

Article

Chlorite-White Mica Pairs' Composition as a Micro-Chemical Guide to Fingerprint Massive Sulfide Deposits of the Bathurst Mining Camp, Canada

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Abstract: The compositions of phyllosilicates, with a focus on fluid-mobile elements, were evaluated as a means to fingerprint the Middle Ordovician metamorphosed (greenschist facies) volcanogenic massive sulfide deposits of the Bathurst Mining Camp (BMC), Canada. Ninety-five drill-core samples from six of the major deposits of the Bathurst Mining Camp (Brunswick No. 12, Heath Steele B zone, Halfmile Lake Deep zone, Key Anacon East zone, Louvicourt, and Restigouche) were analyzed using electron microprobe and laser ablation inductively coupled plasma-mass spectrometry. Typically, phyllosilicates (chlorite, white mica, and to a lesser extent biotite) are ubiquitous phases in the host rocks of the massive sulfide deposits of the BMC. Electron microprobe analysis results show a wide compositional variation in chlorite and white mica. Laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) analysis was performed to measure fluid-mobile elements, showing that Tl is distinctly enriched in all white mica (up to 719 ppm) relative to chlorite (up to 50.1 ppm). Chlorite hosts Sn (up to 4600 ppm), Hg (up to 7.3 ppm), Sb (up to 35.4 ppm), As (up to 1320 ppm), In (up to 307 ppm), Cd (up to 83.2 ppm), and Se (up to 606 ppm). White mica hosts Sn (up to 1316 ppm), Hg (up to 93 ppm), Sb (up to 1630 ppm), As (up to 14,800 ppm), In (up to 1186 ppm), Cd (up to 98 ppm), and Se (up to 38.8 ppm). Limited LA-ICP-MS analysis on biotite indicates a higher overall concentration of Tl (mean = 14.6 ppm) relative to co-existing white mica (mean = 2.18 ppm). On average, biotite is also more enriched in Hg, Sn, and Ba relative to chlorite and white mica. Laser Ablation ICP-MS profiles of chlorite, white mica, and biotite demonstrate smooth time-dependent variations diagnostic of structural substitution of these elements. Compositional variation of chlorite-white mica pairs presented in the current study shows systematic variations as a function of distance from the mineralized horizons. This highlights the potential to use trace-element signatures in these phyllosilicate pairs to identify proximal (chlorite) and distal (white mica) footprints for volcanogenic massive sulfides exploration.

Keywords: Bathurst Mining Camp (BMC); biotite; chlorite; fingerprint; fluid-mobile elements; LA-ICP-MS; massive sulfide deposit (VMS); phyllosilicate; vectoring tool; white mica

1. Introduction

The volcanogenic massive sulfide deposits are major sources of Zn, Cu, Pb, Ag, and Au, and significant sources of Co, Sn, Se, Mn, Cd, In, Bi, Te, Ga, and Ge. These metals may be sourced by the

leaching of footwall rocks or supplied directly from magmatic fluids. The metal-bearing hydrothermal fluid migrates to the site of deposition (seafloor) via convective up-flow. Mineralogical changes in the footwall rocks (e.g., distal white mica to proximal chlorite, depending on the massive sulfides subtypes) are symmetrically zoned about the up-flow conduit and define distinct alteration haloes [1]. These haloes are commonly more extensive than their respective deposits thereby providing a larger (up to several km radiuses) target area within which mineralization may exist. The primary challenge is discriminating mineralized from barren alteration systems and recognizing the fringes to ore horizons.

Phyllosilicates (chlorite, white mica, and biotite) are ubiquitous in the hydrothermal alteration zones associated with the Bathurst Mining Camp (BMC), Canada, yet the trace-element geochemistry of these phyllosilicates is poorly understood [2]. Phyllosilicate geochemistry is more commonly investigated for major, minor, and a limited number of trace elements and variations in such features as the Fe/Mg of chlorite can reflect spatial and temporal relationships with respect to the proximity of massive sulfide mineralization. Some volcanogenic massive sulfide systems show patterns of increasing Mg content of chlorite with proximity to the core of the footwall alteration system (e.g., Seneca, Southbay, and Corbet deposits [3], Hellyer deposit [4], Mount Read and Mount Windsor deposits [5,6], and Thalanga deposit [7]). On the other hand, the reverse pattern has been recorded with the Fe content of chlorite increasing with proximity to the core of the alteration pipe (e.g., Heath Steele [8], Brunswick No. 12 [9–11], Halfmile Lake [12], Caribou [13], Restigouche [14], Key Anacon [15], Horne [16], Hercules in Australia [17], Kuroko deposits of Japan [18], and Matagami, Quebec [19]). White mica from massive sulfide deposit (VMS) deposits shows two main compositional affinities: 1) Ba-rich phengitic white mica that occurs proximal to the ore horizon (e.g., Hellyer [20], and Rosebery [21], Tasmania, Australia; Heath Steele B zone [8]; Brunswick No. 12 [22], BMC, Canada; Neves-Corvo [23], Iberian Pyrite Belt), or 2) muscovitic white mica from the inner alteration zone proximal to ore (e.g., Western Tharsis and Mt. Lyell, Tasmania, Highway Reward and Mt. Windsor sub-province, Queensland [6]).

Recently, micro-analytical techniques, in particular, laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) have been applied to measure a wider range of elements than previously possible in phyllosilicates [24–28]. In particular, the fluid-mobile elements suite (Ag, Cd, Au, Hg, Ga, In, Sn, Tl, Bi, Pb, Ge, As, Sb, Te, Se) occur in the Fe-, Cu-, Zn-, and Pb-sulfide and sulphosalt minerals, as well as phyllosilicates typical of the alteration zones of VMS deposits (see [27]). The association of these elements with base metal mineralization makes them particularly important in the exploration for VMS deposits. Therefore, establishing the major host minerals of these elements and variation in concentration with respect to location in the alteration halo is relevant to improved mineral deposit and exploration models.

Work published by [28] described the fluid-mobile element variability of white mica in the alteration zones associated with the VMS deposits of the BMC. Work presented herein builds on this earlier work and introduces the chlorite-white mica pairs as a more robust assessment of fluid-mobile element distribution in the alteration zones of VMS deposits. Fluid-mobile element concentrations in phyllosilicates were measured throughout the footwall and hanging wall zones (Ninety-five samples) from six of the major deposits of the Bathurst Mining Camp (Brunswick No. 12, Heath Steele B zone, Halfmile Lake Deep zone, Key Anacon East zone, Louvicourt, and Restigouche). The significance of this research is the assessment of fluid-mobile element dispersion haloes associated with VMS deposits of the BMC to introduce the application of chlorite-white mica pairs as potential micro-chemical tools for VMS exploration.

2. Geological Setting

2.1. Regional Geology

The Bathurst Mining Camp, located in northern New Brunswick, Canada contains 45 Zn-Pb-Cu-Ag type VMS deposits that range in size from <1 to 230 million metric tons (Mt) in the

case of the giant Brunswick 12 massive sulfide deposit. These deposits are hosted by a poly-deformed Middle Ordovician sequence of bimodal volcanic and intercalated sedimentary rocks deposited in the Tetagouche-Exploits back-arc basin. This sequence was deposited on siliciclastic rocks (Miramichi Group) on the stable Gondwanan margin [29–31]. The Cambro–Ordovician Miramichi Group (490–478 Ma) occurs at the base of the sequence and consists of a passive-margin, continentally-derived turbidite sequence consisting of quartz wacke, quartzite, siltstone, and shale. The Miramichi Group was succeeded by the Bathurst Supergroup, which is divided into the Sheephouse Brook, Tetagouche, and California Lake groups and overlain by the Fournier Supergroup (Figure 1; [29–32]). The first three groups are coeval (471–465 Ma) and mainly include ensialic bimodal volcanic and sedimentary rocks. The Sheephouse and Tetagouche groups are dominated by two distinct cycles of felsic volcanism that transition up section into tholeiitic mafic rocks, whereas the California Lake Group has only one cycle of felsic volcanic rocks. The Fournier Supergroup is the youngest group (~465 Ma); it is dominated by ocean-floor mafic volcanic and related sedimentary rocks that were thrust onto the para-autochthonous sequences. Closure of the Tetagouche-Exploits back-arc basin in the Late Ordovician to Early Silurian resulted in the incorporation of Miramichi Group and the Bathurst and Fournier Supergroups into the Brunswick subduction complex [33]. Salinic Orogeny in the BMC caused poly-phase deformation (thrust faulting and tight to isoclinal folding) associated with middle- to upper-greenschist and locally blueschist facies metamorphism. The subsequent Acadian orogeny (Late Silurian in this region) refolded pre-existing Salinic structures leading to complex re-folded fold structures [34] (Figure 1).

Most of the deposits in the BMC are associated with the first-erupted felsic volcanic units in the Tetagouche, California Lake, and Sheephouse Brook groups. In the case of the Tetagouche Group, 24 of 32 deposits are associated with the Nepisiguit Falls Formation. In the California Lake Group, 12 of 13 deposits are spatially associated with the only phase of felsic volcanic rocks of the Spruce Lake and Mount Brittain formations [35], whereas the Sheephouse Brook Group, in the southern BMC, hosts only one VMS deposit which is hosted by the Clearwater Stream Formation [32] (Figure 1).

2.2. Geology of the Studied Deposits

Tetagouche Group deposits: The Tetagouche Group comprises mainly felsic and mafic volcanic rocks, which occur in several internally imbricated and folded nappes. This group shows a general progression up-section from sub-alkalic felsic volcanic rocks (Nepisiguit Falls Formation) to felsic-dominated bimodal volcanic rocks (Flat Landing Brook Formation) to alkalic basalts (Little River Formation) [36]. Most of the deposits examined as part of this study, including Brunswick No. 12, Heath Steele B zone, Halfmile Lake Deep zone, Key Anacon East zone, and Louvicourt are hosted by the Tetagouche Group, (see Figure 1).

California Lake Group deposits: The California Lake Group consists mainly of volcanic rocks that occur in three major, internally imbricated nappes, namely: The Canoe Landing, Spruce Lake, and Mount Brittain nappes [31]. The Restigouche deposit is hosted by Mount Brittain Formation and is included in the present study. A detailed description of the Restigouche deposit is presented by [27].

