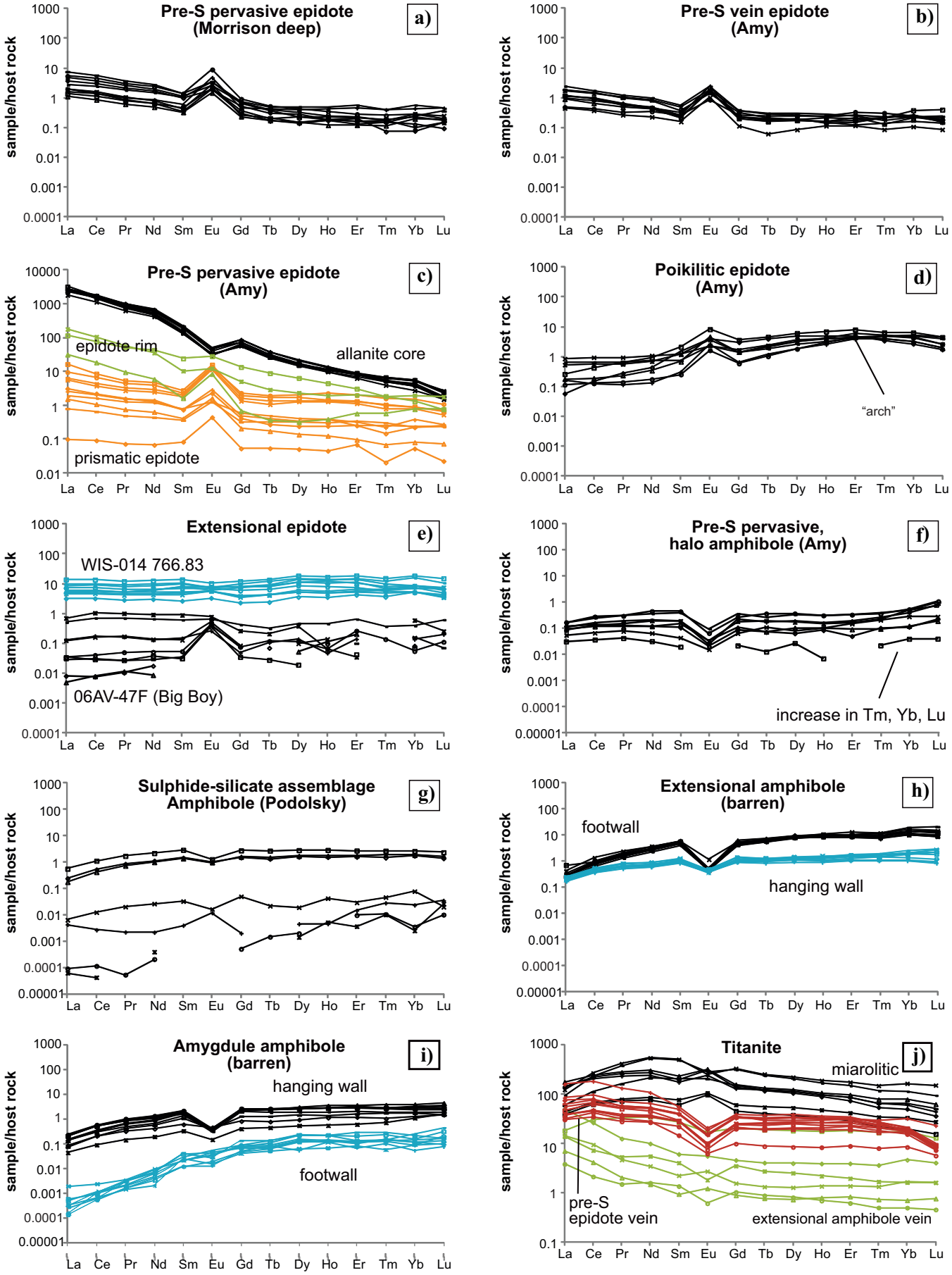
The overall REE content of the alteration assemblages is strongly dependent on the presence of allanite and titanite. Miarolitic cavities and pervasive epidote-amphibole alteration contained minerals bearing the highest concentrations of REE (titanite average REE_{tot} = 9,256 ppm, and allanite average REE_{tot} =144,260 ppm, respectively), (Fig. 5). Titanite in amphibole amygdules in the Trill Sudbury breccia has similar REE levels as the titanite in pre-sulphide epidote veins (Fig. 5a,e). The REE content of titanite decreases more in the pre-sulphide epidote veins than in the mineralization-related extensional actinolite veins (Fig. 5f). Epidote is the main REE-carrier in extensional epidote veins, mineralized sulphide-silicate assemblages, and late shear-type veins; these assemblages are generally low in REE (REE_{tot} = 76–286 ppm) with the exception of extensional epidote and actinolite veins from the vicinity of the Broken Hammer sperrylite zone, which are unusually enriched (average REE_{tot} = 1,382 ppm).