2.3. Metamorphism and Deformation

The rocks and alteration assemblages in the BMC have been affected by regional and contact metamorphism, and polyphase deformation. In the BMC, the metamorphic grade varies from lower- to upper-greenschist to locally blueschist facies ([34] and references therein). Metamorphic conditions of the BMC are estimated to lie in a narrow range 350–400 °C, and 5.5–5.8 kbar and are most likely equivalent to M_1 (metamorphism) or post- M_1 [34]. Petrographic evidence of porphyroblasts of stilpnomelane, biotite, and garnet grown across S_1 (schistosity/foliation) indicate a late phase of M_1 metamorphism, and peak thermal conditions [34]. In the eastern part of the BMC, upright F_2 (fold) folds that refold D_1 (deformation) structures are well-developed [37]. A differentiated crenulation cleavage (S_2), formed partly by rotation of S_1 and partly by dynamic recrystallization and neo-crystallization of white mica, chlorite, and clinoamphibole parallels kink band boundaries in the

hinges of F_2 micro-kinks and segments of old deformed grains. This was interpreted by [31] as an early M_2 stage of deformation which occurred at metamorphic temperatures below the Ar diffusion closure temperature of phengite (350 ± 50 °C). Subsequent contact metamorphism occurred as a result of upper Silurian–lower Devonian intrusions, defining the peak M_2 conditions, and is marked by the occurrence of cordierite and andalusite [15,38]. The superimposed D_3 - and D_4 -related folds and kinks locally overprint D_2 fabrics and M_2 porphyroblasts by mechanical rotation of earlier phyllosilicates; however, in zones of higher strain, some neo form growth of white mica and chlorite occurred [34].

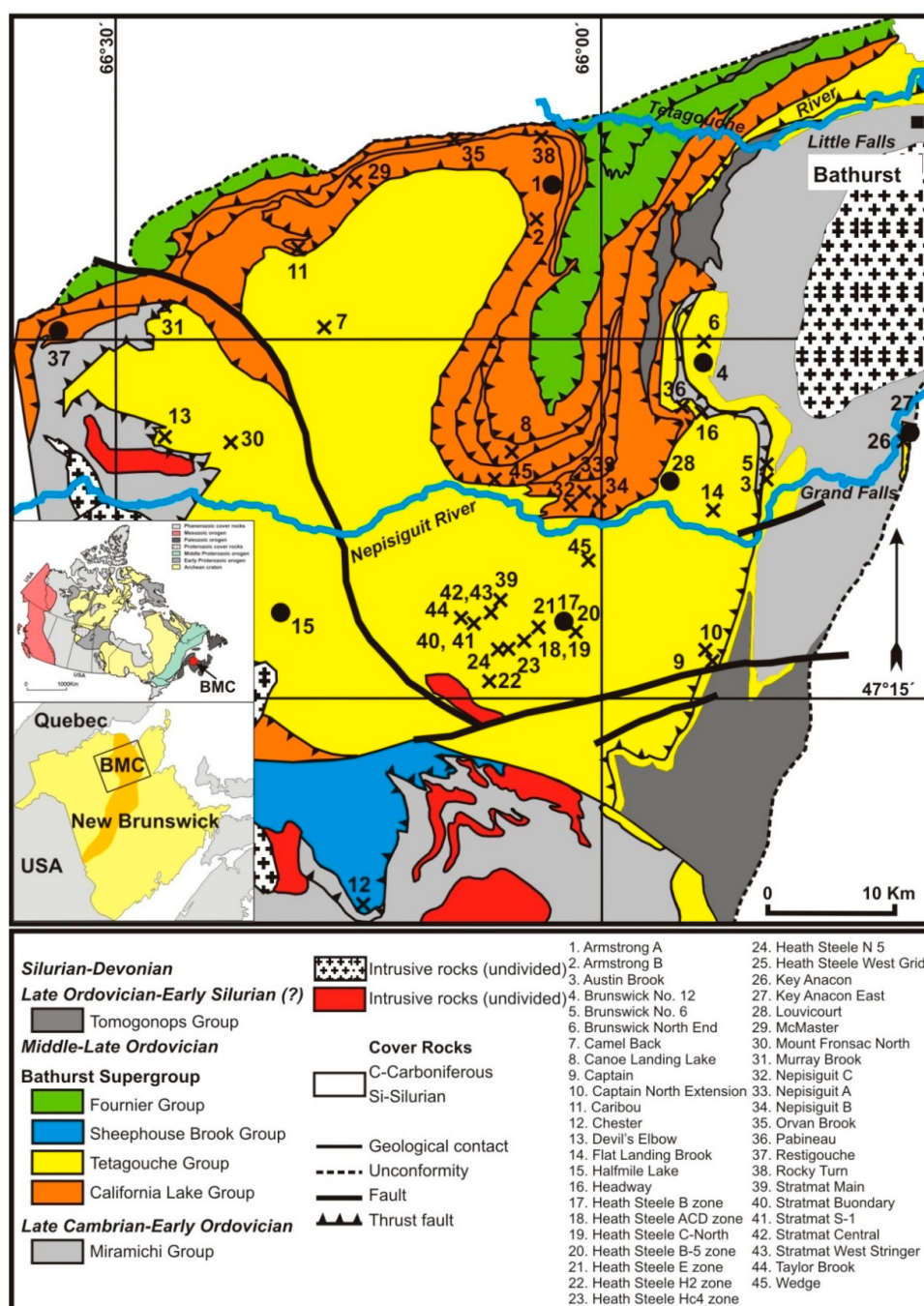


Figure 1. Simplified geological map of the Bathurst Mining Camp, northeastern New Brunswick, showing the location of massive sulfide deposits marked by numbered (x) and listed in the legend. Deposits examined during this study are marked by numbered black filled circles and listed in the legend (modified from [12]). Geological maps of the studied deposits, as well as drill-hole profiles, are provided by [27].

2.4. Hydrothermal Architecture of the BMC

The geochemistry of the altered volcanic and sedimentary rocks hosting the massive sulfide deposits of the BMC is variable and reflects the diversity and intensity of alteration processes that occurred during VMS mineralization [9,11,13,39–41]. Hydrothermal alteration zones enveloping the feeder zones of VMS deposits in the BMC are laterally (1–5 km) and vertically (hundreds of meters) extensive and distinguishable on the basis of mineralogy and bulk-rock geochemistry (Figure 2). At the Brunswick No. 12 deposit, four deposit-related hydrothermal alteration zones (zones from I to IV) are recognized [9,11,39–41] (Figure 2). Zone I is associated with the upper part of the alteration pipe (stringer zone) and lies immediately below the massive sulfides. This zone is characterized by silicic alteration [40,41] and consists of fine-grained milky quartz (40%–90%), Fe-rich chlorite (3%–15%), carbonate (5%–12%, mainly calcite) with variable sericite (10%–20%), and sulfides (5%–25%, mainly pyrrhotite, chalcopyrite, pyrite, tetrahedrite, and arsenopyrite). Zone I is transitional downward into Zone II (potassic alteration zone from [40,41]), which consists of K-feldspar (5%–25%), Fe-rich chlorite (3%–10%), sericite (10%–55%, compositionally phengitic), minor quartz (10%–15%), and sulfides (5%–10%, mainly pyrite, pyrrhotite, chalcopyrite, sphalerite). Zones I and II are transitional outward into zone III (Na-Mg alteration zone by [40,41]), which consists of sericite (30%–60%, muscovitic), Fe-Mg-chlorite (15%–60%), albite (5%–20%), and subordinate sulfides (0%–15%). Zone III is transitional outboard into zone IV, the most distal of the footwall alteration zones, and is dominated by albite (30%–70%) and Mg-rich chlorite (40%–50%). In some deposits, continued post-ore hydrothermal activity results in the extension of alteration zones III and IV into the hanging wall for up to several 10s of meters [9,11,40,41].

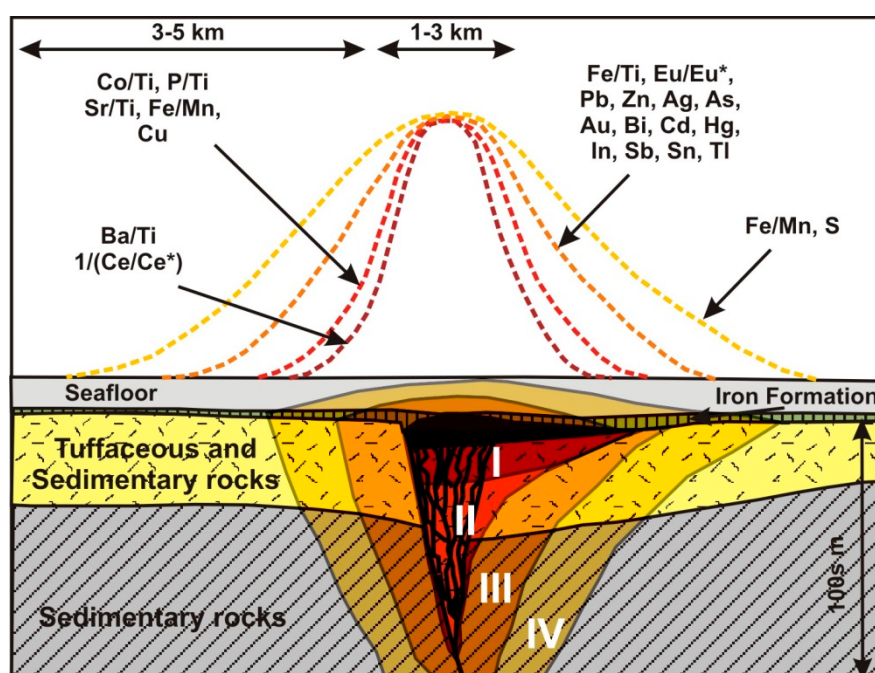


Figure 2. Schematic diagram illustrating the lateral extent of chemical haloes, forming different hydrothermal alteration zones surrounding the Brunswick No. 12 deposit, BMC (modified from [9]). See text for description of alteration zones I, II, III, and IV.

3. Analytical Methods

3.1. EPMA

Electron probe micro-analysis (EPMA) was utilized to determine the chemical variation (major and some minor elements) of the phyllosilicates. Analyses of selected phyllosilicate minerals were

carried out at the University of New Brunswick on a JEOL JXA-733 Superprobe (Tokyo, Japan) operated in wavelength-dispersive mode at a 15 kV accelerating voltage, 30 nA focused beam, and rastered over 5 μm^2 area with a peak counting time of 40 s. For more information on the methodology see [22].

3.2. LA-ICP-MS

The major and trace-element chemistry of chlorite, white mica, and a limited number of biotite grains was determined by LA-ICP-MS at the University of New Brunswick, Canada, following the methods described previously (see the system setup presented by [42,43]). The system comprises a Resonetics Resolution™ 193 nm ArF (excimer) and a Laurin Technic Pty (Canberra, Australia) S-155 large format sample cell that connected via Nylon™ transfer tubes to an Agilent 7700x ICP-MS equipped with dual external rotary vacuum pumps (see [27] for lab and methodology information). Carrier gas flows and ICP-MS lens tuning was carried out by rastering across NIST610 glass while optimizing settings to obtain maximum sensitivity while maintaining oxide production (monitored as $^{248}(\text{ThO})^+ / ^{232}\text{Th}^+$) and doubly-charged production (monitored as $^{22}\text{M}^+ / ^{44}\text{Ca}^{++}$) to <0.1% and <0.2% respectively.

Data acquisition consisted of a measurement of the gas background for 40 s, followed by 40 s of ablation, pulsed at 4 Hz, using a crater diameter of 66 μm . Fluence was regulated at $\sim 1.5 \text{ J}/\text{cm}^2$. Raster lines on phyllosilicates were obtained using the same ablation conditions as spot analysis with the raster speed assigned as half of the beam size, i.e., 33 $\mu\text{m}/\text{s}$. Since the concentration of fluid-mobile elements is commonly low in phyllosilicates, the dwell time and total integration time (see Supplementary Table S1) was adjusted for each analyte to be able to measure them with better detection limits. A total of 32 isotopes were examined (fluid-mobile elements of interest in this study in *italic*): (^7Li , ^{23}Na , ^{24}Mg , ^{27}Al , ^{29}Si , ^{35}Cl , ^{39}K , ^{44}Ca , ^{49}Ti , ^{53}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{75}As , ^{77}Se , ^{81}Br , ^{85}Rb , ^{88}Sr , ^{111}Cd , ^{115}In , ^{118}Sn , ^{123}Sb , ^{125}Te , ^{133}Cs , ^{137}Ba , ^{202}Hg , ^{205}Tl , ^{208}Pb , and ^{209}Bi) from which element concentrations were calculated. Elements were chosen on the basis of lowest abundance and the heavier isotopes with the least interference. Since isotopic interferences are one of the challenges of the accurate measurement by LA, assuming a more suitable isotope should be considered based on the suite of elements of interest. In this case, better results can be obtained for ^{77}Se and ^{121}Sb instead of ^{78}Se and ^{123}Sb . In addition, ^{115}Sn (0.34% abundance) is isobaric on ^{115}In (95.71% abundance), so where ^{118}Sn is being counted, the net ^{115}In - ^{115}Sn and overestimation of small ^{115}Sn interference on ^{115}In needs to be assessed. Herein, In concentration in Sn-rich samples is expected to be overestimated by about 10% (these points are flagged in the dataset).

Data calculation was undertaken offline using the Iolite™ 2.5 Trace Element Data Reduction Scheme [44] (see Supplementary Tables S6–S8 for detection limits). The quality of the obtained data was checked by monitoring NIST612 (National Institute of Standards and Technology) and BCR-2G (Basalt, Columbia River) as consistency standards with accepted values reference from GeoREM website. The NIST612 and BCR-2G standards were calibrated versus NIST610, using published values for Si as the internal standard ($\text{Si}_{\text{NIST612}} = 33.6 \text{ wt } \%$ and $\text{Si}_{\text{BCR-2G}} = 25.4 \text{ wt } \%$) (see the summary statistics, Supplementary Table S2). The obtained values have an acceptable degree of accuracy within 2 standard deviations ($\pm 2\sigma$) of the published values for NIST612 and BCR-2G (Supplementary Figures S1 and S2, respectively). The measured mean for In (35.5 ppm), Sb (31.1 ppm), and Sn (34.2 ppm) values of NIST612 vary from the published values of 38.9, 34.7, and 38.6 ppm, (GeoReM database), respectively Supplementary Table S2). However, reproducibility is typically within 10% relative standard deviation (RSD %) for all the volatile elements, except Tl and Hg (Supplementary Figure S1). The results for BCR-2G agree well with the published values (GeoReM database) for all elements except As (3.43 ppm), Sn (1.85 ppm), and Zn (157), which vary from the published values of 7.2, 2.6, and 125 ppm, respectively (Supplementary Figure S2). Replicate analyses of BCR-2G yielded a precision of less than 10% RSD for all of the elements, except As, Se, Cd, In, Sb, Hg, Tl, and Bi (Supplementary Table S2).

In the current study, the NIST610 certified glass ([45], modified by GeoReM database) was used as the external reference for sensitivity calibration. The NIST610 glass has not been quantified for Hg

previously. In the current study, the Hg value of the NIST610 is obtained using MASS-1 as external standard ($Hg_{\text{information value_NIST610}} = 0.46 \text{ ppm}$). Therefore, Hg values presented in the current study for phyllosilicates should be considered semi-quantitative. Internal standardization was done using potassium for reduction of white mica. Not all the samples examined by LA-ICP-MS had EPMA data, so data reduction using internal standard obtained from EPMA was not an ideal choice. In addition, based on variable K values (7.7 wt %–9.2 wt %) presented by [8] for a complete sample set of Heath Steele B zone (HSB-3409 drill hole), it is necessary to address the effect of using different K values. Herein, we reduced a small set of data using the lowest, highest, and average K values as internal standard (Supplementary Table S3). In all cases, there is a ca. 20% difference between the values that reflects the difference between 9.2 and 7.7. In some cases, especially for very low-concentration analytes (e.g., <1 ppm), internal errors were larger than the effect of changing internal standard values. Those analytes at a few ppm do not generally overlap within error, but if errors are expanded only slightly (e.g., by propagating error from standard), then many trace elements would likely overlap within the 7.7–9.2 internal standard range. In addition, changing the internal standard value will not, of course, change any relative chemical trends. Based on these observations, we have opted to use mean stoichiometric values of K ($K_{\text{mean stoichiometric}} = 9.5 \text{ wt \%}$) (muscovite and celadonite end members) as internal standards to preserve the internal consistency of the dataset. We also recognize the potential $\pm 20\%$ absolute error for important fluid-mobile elements imposed by this assumption [27]. Chlorite calibration was done using Si as the internal standard ($Si_{\text{mean in chlorite}} = 11.8 \text{ wt \%}$) from the representative chlorite of the BMC reported in [22]. LA-ICP-MS analysis on biotite was corrected using $Si = 17 \text{ wt \%}$ (obtained from EPMA; [8]).

LA-ICP-MS time-series data for each analyte can be used to assess the homogeneity of elements within an ablated volume. This can help reveal zoning patterns and micro-inclusions in mineral grains. However, this technique cannot distinguish inclusions that are below the resolution of the time-resolved signal: micro- and nano-inclusions may not be manifest in the signal. Figure 3 shows selected representative LA-ICP-MS time-series (counts per second versus time) for spot analyses on chlorite and white mica from the Louvicourt deposit (the highest fluid-mobile element concentrations among the studied deposits) and biotite from Heath Steele B zone deposit. Signals exhibit smooth patterns over time for Zn, In, and Pb in chlorite (Figure 3A), Sb, Pb, Tl, As, Zn, and Hg in muscovite (Figure 3B) and Tl and Zn in biotite, which can be interpreted to reflect structural substitution (Figure 3C).

Line scans across grains were performed to investigate trace element variability within masses of chlorite and white mica. This work was conducted using a beam size of 33 μm , which was sufficient considering the grain size (from several microns to areas with a massive occurrence of phyllosilicates in centimeter scale) and textures of the samples analyzed. LA raster lines conducted on masses of white mica display varying levels of inhomogeneity depending on the texture (Figure S3). Distinct spiky signals for Bi, Pb, and Sb suggest the presence of sulfide or sulfosalt inclusions, although they are not optically visible. In other cases, white mica masses devoid of textural variability have more homogeneous elemental patterns. LA raster lines across chlorite masses indicate generally very high concentrations of Mn and Zn, with some slight irregularities (Figure S4). The other fluid-mobile elements have highly irregular patterns at very low concentrations with no distinct chemical zonation. These data suggest that to determine a representative and accurate chemical variation in phyllosilicates, textural criteria must be taken into consideration in addition to careful data reduction to exclude the data contaminated with inclusions. Furthermore, increasing the number of spot analyses is recommended to obtain a sufficiently large database.

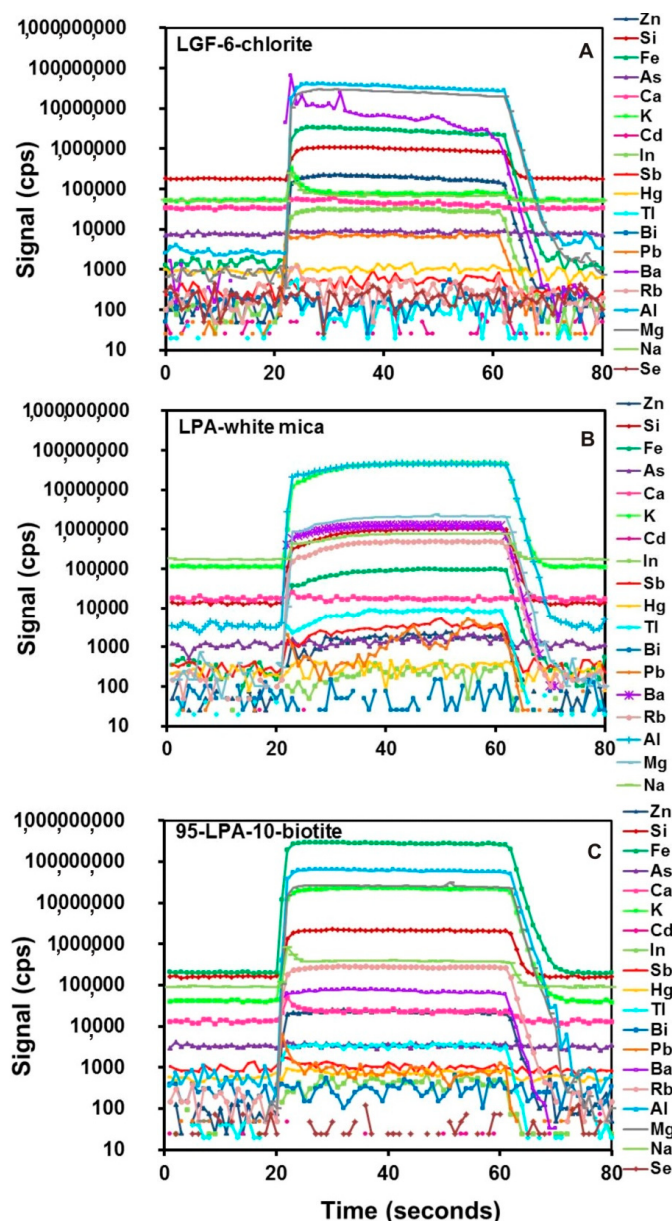


Figure 3. Single-spot laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) spectra for selected elements (A) chlorite from LGF-6 at 65.5 m, and (B) white mica from LGF-6 at 68 m; both (A,B) from Louvicourt deposit, and (C) 95-LPA-10 at 90 m, Heath Steele B zone deposit. These samples have the highest fluid-mobile element concentrations.

4. Results

4.1. Petrography

The host rocks of the BMC can be divided into three main categories, including felsic volcanic rocks, sedimentary rocks, and mafic volcanic rocks. All the volcanic host rock samples examined during this study have foliated and recrystallized groundmasses (see [27] for host rock description). Chlorite and white mica are common components in all samples examined. The dominant petrographic characteristics of chlorite, white mica, and biotite are described below.

4.1.1. Chlorite

Chlorite is ubiquitous in the BMC and is a major component of exhalative sedimentary rocks, including Algoma-type iron formation and in chloritic tuff in areas distal to mineralization.