Epidote and amphibole in the different alteration assemblages exhibit host–rock-normalized REE patterns with characteristic topologies that are best described with nLREE to nHREE relations (Fig. 4). High-REE (with additional Y, Th, and U) assemblages are found in miarolitic cavities and pervasive epidote-amphibole alteration that predate the Sudbury footwall mineralization as these contain the REE-rich minerals allanite and titanite, whereas, in other alteration styles these minerals are absent. Vein-type pre-sulphide assemblages are comparably lower in REE, whereas sulphide-silicate assemblages of footwall mineralization and associated extensional silicate veins, as well as post-Sudbury shear-type veins are REE-poor.

Pathfinder Mineral Chemistry of Epidote-Allanite and Amphibole

Epidote-Group Minerals

Of all of the >25 trace elements analysed in epidote, Pb and Ni proved to be most useful for classifying the alteration groups. Epidote-bearing assemblages predating the sulphide Cu-PGE mineralization are dominantly lower in Pb (<5 ppm) than those associated with the sulphide-bearing system, although the two groups overlap slightly (Fig. 6a,b). Among the pre-sulphide assemblages, Ni is lowest (<1 ppm) in the miarolitic epidote, and highest (typically a few 100 ppm) in the high-PGE pervasively epidotized alteration. Vein-type epidote and most of the low-PGE pervasive epidote plot in between. Nickel in poikilitic epidote of the sulphide-silicate assemblage and in extensional veins ranges widely from ~0.1 to 300 ppm). Although the pre-sulphide and sulphide-bearing systems may be distinguished based on the Pb content of epidote, the Pb and Ni values of epidote in post-Sudbury shear-type veins overlap with both groups. The observations regarding Pb and Ni patterns as discussed above are


a)
Pre-S pervasive epidote
(Morrison deep)
b)
Pre-S vein epidote
(Amy)
c)
Pre-S pervasive epidote
(Amy)
epidote rim
allanite core
prismatic epidote
d)
Poikilitic epidote
(Amy)
"arch"
e)
Extensional epidote
WIS-014 766.83
06AV-47F (Big Boy)
f)
Pre-S pervasive,
halo amphibole (Amy)
increase in Tm, Yb, Lu
g)
Sulphide-silicate assemblage
Amphibole (Podolsky)
h)
Extensional amphibole
(barren)
footwall
hanging wall
i)
Amygdule amphibole
(barren)
hanging wall
footwall
j)
Titanite
miarolitic
pre-S
epidote vein
extensional amphibole vein
sample/host rock
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

generally in agreement with the findings of Tuba et al. (2014).

The positive correlation previously found between Co and Ni in epidote (Tuba et al., 2014) is less pronounced in this extended database (Fig. 6c,d). A strong positive correlation between these elements does occur in poikilitic epidote (and a weaker correlation in the shear-type epidote group); however, there is no clear linear relationship between Co and Ni in other alteration groups. There is a link between these elements in the fluids associated with footwall PGE mineralization. Furthermore, comparison of the absolute and host-rock normalized Co versus Ni plots (Fig. 6c,d) shows that the host-rock composition influenced the concentration of Co in epidote in most alteration assemblages. Significantly, the late shear-type and PGE-mineralized poikilitic epidote samples do not show a major change in the topology of Co versus Ni plots and thus, are not affected by wall rock.