Chlorite abundance increases with proximity to the vent zone where it is commonly associated with disseminated to semi-massive sulfides in proximal footwall alteration zones (Si alteration zone). Chlorite color in thin section varies from olive–green to brown–yellow, with anomalous interference colors, ranging from very pale gray to grayish green- to deep blue–green, deep blue–violet (Berlin-blue; Figure 4). Chlorite in quartz–feldspar augen schist (QFAS) and quartz augen schist (QAS) of the Nepisiguit Falls Formation occurs as disseminated, medium- to fine-grained flakes and masses or patchy aggregates and bands (Figure 4A), and as epitaxial growths associated with sericite, feldspar, and quartz in more distal part of the hydrothermal system (Figure 4B). In some samples, chlorite fills extensional (pull-apart) fractures in porphyroblasts (Figure 4C). Chlorite in tuffaceous sedimentary rocks of the Patrick Brook Formation is commonly associated with sulfide veins (Figure 4D). Proximal to the ore horizons, chlorite typically occurs as chloritic bands/layers in close association with sulfides. In addition, the formation of beards, fringes, and shadows of chlorite on the margins of individual sulfide porphyroblasts (e.g., pyrite), and as an interstitial component with sulfide phases commonly occur (Figure 4E). In semi-massive sulfide samples, chlorite may be associated with quartz and carbonates (Figure 4F).

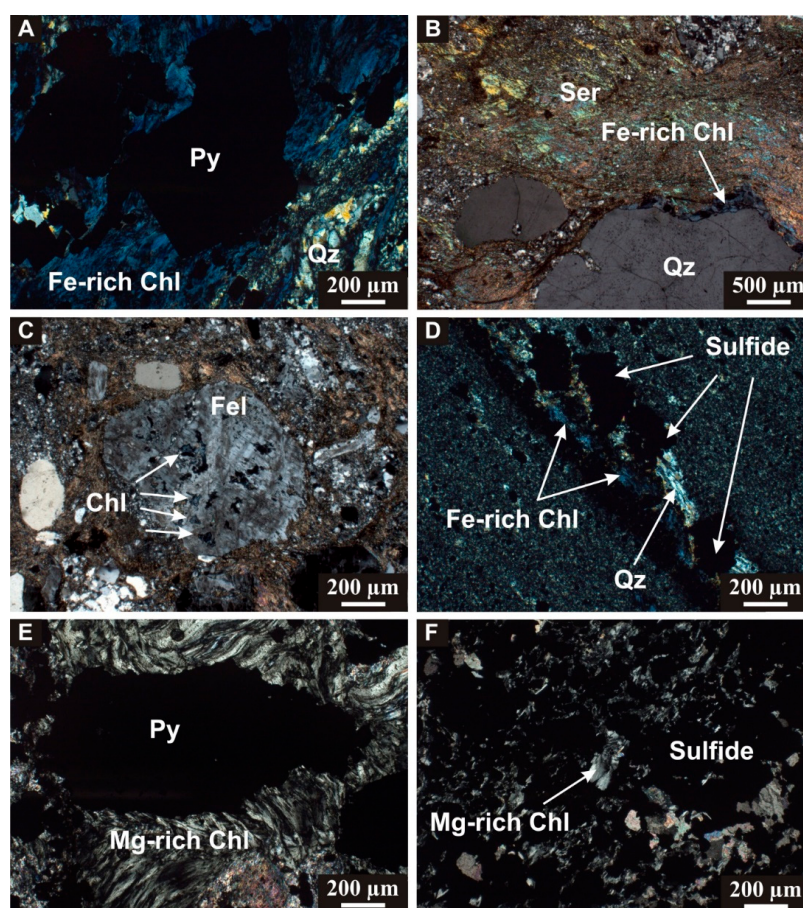


Figure 4. Photo-micrographs (crossed-polarized light) of chlorite varieties from the Bathurst Mining Camp (BMC). (A) Chlorite mass enclosing pyrite porphyroblast (A1-028 at 158 m). (B) Wispy chlorite surrounding quartz phenocryst in fine-grained groundmass of quartz and phyllosilicates (95-LPA-5 at 165 m). (C) Turbid K-Feldspar phenocryst hosting blebs of chlorite (see arrows) (95-LPA-8 at 219 m). (D) Sulfide–chlorite–quartz vein in very fine-grained matrix (A1-023 at 120 m). (E) Massive chlorite enveloping a pyrite grain (HN-99-119 at 1250 m). (F) Semi-massive sulfide sample, in which tension gashes are filled by chlorite, recrystallized quartz, carbonate mainly calcite, and subordinate white mica (94-DL-70 at 426 m).

4.1.2. White Mica

Varying proportions of white mica occur in VMS-related hydrothermal alteration zones of the BMC. In particular, white mica is commonly present in potassically-altered (sericitic) zones developed in quartzo–feldspathic volcanic and volcanoclastic rocks of the Nepisiguit Falls, Flat Landing Brook, and Mount Brittain formations and in clastic and exhalative sedimentary rocks interbedded with the above-mentioned units or in the underlying Patrick Brook Formation. In these units, white mica typically occurs as fine-grained fibers, locally formation centimeter-scale felty clusters, or isolated pods intermixed with quartz and chlorite. K-feldspar phenocrysts and the groundmass of volcanic rocks may be partially to completely replaced by sericite, chlorite, and quartz (Figure 5A,B). Sericite-rich bands or septa (Figure 5C), defining penetrative S1 foliation, are common in the samples analyzed. Likewise, kink bands and crenulation cleavages are commonly recognized in sericitic bands (Figure 5D).

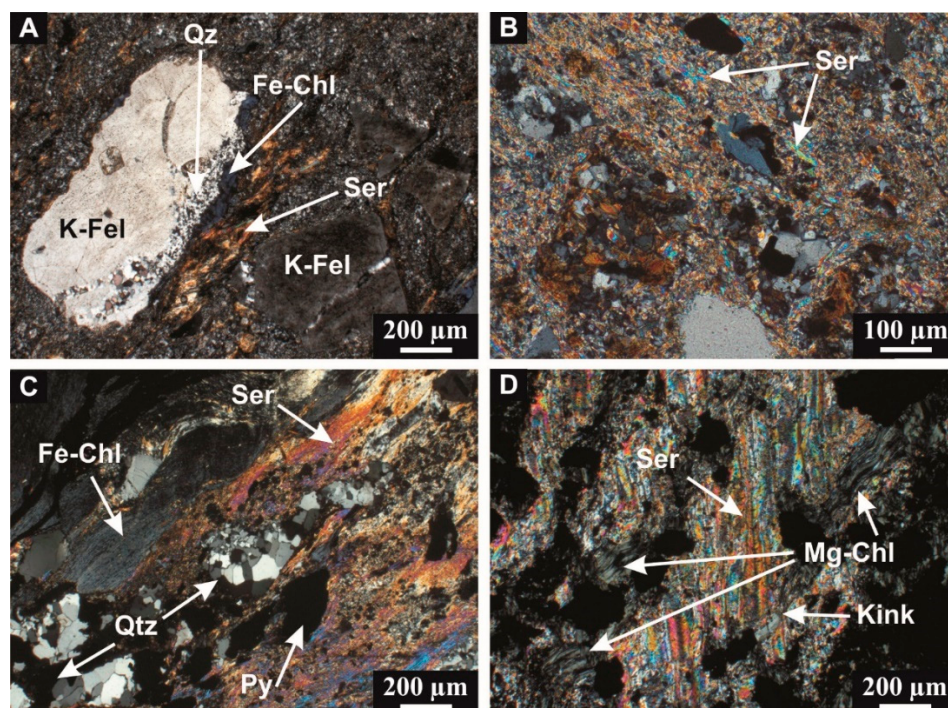


Figure 5. Photomicrographs (crossed-polarized light) of representative white mica varieties from the BMC. (A,B) K-feldspar phenocrysts in volcanic rocks with groundmass partially or completely are replaced by an intergrowth of sericite, chlorite, and quartz (HN-99-119 at 308 m and 95-LPA-10 at 239 m). (C) Sericite-rich bands or septa quartz-feldspar tuff (LPA-054 at 369 m). (D) Kink bands and crenulation cleavages in sericitic and chloritic bands (HN-99-119 at 1250 m).

4.1.3. Biotite

Biotite porphyroblasts typically occur in sericitic zones developed in quartzo–feldspathic volcanoclastic rocks of the Nepisiguit Falls Formation. Most of the biotite grains are partially or completely retrograded to chlorite (see Figure 6).

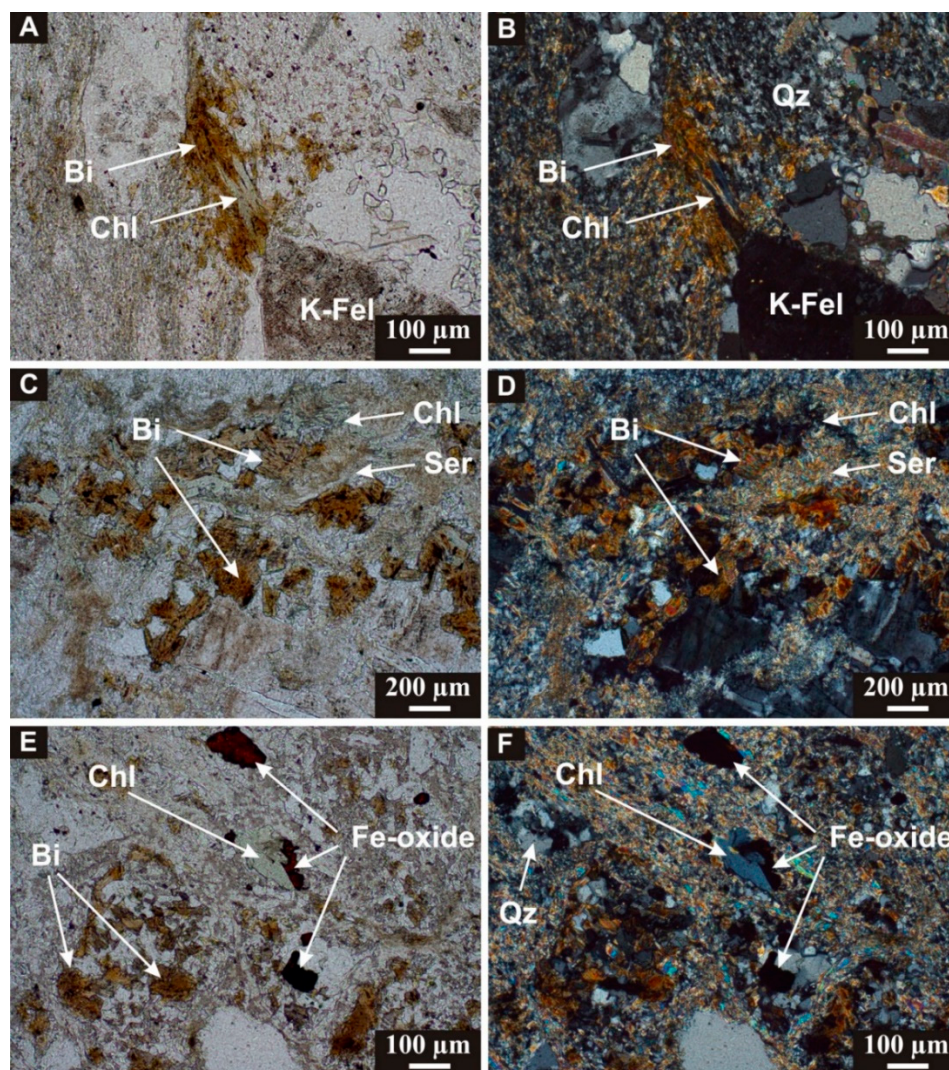


Figure 6. Photomicrographs showing textural relationships indicative of biotite alteration to chlorite; (A,B) 95-LPA-23 at 580 m, (C,D) HN-99-119 at 629 m, (E,F) alteration of iron-oxide to chlorite (95-LPA-10 at 239 m). Photo-micrographs (aA), (C) and (E) are in plain-polarized light, whereas (B), (D) and (F) are under crossed-polarized light.