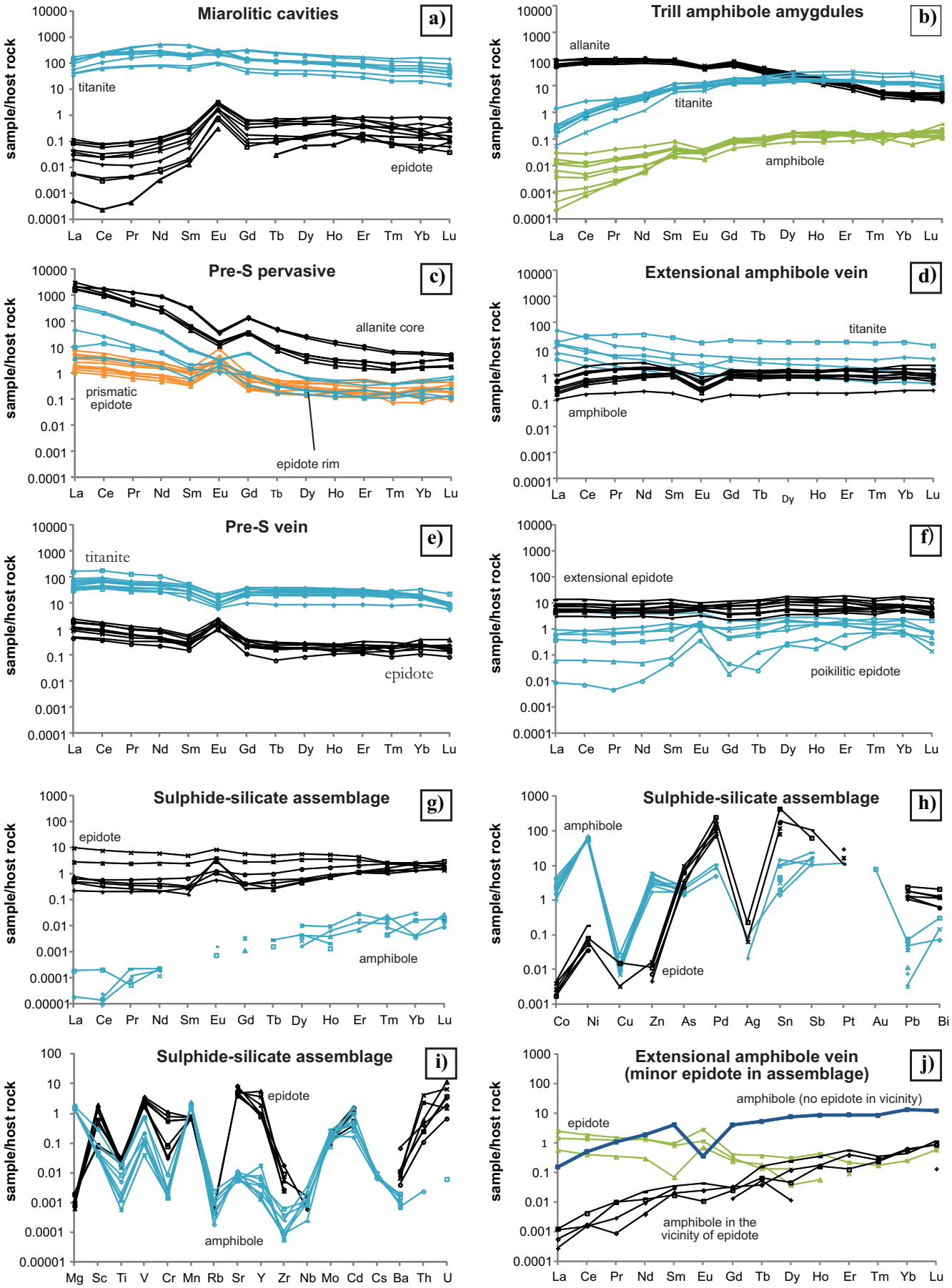
Amphibole and Chlorite

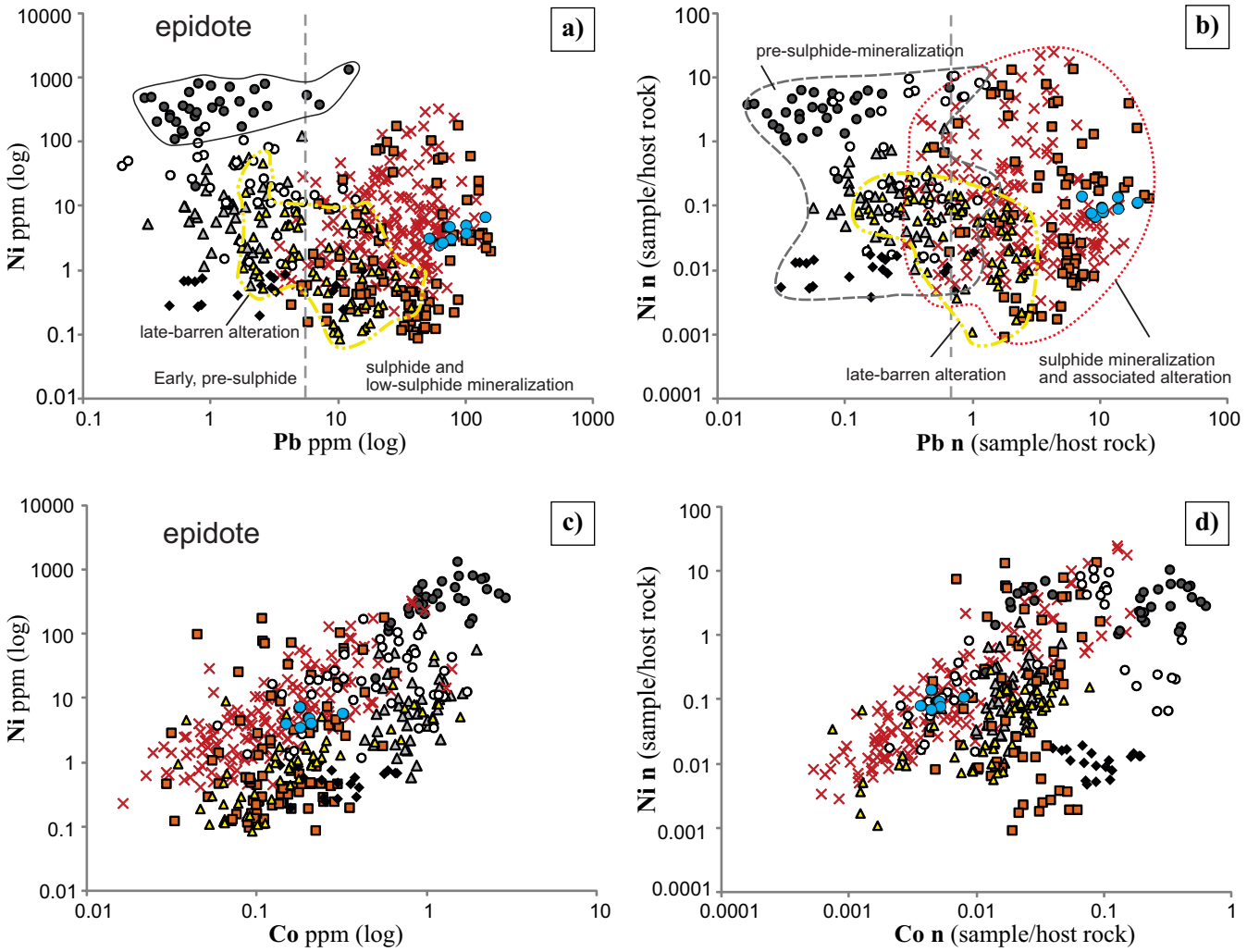
The Ni content is highest in chlorite (<3.4 wt%), followed by amphibole (<1.3 wt%) and biotite (<1 wt%) and also occurs in epidote and stilpnomelane in the mineralized footwall environment (Ames et al., 2013). The magnesian- and nickel-rich compositions of chlorite associated with both low-sulphide-PGE and sharp-walled-vein Cu-PGE mineralization has been recognized (Péntek et al., 2008; Tuba et. al., 2010; Ames and Kjarsgaard, 2013) and is also manifested by Ni-rich amphibole in alteration assemblages produced in higher contact metamorphic grades in the thermal aureole of the SIC (Hanley and Bray, 2009). Ni-enriched ferromagnesian phases identified proximal to Ni-Cu-PGE mineralization include amphibole, chlorite, and biotite (Farrow and Watkinson, 1992; Hanley et al., 2011; White, 2010; Warren et al., 2015). Systematic sampling towards high-sulphide Cu-PGE veins in the footwall identified a vectoring tool using Ni in amphibole (Hanley and Bray, 2009). However, the usefulness of these observations are significant to PGE fertility only when comparing these compositions with other amphibole in the Sudbury environment to detect a unique signature for alteration related to the high-tenor PGE mineralization.