4.2. Geochemical Results of Individual Phyllosilicates

The entire dataset and summary statistics of the EPMA and LA-ICP-MS spot analyses on chlorite, white mica, and biotite are presented in Supplementary Tables S4–S8. Since the composition of white mica was previously presented [28], the current contribution presented a summary of the fluid-mobile elements of white mica and focused on the chlorite elemental variation. In general, up to six LA-ICP-MS spot analyses on chlorite and white mica were collected from each polished thin section ($n = 96$). EPMA analysis revealed a wide variation in the composition of chlorite (sheridanite to brunsvigite–diabantite) (Figure 7A) and white mica (muscovite to celadonite Figure 7B). The key difference, in terms of fluid-mobile elements, based on LA-ICP-MS analysis of chlorite and white mica, is the thallium (Tl) content, which is typically lower in chlorite. The trimmed mean (10% trimming) Tl content of chlorite averages 0.3 ppm for all deposits, and includes the atypically high values from Louvicourt that has a trimmed mean Tl content of 7.83 ppm. A similar pattern was recognized in white mica, which has a trimmed mean Tl value of 6.56 ppm for all deposits examined (not including the Louvicourt deposit that has anomalously high trimmed mean Tl contents of 209 ppm (see Supplementary Tables S6 and

S7). Binary plots, using Ti as a proxy element versus Sb, Hg, As, Sn, In, and Bi are presented for chlorite and white mica separated on deposit basis (Figure 7).

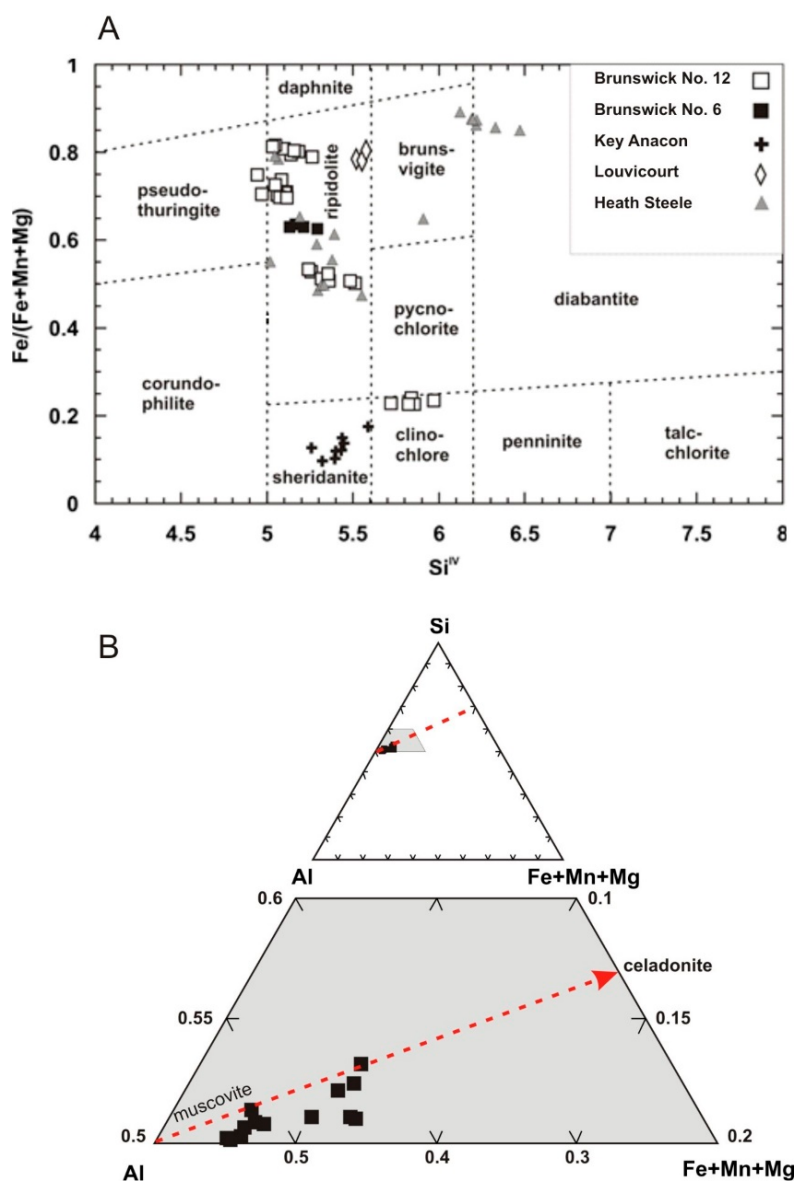


Figure 7. (A) $Fe/(Fe+Mn+Mg)$ vs. Si^{IV} discrimination diagram for the classification of chlorite from the BMC (see Supplementary Table S4) and consistent with compositions reported for footwall alteration zones [8,11] and iron formation [46,47]. Field boundaries acquired after [48]. (B) Al-Si-(Fe+Mn+Mg) discrimination diagram for 13 electron-microprobe analyses of muscovite from the BMC (see Supplementary Table S5). Note the tight clustering of data points with compositions falling between end member muscovite and celadonite.

4.2.1. Chlorite Chemical Variations

Chlorite in massive sulfides from the BMC is, for the most part, Fe-rich with an average formula $(Mg_{4.0}Al_{2.7}Fe_{5.2})[(Si_{5.4}Al_{2.6})O_{20}](OH)_{16}$; according to the EPMA compositions which are based on an anhydrous structural formula with 28 oxygen (see Supplementary Table S4). Analysis totals were consistently between 84.0% and 91.3% indicating the presence of hydroxyl groups in alternating sheets of brucite and talc. Contents of Al_2O_3 range from 13.8% to 25.7%, with Al (average 5.34 *apfu*) exhibiting a negative correlation with Si ($r' = -0.83$; 99% confidence interval, $r' > 0.28$) and Ca ($r' = -0.53$). Contents of Fe averaged 28.8% FeO, but are quite variable (5.21%–44.1%) with chlorite compositions

ranging from sheridanite to daphnite, and exhibit a negative correlation with Mn ($r' = -0.72$). The magnesium average is 12.8% MgO, which ranges from 2.89% to 28.3%. Magnesium shows a positive Spearman Rank correlation with Mn ($r' = -0.70$) and a negative correlation with Fe ($r' = -0.99$), indicating substitution for Fe in the chlorite structure (see Figure S5). The average $\text{Fe}/(\text{Fe}+\text{Mn}+\text{Mg}) = 0.57$, consistent with a ripidolite composition based on the classification scheme of [46]; however, this ratio can vary from 0.09 to 0.89, indicating the presence of sheridanite and daphnite compositions (Figure 7A). Contents of SiO_2 range from 22.2% to 29.3% with Si^{IV} (based on 28 oxygen) ranging from 4.94 to 6.47, indicating compositions trending towards brunsvigite and diabantite.

LA-ICP-MS data show that Sb content within chlorite varies from <hmdl (half mean detection limit) to 35.4 ppm with a few sporadically higher Sb contents in chlorite from Brunswick No. 12 and Heath Steele B zone (Figure 8A–C). The Hg content of chlorite is somewhat variable with values of up to 7.3 ppm, 5.5 ppm, and 3.33 ppm from the Louvicourt, Restigouche, and Heath Steele B zone deposits, respectively (Figure 8D–F). The concentration of As in the majority of analyzed chlorite samples is below 10 ppm and does not correlate with Tl ($r' = 0.01$) (Figure 8G–I). Tin weakly correlates with Tl ($r' = 0.24$) in chlorite, with Sn contents ranging from <hmdl to 100 ppm, with a few anomalously enriched grains from Louvicourt having up to 983 ppm (Figure 8J–L). The In content fluctuates from <hmdl to a maximum of 307 ppm in samples from the Louvicourt deposit (Figure 8M–O). Also, some chlorite grains from Halfmile Lake Deep Zone deposit have higher In contents (up to 42.2 ppm). The Bi content of chlorite is generally low with over 70% of the analyses reporting below the detection limit, with some chlorite grains returning Bi contents of up to 19 ppm (Figure 8P–R). Also, trimmed mean Se and Cd contents in all chlorite samples are low with the exception of a few anomalously high values from the Halfmile Lake Deep zone, that are likely due to the presence of inclusions (not shown) (see Supplementary Table S6).

Based on the petrography of the samples, chlorite occurs in several generations. Herein, two distinct generations of chlorite have been investigated for fluid-mobile element variations (Figure S6). Chlorite that crystallized at the fringes of pyrite grains have higher As, Se, and Sb contents in both examples examined and distinctly higher values of Cd, In, Sn, and Bi relative to larger masses of chlorite.

4.2.2. White Mica Chemical Variations

Muscovite compositions determined by EPMA ($n = 13$) have an average formula of $\text{K}_{1.2}\text{Na}_{0.05}\text{Ba}_{0.05}\text{Al}_{3.7}[\text{Si}_{6.3}\text{Al}_{1.7}\text{Mg}_{0.25}\text{Fe}_{0.28}\text{Ti}_{0.03}\text{O}_{20}](\text{OH})_2$ based on an anhydrous structural formula of 22 oxygen (see Supplementary Table S5). Contents of SiO_2 average 51.3% and range from 48.1% to 54.0% with an excess of Si^{IV} ranging from 6.14 to 6.56 *apfu* and exhibit a negative Spearman Rank correlation with Al ($r' = -0.95$; 99% confidence interval, $r' > 0.63$) and a positive correlation with Fe ($r' = 0.65$) and Mg ($r' = 0.83$). Contents of Al_2O_3 range from 34.9% to 41.3% with Al^{VI} ranging from 3.49 to 3.98 *apfu* and exhibit a negative correlation with Mg ($r' = -0.92$) and Fe ($r' = -0.88$) (Figure S7). Values of $\text{Si}^{\text{IV}}/\text{Al}^{\text{IV}}$ range from 3.30 to 4.57, consistent with a phengitic composition with minor contributions from other end member micas (Figure 6B). Interlayer cations are dominated by K (Mean 7.56% K_2O) and Na (Mean 0.21% Na_2O), with a deficiency in total interlayer cations, averaging 1.3 *apfu*.

The white mica from the deposits investigated have a wide range of fluid-mobile element contents (see Figure 8), with samples from the Louvicourt having the highest concentrations of fluid-mobile elements. The Sb content of white mica from Louvicourt ranges from 0.82 to 1630 ppm. At the Halfmile Lake Deep zone, Heath Steele B zone, and Restigouche deposits white mica had trimmed mean Sb contents of 1.23, 1.11, and 1.43 ppm, respectively (Figure 8A–C). The Hg content of white mica varies between 0.09 and 3.96 ppm in white mica from most deposits. However, white mica from the Louvicourt deposit contains up to 93 ppm Hg (Figure 8D–F). The pattern for As is similar to the majority of white mica containing less than 10 ppm. The exceptions are elevated values from the Louvicourt deposit which returned up to 14,800 ppm As (Figure 8G–I). The Sn content of white

mica from all deposits falls within a range from 2.52 to 1316 ppm, and there is a good positive correlation between Sn and Tl (Figure 8J–L). The In and Bi contents of white mica are similar to those of chlorite with the majority of the grains containing <10 ppm (Figure 8M–R), with some grains from the Louvicourt deposit having anomalously high In and Bi contents (see Supplementary Table S7).

4.2.3. Biotite Chemical Variations

Two of the thin sections from Heath Steele B zone deposit were examined for the concentration of fluid-mobile elements in biotite. The fluid mobile composition of biotite is presented in Supplementary Table S7. Comparing the results with white mica and chlorite in the same thin section shows that the distribution of Tl among phyllosilicate phases (Figure S8) is in the order: biotite (primary/secondary) > white mica (distal alteration) > chlorite (proximal alteration). Other elements do not show reproducible orders of abundance in the three minerals for the two thin sections. Antimony in sample 95-LPA-10 increases in the order of chlorite < white mica < biotite, but this pattern does not exist in the other sample (Figure S8A). On average, biotite is more enriched in Hg, Sn, Ba, relative to chlorite and white mica (Figure S8B–D). The average Mn and Zn are distributed among phyllosilicates in both thin sections in the order of biotite > chlorite > white mica (Figure S8E,F).

4.3. Fluid-Mobile Elements Variation of Phyllosilicates from the Studied Deposit Profiles

The previous section described the overall inventory of fluid-mobile elements and crystal-chemical variations in phyllosilicates. Below we investigate variations of fluid-mobile elements along stratigraphic (drill-core) profiles of the studied deposits.

4.3.1. Tetagouche Group Deposits

White mica from the footwall of the Heath Steele B zone shows a pattern of increasing Tl, Sb, and to a lesser extent Sn and In with proximity to the ore horizon. In the footwall, enrichment of As, Sb, Pb, and to a lesser degree Hg is more prominent in white mica in the sedimentary rocks relative to the interbedded crystal tuff. With the exception of Zn and Mn, chlorite at Heath Steele typically has lower fluid-mobile element contents than white mica (Figure 9; Supplementary Tables S6 and S7), and is highly variable within footwall chlorite but tends to increase with proximity to the ore horizon. White mica from crystal tuff in the hanging wall at Heath Steele (Figure 9) displays increasing contents of Tl, Sb, Hg, and to a lesser extent Sn and In with proximity to the ore horizon. Likewise, in the hanging wall, the Ba content of white mica increases with proximity to the ore horizon. Chlorite in the hanging wall, proximal to the ore horizon (≤ 150 m above), has Tl contents up to 5.21 ppm and is enriched relative to chlorite from the proximal footwall. The abundances of As (0.3–11 ppm), Sb (0.07–5.76 ppm), Hg (0.07–3.33 ppm), Zn (176–2300 ppm), and Mn (457–6635 ppm) in chlorite from the proximal hanging wall is similar to those in proximal footwall; however, the Sn (0.03–22.8 ppm) and In (<hmdl–11.8 ppm) contents of hanging wall chlorite are higher than chlorite from the footwall.

At the Brunswick No. 12 deposit, footwall crystal tuff and tuffaceous sedimentary rocks of the Nepisiguit Falls Formation (NF Fm) contain white mica that is highly enriched in Tl, Sn, In, and Zn, with trimmed mean concentrations of 36.4, 83.2, 1.79, and 166 ppm, respectively. The Tl, As, Sb, and Pb content of white mica from the K-Na-Mg alteration halo (zone II and III) in the NF Fm (shallow footwall) are elevated relative to white mica from more proximal alteration zones (Figure 10). In comparison, white mica in the hanging wall rocks of the Flat Landing Brook Formation (FLB Fm) has higher concentrations of Sb and Ba with mean contents of 9.36 and 3309 ppm, respectively. Chlorite in the footwall has lower fluid-mobile element contents than white mica. The Tl, As, Sn, and Ba contents of chlorite in the footwall increase with proximity to the ore horizon (see Figure 10). Limited data on chlorite from the hanging (FLB Fm) suggest similar or higher fluid-mobile element contents relative to coexisting white mica.

At the Halfmile Lake Deep zone (Figure 11), the fluid-mobile element contains (Tl, As, Sn, In, Pb, and to a lesser extent Sb and Hg) of white mica from the immediate hanging wall and

footwall. Chlorite displays a similar pattern for these elements as well as Zn. In the structural hanging wall (upward-facing limb), crystal tuff and interlayered volcanoclastic rocks of the Nepisiguit Falls Formation (stratigraphic footwall) show marginally higher fluid-mobile element concentrations in white mica (Sb, Sn, Hg, as well as Mn and Ba) relative to clastic sedimentary rocks of Patrick Brook Formation (Figure 11). The Tl, Sb, Sn, Hg, In, and Ba contents of chlorite are lower than white mica but follow similar trends. Chlorite in the massive sulfides and iron formation contains elevated contents of In, Zn, Pb, Sb, and As.

Crystal tuff from the footwall of the Key Anacon East zone (Figure 12) contains white mica in which Tl (3.56–8.08 ppm), As (1.52–6.3 ppm), Hg (0.53–1.86 ppm), Zn (14–194 ppm), Pb (0.75–51.7 ppm), and Ba (362–2469 ppm) increase, to varying degree, with proximity to the ore horizon and are detected at depths of up to 100 m below the ore horizon. In contrast, Sb, Sn, and In contents of white mica tend to decrease slightly with proximity to the ore horizon. White mica in mafic volcanic rocks of the Little River Formation (LR Fm) tend to have higher Tl contents in proximity to the sulfide horizon, whereas As, Sn, In, and Zn contents are higher in more distal parts of LR Fm. Rhyolite of Flat Landing Brook Formation, in the immediate hanging wall, contain white mica with Tl contents ranging between 4.67 and 10.1 ppm, and are slightly higher than mafic volcanic rocks of the LR Fm higher in the hanging wall (Figure 12). Chlorite at Key Anacon East is best developed in the mafic volcanic rocks of the LR Fm. Here the Tl (<hmdl–3.43 ppm), Sn (<hmdl–25.2 ppm), Hg (0.19–2.16 ppm), and In (0.01–2.89 ppm) contents of chlorite are higher in rocks more distal to the massive sulfide horizon. Zinc and Mn contents of chlorite are high relative to white mica but do not seem to show any trend, either increasing or decreasing, with respect to proximity to the sulfide horizon (Figure 12).

At the Louvicourt deposit (Figure 13), white mica from the footwall is marked by increasing Tl (95.6–229 ppm), Sb (1.26–18.8 ppm), Hg (0.66–1.44 ppm), Pb (1.23–85,400 ppm), and Ba (7606–16,450 ppm) with proximity to the sulfide horizon. As in the footwall, white mica from the hanging wall tuff and magnetic argillite tend to be enriched in fluid-mobile elements (Tl, Sn, Hg, Zn, Mn, and Ba) with proximity to the massive sulfide horizon. The concentration of Sn and In in white mica from the sulfide horizon is higher than that of white mica from the hanging wall or footwall.

At Louvicourt, the development of chlorite is restricted to the hanging wall tuff and magnetic argillite (a narrow interval of about 3 m immediately above the ore horizon). The fluid-mobile element content of chlorite from the hanging wall tuff are elevated in Tl (0.05–50.1 ppm), As (1.67–11.8 ppm), Hg (0.45–2.41 ppm), Zn (99.9–2832 ppm), Ba (2.27–87,000 ppm), and Mn (151–6170 ppm) and tend to increase with proximity to the ore horizon. The Sb (0.07–1.91 ppm), Sn (0.03–1.92 ppm), In (0.02–0.16 ppm), and Pb (0.12–9900 ppm) contents define less significant trends; however, Sb, Sn, In, and to a lesser extent As and Hg are highly enriched in chlorite from the top of the sulfide horizon.

4.3.2. California Lake Group Deposit

At the Restigouche deposit (Figure 14), white mica in the footwall shows increasing Tl, As, Pb, Sn, and to a lesser extent Hg and Sb with proximity to the ore horizon. The limited data for white mica from very proximal hanging wall suggest comparable abundances of Tl, As, and Sn, and higher Pb, Mn, and to a lesser extent Sb relative to white mica from the proximal footwall. Fluid-mobile element contents of chlorite over a distance up to 100 m below the sulfide zone show increasing trends of Tl, Sb, Hg, In, Zn, and Mn with proximity to the ore horizon, whereas As and Pb decrease with proximity to the massive sulfide horizon (Figure 14).