Amphibole-bearing assemblages may be fingerprinted based on their Ni and Sn content (Fig. 7). Pre-sulphide, pervasively altered assemblages associated with high-PGE contain the highest amounts of Ni (0.2 wt% Ni average) in amphibole that occurs with both prismatic epidote and forms the finer grained actinolite halo around the alteration (Fig. 3b). The actinolite halo around pre-sulphide epidote veins, as well as amphibole-filled amygdules in Sudbury breccia are both Ni-poor (<300 ppm). Euhedral amphibole in sulphide-silicate assemblages in the low-sulphide footwall mineralization is enriched in Ni, with values above 0.1 wt% and as high as 1 wt% Ni. Such high concentration of Ni in this type of amphibole was already known from the Sudbury footwall (Farrow, 1994; Magyarosi et al., 2002; Kjarsgaard and Ames, 2010; Tuba et al., 2010, 2014). Unmineralized extensional amphibole veins fall into the low-Ni area of the diagrams, typically with 100–200 ppm Ni; among them, however, two samples with trace microscopic chalcopyrite had anomalous bulk PGE contents (0.01 ppm) and plot closer to the high-PGE field. The Ni content of amphibole in high-PGE extensional veins (samples 12AV-15B and BLT-06) is typically 0.04 to 0.1 wt%.

Nickel content in extensional amphibole as a function of bulk total precious metal content and/or proximity to footwall mineralization was documented by Hanley and Bray (2009) and Tuba et al. (2010). Tin in amphibole is also enriched (>1 ppm) in sulphide-silicate assemblages and extensional amphibole veins in footwall ore systems, whereas the concentrations of Sn in the extensional amphibole veins from the hanging wall (Onaping Formation) are below 1 ppm.