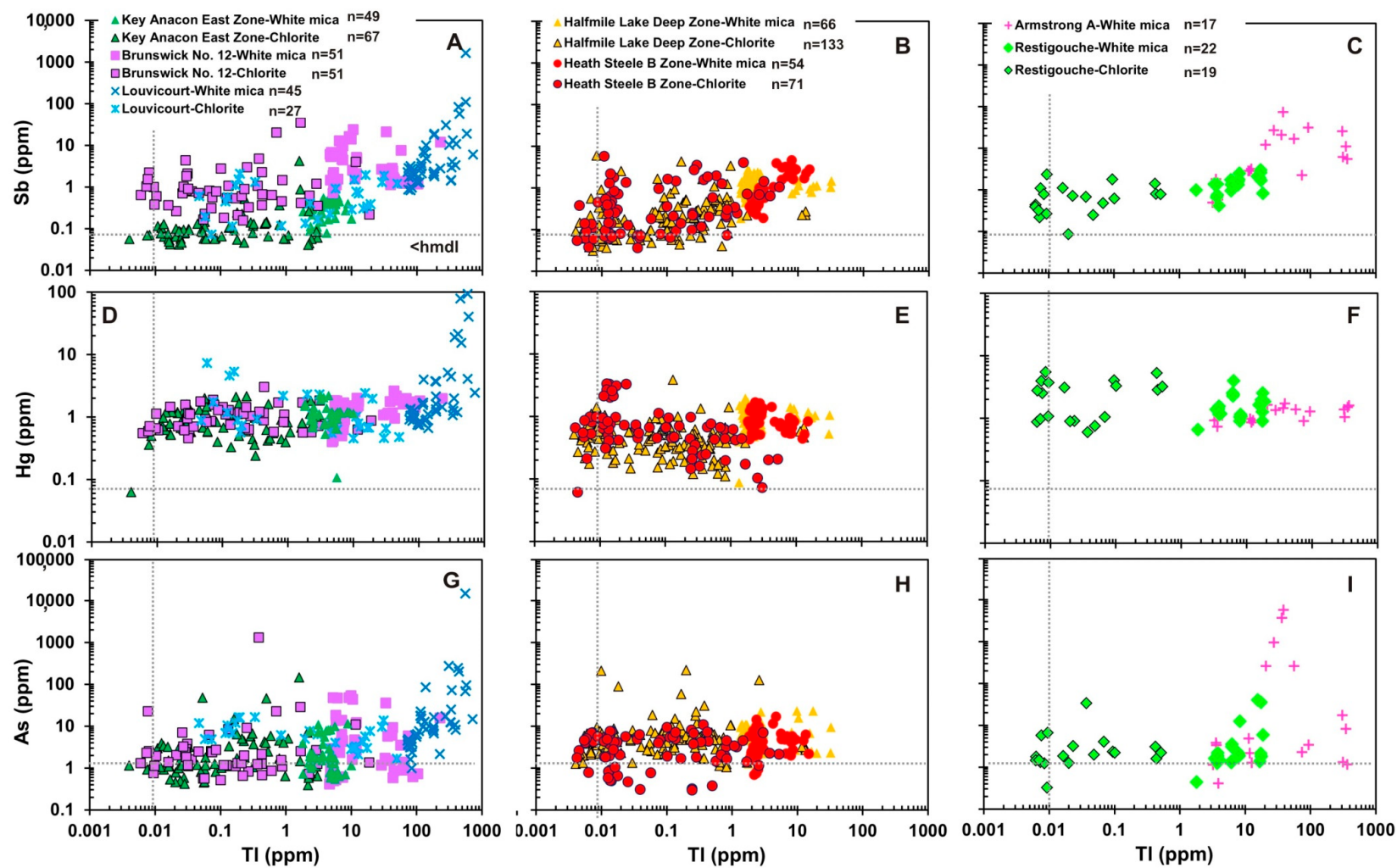


Figure 8. Cont.

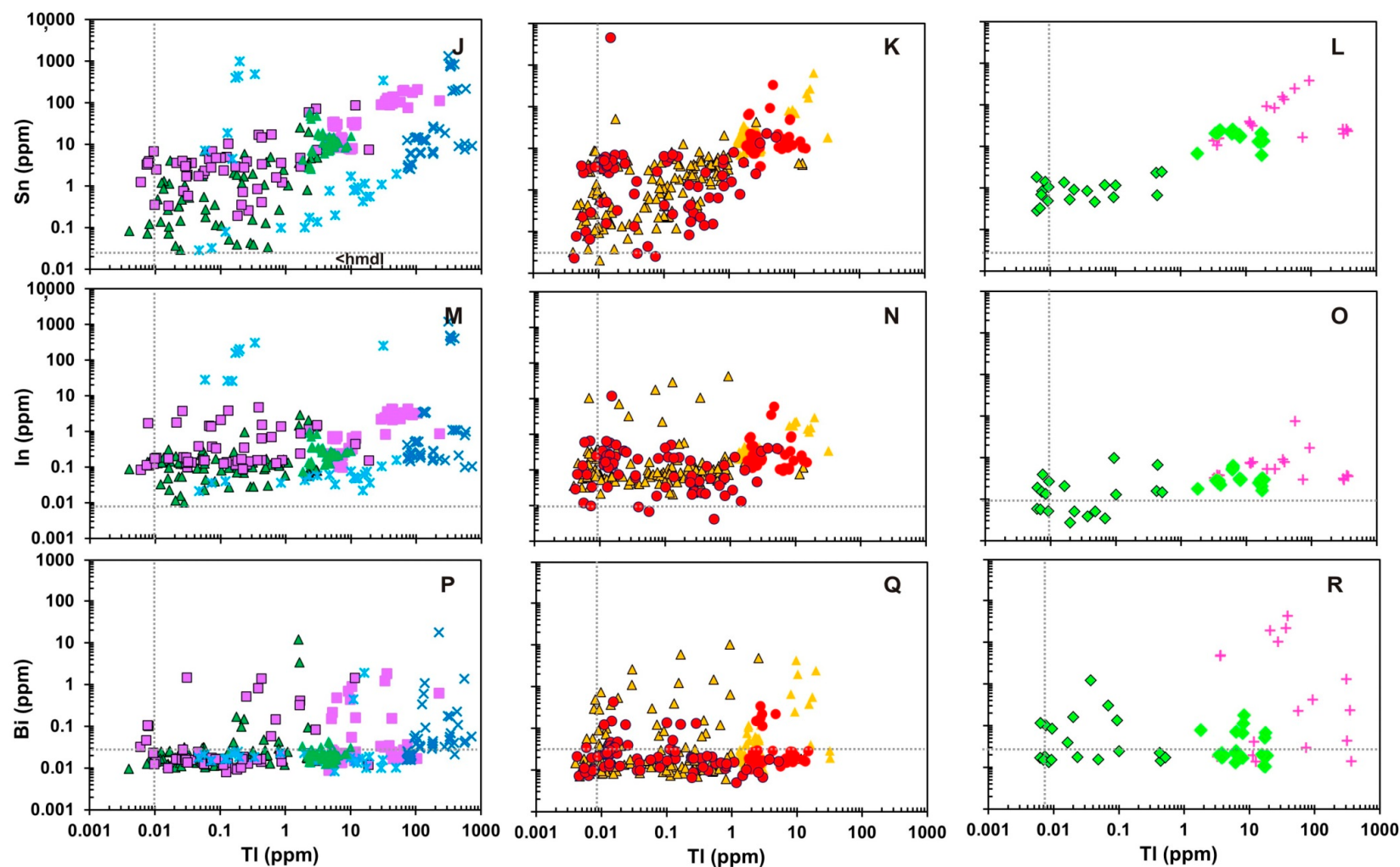


Figure 8. Binary plots of Tl (in ppm) vs. Sb, (A, B and C); Hg, (D, E and F); As, (G, H and I); Sn (J, K and L); In, (M, N, and O); and Bi, (P, Q and R), for chlorite and white mica from selected massive sulfide deposits of the BMC as determined by LA-ICP-MS during this study (see Supplementary Tables S6 and S7). The dotted lines are equivalent to $\frac{1}{2}$ of the mean detection limit (<hmdl of the presented element).

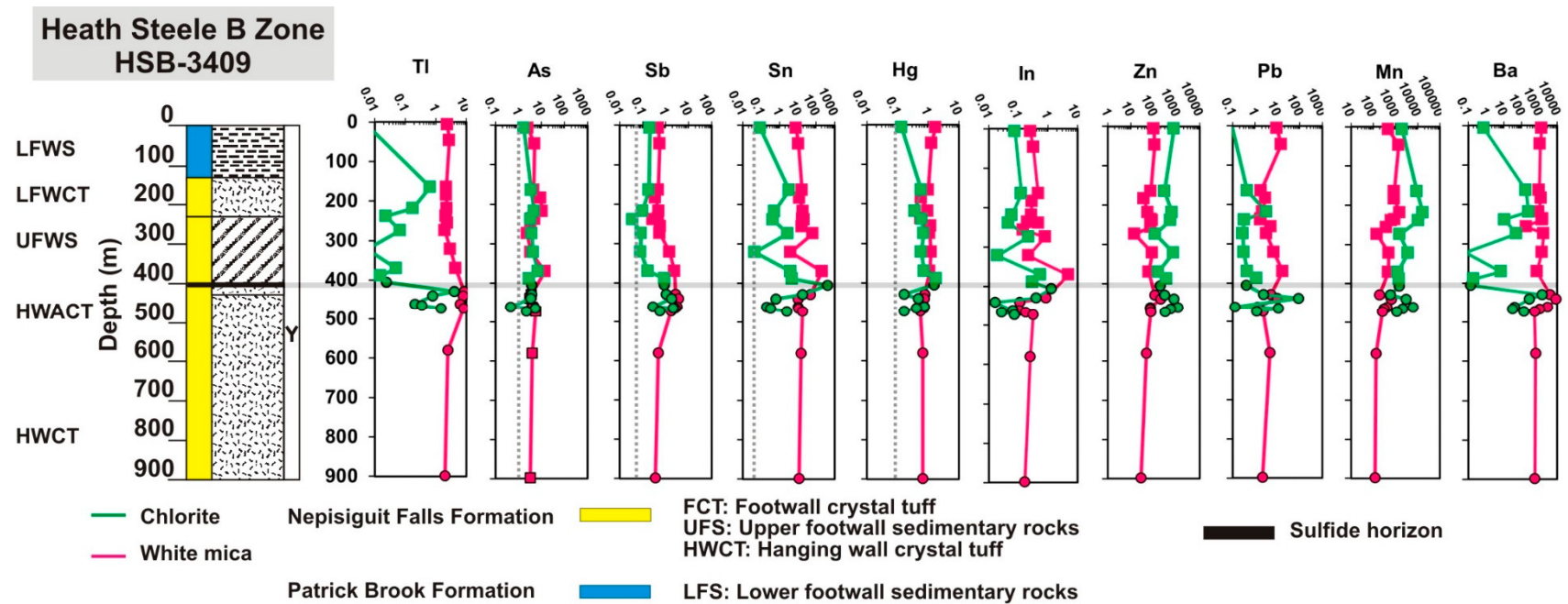


Figure 9. LA-ICP-MS geochemical data profiles illustrating fluid-mobile elements, as well as Zn, Pb, Mn, and Ba content (in ppm) of chlorite (green symbols and lines) and white mica (pink symbols and lines) plotted with respect to stratigraphic profile of the Heath Steele B zone deposit along drill hole HSB-3409 (see Supplementary Tables S6 and S7). Black outline on squares denotes hanging wall samples.