Figure 4 (opposite page). Representative examples of the rare earth element (REE) distribution patterns in pre-sulphide epidote, amphibole, titanite, and sulphide-silicate assemblages. Typical REE pattern of pre-sulphide epidote in **(a)** pervasive replacement (sample 08AV-05A) and **(b)** vein epidote (sample 12AV-63) assemblages with moderate negative slope and pronounced Eu anomaly. The slightly negative slope is characteristic and discriminatory of pre-sulphide epidote. **c)** REE patterns of pre-sulphide pervasive alteration with coexisting allanite and epidote (sample 12AV-60). **d)** "Arch-like" heavy REE pattern of poikilitic epidote associated with platinum-group element (PGE) mineralization (sample FAL-12). **e)** REE pattern in extensional epidote is commonly flat with a slight Eu anomaly. The anomaly increases with decreasing concentrations of REE. **f)** A slight increase in Tm, Yb, and Lu is visible in the REE plots of pre-sulphide amphibole (sample 12AV-60). **g)** Euhedral amphibole from the mineralized sulphide-silicate assemblage is usually low in REE and may show large intra-sample variations (sample 11AV-62F). **h)** Typical REE pattern of extensional amphibole from both the footwall (sample BLT-05) and hanging wall (sample AV-488B) of the Sudbury Igneous Complex(SIC), which show a similar topology to the **(i)** hanging-wall actinolite amygdules (Joe Lake Onaping Formation, sample AV-524A) as they are all mono-mineralic assemblages. This is in contrast to the amphibole assemblage with allanite and titanite in the footwall amygdules (Trill Sudbury Breccia) below the SIC. **j)** REE in titanite decreases from the miarolitic cavities (sample 12AV-57) to pre-sulphide (pre-S) epidote veins (sample 12AV-63) and extensional amphibole veins (sample 12AV-78).


a)
Miarolitic cavities
titanite
epidote
b)
Trill amphibole amygdules
allanite
titanite
amphibole
c)
Pre-S pervasive
allanite core
prismatic epidote
epidote rim
d)
Extensional amphibole vein
titanite
amphibole
e)
Pre-S vein
titanite
epidote
f)
extensional epidote
poikilitic epidote
g)
Sulphide-silicate assemblage
epidote
amphibole
h)
Sulphide-silicate assemblage
amphibole
epidote
i)
Sulphide-silicate assemblage
epidote
amphibole
j)
Extensional amphibole vein
(minor epidote in assemblage)
amphibole (no epidote in vicinity)
epidote
amphibole in the vicinity of epidote
sample/host rock
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Co Ni Cu Zn As Pd Ag Sn Sb Pt Au Pb Bi
Mg Sc Ti V Cr Mn Rb Sr Y Zr Nb Mo Cd Cs Ba Th U



Epidote legend

Pre-sulphide-mineralization

- miarolitic cavities
- pervasive epidote-amphibole (high-PGE)
- pervasive epidote-amphibole (low-PGE)
- epidote vein

Footwall mineralization

- sulphide-silicate assemblage
- extensional epidote-quartz veins
- epidote-quartz-sperrylite assemblage (Broken Hammer)

Post-Sudbury alteration

- shear-type veins

Figure 6. Results for epidote from multiple hydrothermal assemblages showing the relationship of important pathfinder elements, Ni, Pb, and Co, on absolute, and host-rock normalized concentration plots. **a)** Absolute concentration plot of Pb versus Ni, and **(b)** host-rock normalized Pb versus Ni diagram. Vertical dashed line at 5 ppm Pb. Barren and PGE-enriched, pre-sulphide assemblages may be distinguished from those associated with low-sulphide footwall mineralization based on the lower Pb content (vertical dashed line is at 5 ppm Pb). Post-Sudbury shear-type veins (yellow outline) overlap with both groups. Among pre-sulphide assemblages, high-PGE pervasive epidote samples show the highest Ni values. **c)** Absolute and **d)** host-rock normalized concentration of Co and Ni in epidote. Note the pronounced difference in the topologies of alteration groups in the two plots, indicating the effect of host-rock composition on the Co concentration in all assemblages, except for poikilitic and shear-type epidote. Co and Ni correlates well in the sulphide-silicate assemblage (poikilitic epidote).

Figure 5 (opposite page). Representative rare earth element (REE) plots of epidote-, amphibole-, titanite-, and allanite-bearing alteration assemblages showing the mineral reservoirs for REE in paragenetic order from early pre-sulphide to syn-sulphide assemblages **(a-f)**. A gradual decrease in bulk REE can be observed with higher REE concentrations associated with pre-sulphide assemblages (pervasive: sample 08AV-05A, vein: sample 12AV-63) and low REE being typical for footwall mineralization systems (poikilitic epidote: sample 06AV-37A, extensional amphibole vein: sample 12AV-78, extensional epidote vein: sample WIS-014 766.83). Allanite and titanite in the Trill amphibole amygdule assemblage (sample TR-1005) shows REE values as high as silicates in the miarolitic cavities (sample 12AV-57) and pre-sulphide epidote veins. **g-j)** Element partitioning between epidote (black) and amphibole (blue) in a mineralized sulphide-silicate assemblage at the Podolsky deposit (sample 02AV-642, bornite-bearing) showing **(g)** REE profiles, **(h)** pathfinder element suite and **(i)** other trace elements. Similar element partitioning between epidote and amphibole was found in additional 11 samples. **(j)** Characteristic epidote-amphibole and amphibole-only REE patterns where the epidote-free pattern has a positive slope and pronounced negative europium anomaly.

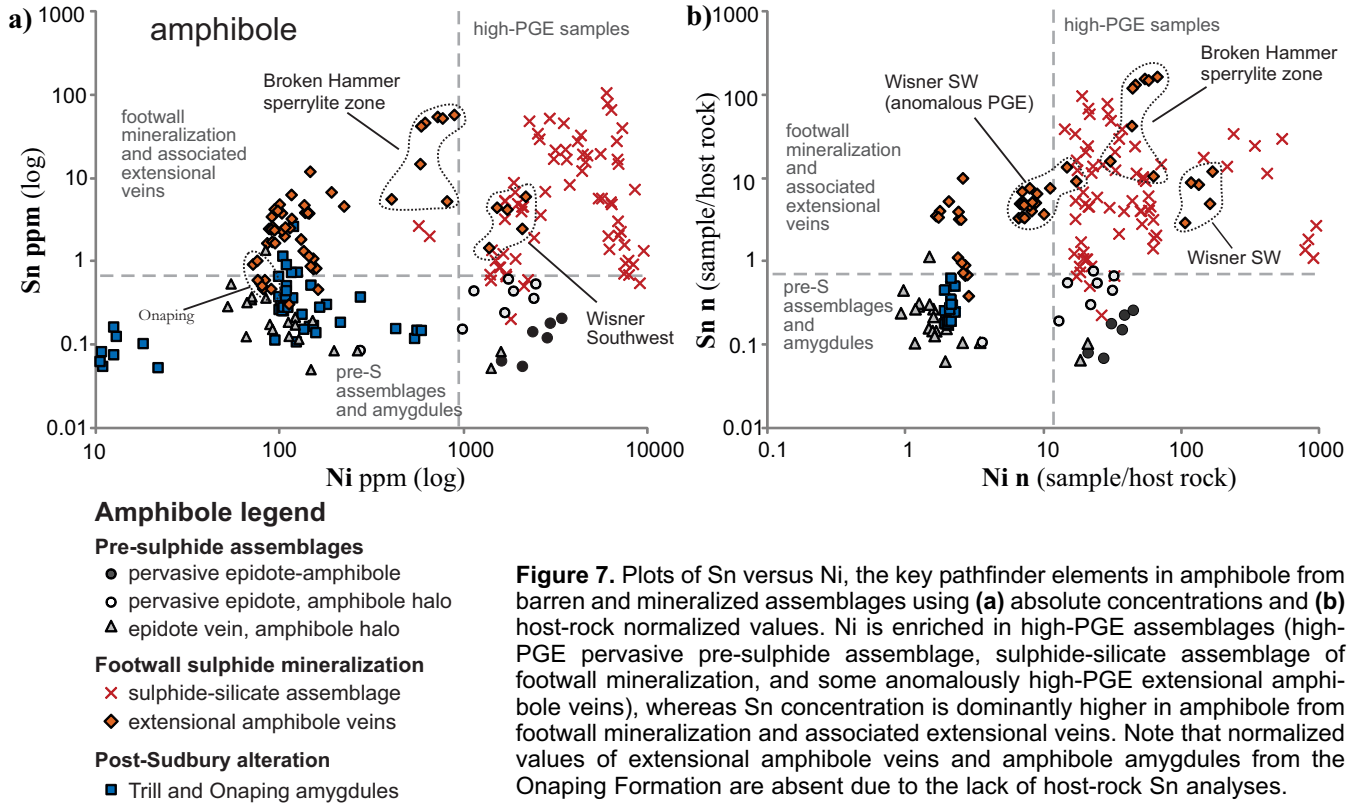


Figure 7. Plots of Sn versus Ni, the key pathfinder elements in amphibole from barren and mineralized assemblages using **(a)** absolute concentrations and **(b)** host-rock normalized values. Ni is enriched in high-PGE assemblages (high-PGE pervasive pre-sulphide assemblage, sulphide-silicate assemblage of footwall mineralization, and some anomalously high-PGE extensional amphibole veins), whereas Sn concentration is dominantly higher in amphibole from footwall mineralization and associated extensional veins. Note that normalized values of extensional amphibole veins and amphibole amygdules from the Onaping Formation are absent due to the lack of host-rock Sn analyses.

DISCUSSION

The alteration minerals quartz, carbonate, chlorite, epidote, and amphibole and accessory titanite and allanite are found in diverse ore-system settings with volcanogenic massive sulphide (VMS), porphyry, gold, and Ni-Cu-PGE deposits. The major elements Fe^{3+} and Al^{3+} of epidote in various mineralizing and barren settings have been used to determine the redox and/or temperature conditions of epidote alteration zones in modern and ancient volcanogenic massive sulphide and recently in porphyry systems (Hannington et al., 2003 and references therein; Frikken et al., 2005; Cooke et al., 2014). Many authors working on different low-sulphide footwall PGE mineralization zones in the Sudbury Ni-Cu-PGE mining district (e.g. White (2010): Vale properties; Tuba (2010): Wallbridge properties; Ames (2005–2010): FNX, Wallbridge and Vale properties) simultaneously recognized poikilitic epidote spatially associated with low-sulphide PGE and some high-sulphide Cu-PGE mineralization.

The trace element contents in minerals are influenced by (1) fluid/melt composition, (2) host-rock composition, and/or (3) co-precipitating minerals. In order to rule out the latter as a major influence on trace element distribution in paragenetically different alteration assemblages, coeval mineral pairs were tested for element partitioning.

Significance of Host-Rock Normalized Mineral Chemistry

Normalization of the data to the composition of the host rock does not usually result in major differences between the topology of the two diagrams — one showing the absolute and the other the normalized values — just "tightening up" the samples within the groups by removing outliers (Figs. 6, 7). As such, the relative position of the groups generally does not change but where it does, it likely indicates that fluid-rock interaction had an impact on certain alteration assemblages. For example, normalizing As in epidote results in a significant shift of poikilitic samples though others preserve their relative position, suggesting that As in the sulphide-silicate assemblage is at least partly dependent on the host rock. Similarly Zn is also host-rock dependent in mineralized and extensional silicate assemblages.

Pathfinder elements Ni, Pb, Sn, and Co are most distinctive in fingerprinting the ore-bearing alteration assemblages. The highest concentrations are associated with silicates from footwall mineralization and the accompanying extensional veins, emphasizing the genetic link between the two assemblages. High-PGE pre-sulphide assemblages are characterized by high Ni and Co but low Pb and Sn values. Other assemblages are notably depleted in these elements. The topologies of the Pb versus Ni diagrams are very similar, regardless of the values plotted (absolute concentrations in

ppm or host-rock normalized values; Fig. 6a and b, respectively), suggesting that the concentrations of these elements are not a function of host-rock composition but rather of fluid composition. The elements Ni, Co, Pb, and Sn are the discriminant elements in epidote and/or amphibole, as the highest amounts of Ni, Co, Pb, and Sn was found in epidote and amphibole in footwall ore as well as in high-PGE pre-sulphide samples that contain Ni-sulphides and significant amounts of Pb- and Sn-bearing trace minerals. High Ni-values in the minerals are also associated with high-PGE pre-sulphide samples, where minor to trace millerite may be present. Sn is more erratic, with only the poikilitic epidote in the selvage of the cassiterite-millerite-bearing sharp-walled vein at Broken Hammer having a high Sn-Ni correlation (Ames et al., 2007). Pre-existing structures provide permeable pathways for the mineralizing fluids; hence, some extensional amphibole and/or epidote-quartz veins are PGE enriched and others are not (Table 1). The amounts of REE, Y, Th, and U are interpreted to reflect the composition of the parental fluids; low-S mineralization is not distinctive based on these elements.

Possible Controls on the Trace Element Distribution in Epidote

Element Partitioning among Minerals

Trace element partitioning between epidote and amphibole, the two most common alteration minerals in the Sudbury footwall, was tested on 12 samples. Element partitioning between titanite and amphibole and between titanite and epidote were tested with a smaller dataset (n= 4 samples; Table 2). The trace element concentration of epidote/amphibole may be influenced by (1) the parental fluid composition (e.g. REE, U, Th, Ni, Pb, Sn), (2) host rock, particularly mafic rocks (e.g. As, Zn), and/or (3) the crystal structural properties of the minerals (e.g. Mg and Sr in epidote).

In samples with coexisting epidote and amphibole, epidote appears to have preferentially incorporated REE, Pb, Bi, and Sn, amphibole is significantly enriched in Co, Ni, and Zn, and As is distributed equally between the two minerals (Table 2; see Fig. 13a to c in Tuba and Ames, in press). The systematic distribution of REE was observed in all of these samples (Fig. 4), and over 90% of the samples showed the same partitioning of the pathfinder elements (Pb, Bi, Sn, Co, Ni, Zn, As, Cu). Copper prefers amphibole or is distributed equally between the two minerals, whereas Pd and Ag are never enriched in amphibole. The behaviour of Sb was found to be erratic.

This partitioning behaviour has a significant effect on the topology of REE plots, and, in fact, may be an explanation for some REE patterns that differ profoundly from the average, most frequent REE patterns in the same alteration group. The typically low-REE content of euhedral actinolite in the mineralized sulphide-silicate assemblage is likely due to the REE-scavenging behaviour of the poikilitic epidote with which the amphibole is associated (Fig. 4a). Whereas, in amphibole-dominated, essentially monomineralic assemblages (e.g. extensional actinolite veins and Onaping amygdules) where the amphibole is the main REE-bearing phase, it is significantly more enriched in REE than the amphibole occurring with epidote, titanite, or allanite in other assemblages (Fig. 4 h,i).

Element partitioning between titanite and amphibole as well as titanite and epidote from four samples representing three alteration groups (miarolitic cavities, extensional amphibole veins, and Sudbury breccia-hosted amygdules) showed that REE, Sn, Zr, Nb, Yb, Th, and U partition preferentially into titanite and Co, Ni and Zn into amphibole (Tuba and Ames, in press).

Table 2. Summary of systematic element partitioning among coexisting minerals in footwall alteration zones.

Mineral	REE and pathfinder elements	Other trace elements
Epidote-amphibole		
ep>amph	REE, Pb, Bi, Sn	Sr, U
amph>ep	Co, Ni, Zn	Mn, Rb
ep~amph	As	
Based on 12 samples representing 4 alteration groups. Observed frequency of given element distribution among mineral pairs: min. 90%.		
Titanite-amphibole		
ttn>amph	REE, Sn, Bi	V, Y, Zr, Nb, Mo, Th, U
amph>ttn	Co, Ni, Zn	Sc, Mn, Ba
ttn~amph	Cu	Rb
Based on 4 samples representing 2 alteration groups. Observed frequency of given element distribution among mineral pairs: 100%.		
Titanite-epidote		
ttn>ep	REE, As, Sn, Pb	Sc, V, Cr, Y, Zr, Nb, Mo, Th, U
ep>ttn	Co	Mn, Sr
ttn~ep	Zn, Sb	Mg, Ba
Based on 2 samples representing 2 alteration groups. Observed frequency of given element distribution among mineral pairs: 100%. For informational purposes only.		

Abbreviations: amph = amphibole; ep = epidote; ttn = titanite.

IMPLICATIONS FOR EXPLORATION

The examination of hydrothermal minerals (epidote, amphibole, titanite, and allanite) formed during multiple pre-, syn-, and post-magmatic hydrothermal events in barren and PGE-fertile assemblages provides diagnostic geochemical signatures of the major minerals epidote and amphibole to aid in the detection of precious-metal mineralization in the Sudbury footwall environment. Pathfinder elements Ni, Pb, Sn, and Co in

epidote and amphibole are the most reliable and robust elements to distinctly fingerprint the PGE-mineralizing alteration in Sudbury's footwall environment.

Trace element partitioning occurs between texturally coeval minerals, such as epidote and amphibole (REE, Pb, Bi, and Sn partition into epidote; Co, Ni, and Zn show affinity to amphibole). In titanite-amphibole assemblages, the elements REE, Sn, Zr, Nb, Yb, Th, and U partition into titanite and Co, Ni, and Zn have an affinity to amphibole. This scavenging phenomenon greatly affects the element distribution of the mineral pairs; therefore, conclusions drawn on the trace element concentrations of a single mineral should be avoided.

An unconventional exploration technique was developed for detection of the "no-see-um" precious-metal (PGE) mineralization in the world-class Sudbury mining district, using alteration-mineral chemical-pathfinder elements. We highlighted the effects of host-rock compositions and mineral-pair partitioning of elements in the indicator minerals, and show that single mineral phases and single elements should not be used.

Although this study only briefly touches on the role of structure, on fluid and metal mobility through the reactivation of older, impact-generated and extensional structures that host the highest grade PGE-only orebodies, a major knowledge gap remaining that has been overlooked is the physical hydrology of the magmatic-hydrothermal system. Determining the physical controls on the magma, multiple fluids (including copper "fluids"), and volatile expulsion is key to understanding the metallogenesis of the world-class camp and thus, help explorers target more efficiently, contributing to the economic potential of the district.

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