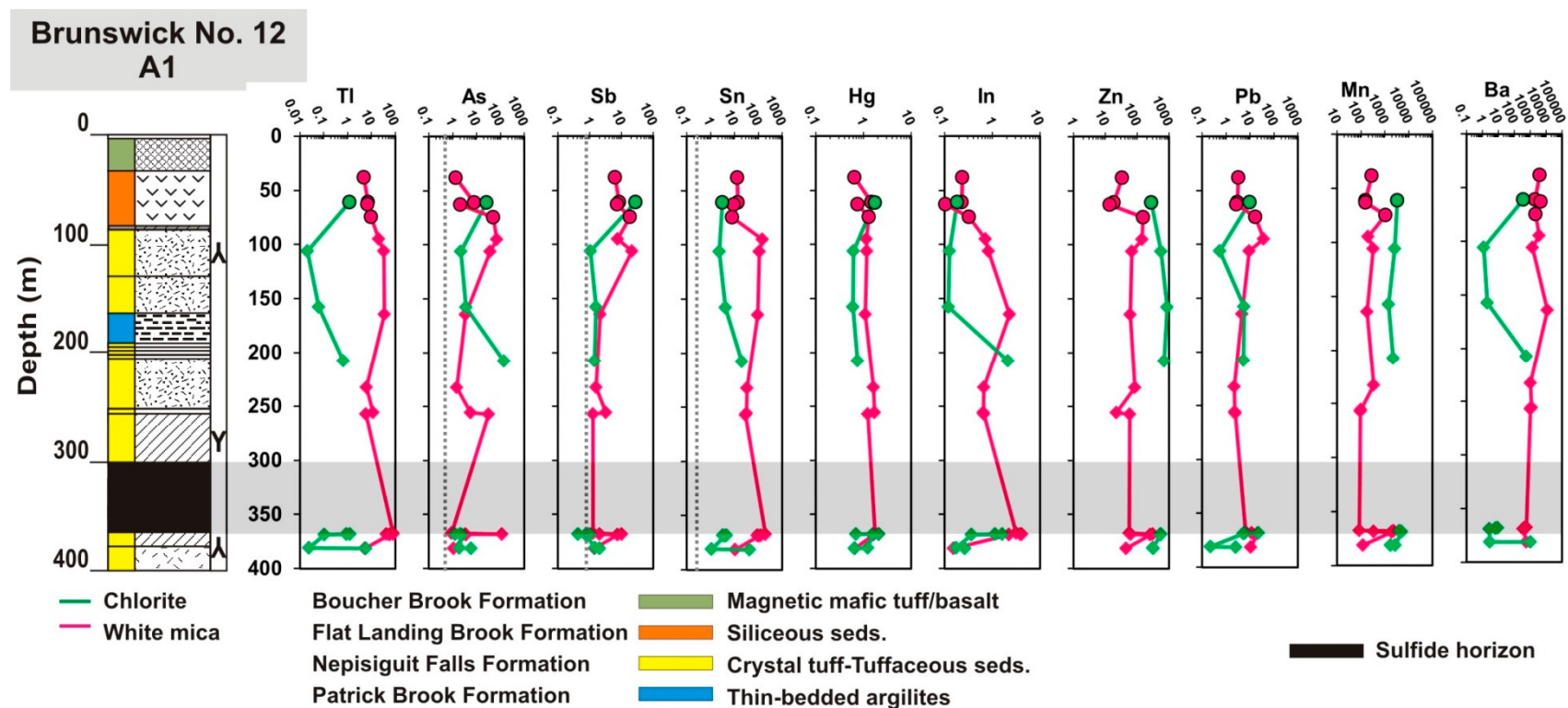


Figure 10. LA-ICP-MS geochemical data profiles illustrating fluid-mobile elements, as well as Zn, Pb, Mn, and Ba content (in ppm) of chlorite (green symbols and lines) and white mica (pink symbols and lines) plotted with respect to stratigraphic profile of the Brunswick No. 12 deposit along drill hole A1 (see Supplementary Tables S6 and S7). Black outline on symbols denotes hanging wall.

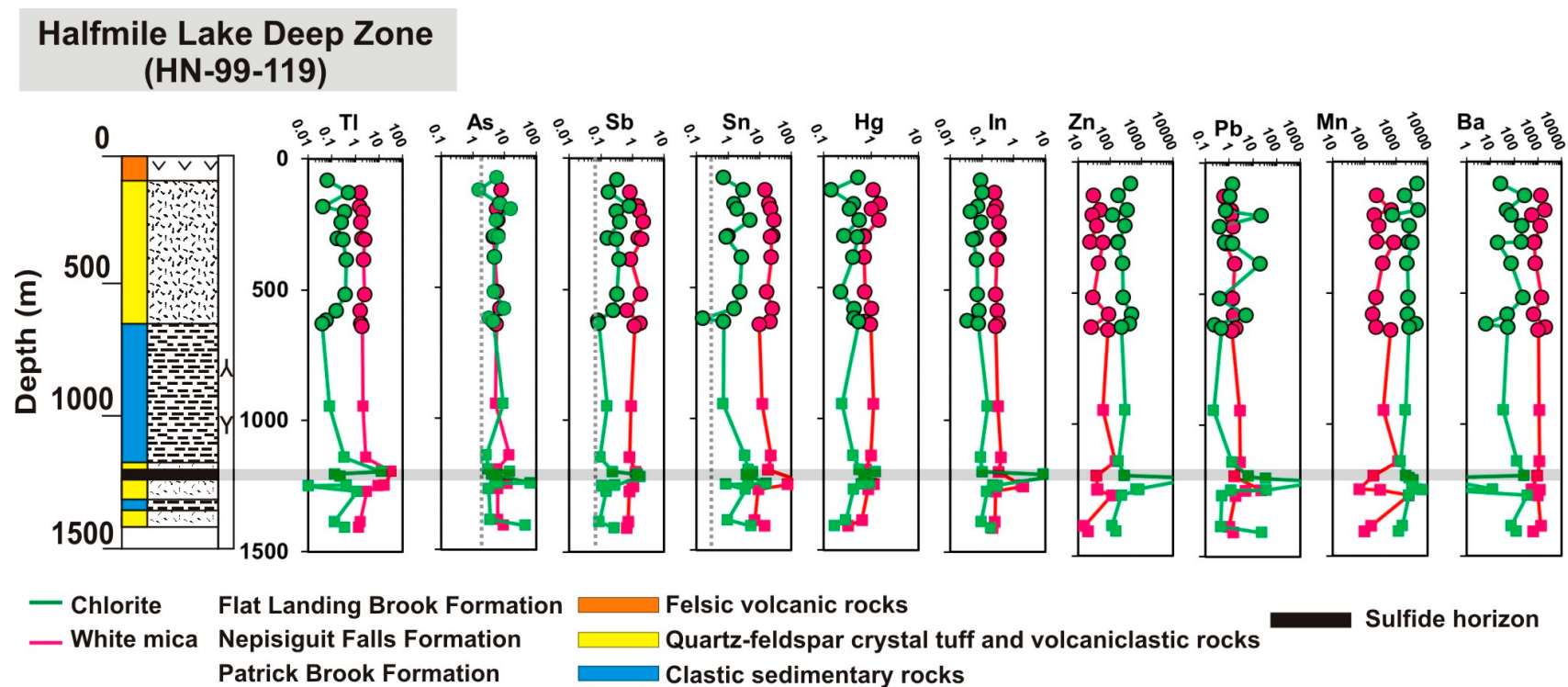


Figure 11. LA-ICP-MS geochemical data profiles illustrating fluid-mobile elements, as well as Zn, Pb, Mn, and Ba content (in ppm) of chlorite and white mica plotted with respect to the stratigraphy of the Halfmile Lake Deep zone deposit intersected by drill hole HN-99-119 (see Supplementary Tables S6 and S7). Black outlined symbols denote hanging wall samples.

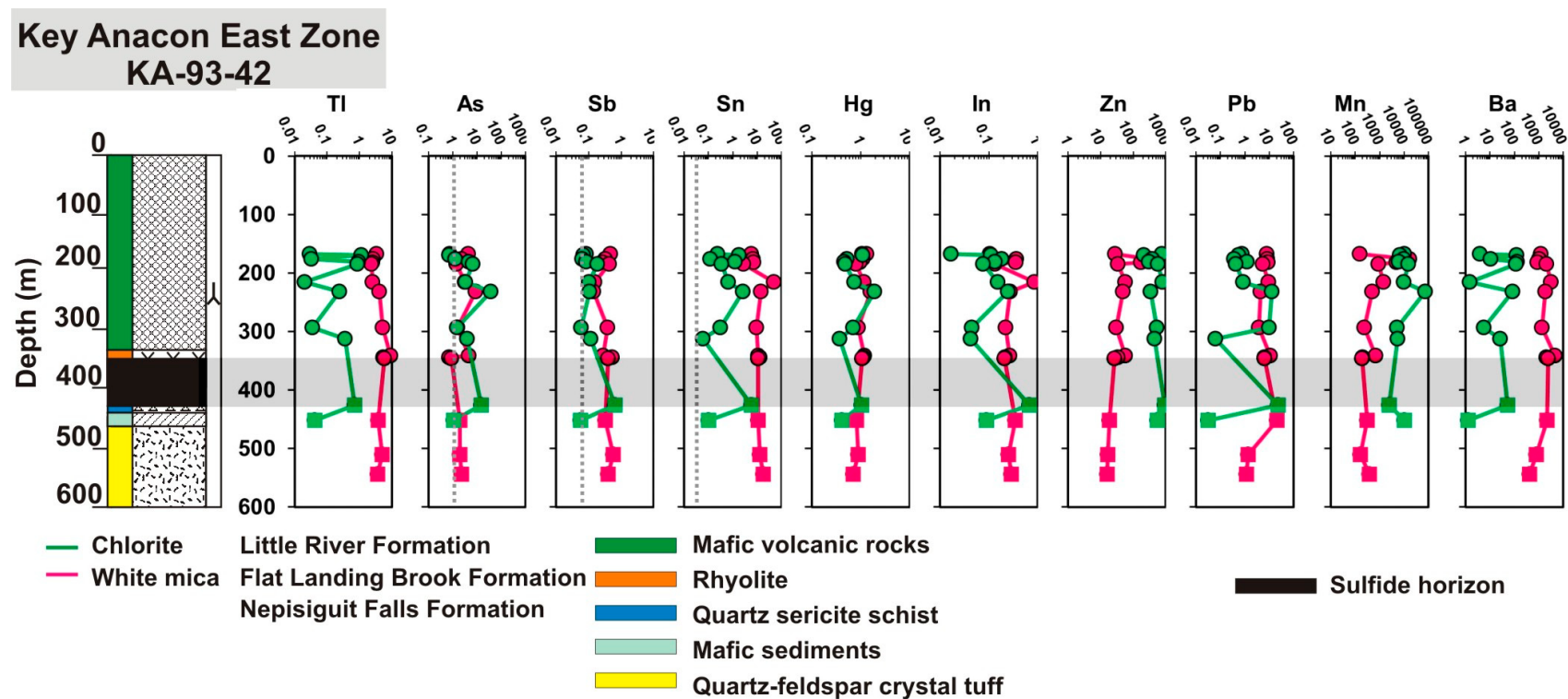
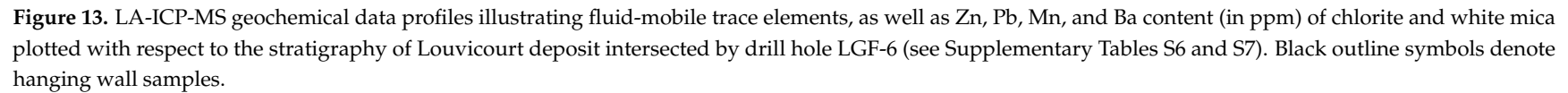


Figure 12. LA-ICP-MS geochemical data profiles illustrating fluid-mobile trace elements, as well as Zn, Pb, Mn, and Ba content (in ppm) of chlorite and white mica plotted with respect to the stratigraphy of the Key Anacon East zone intersected by drill hole KA-93-42 (see Supplementary Tables S6 and S7). Black outlined symbols denote hanging wall samples.



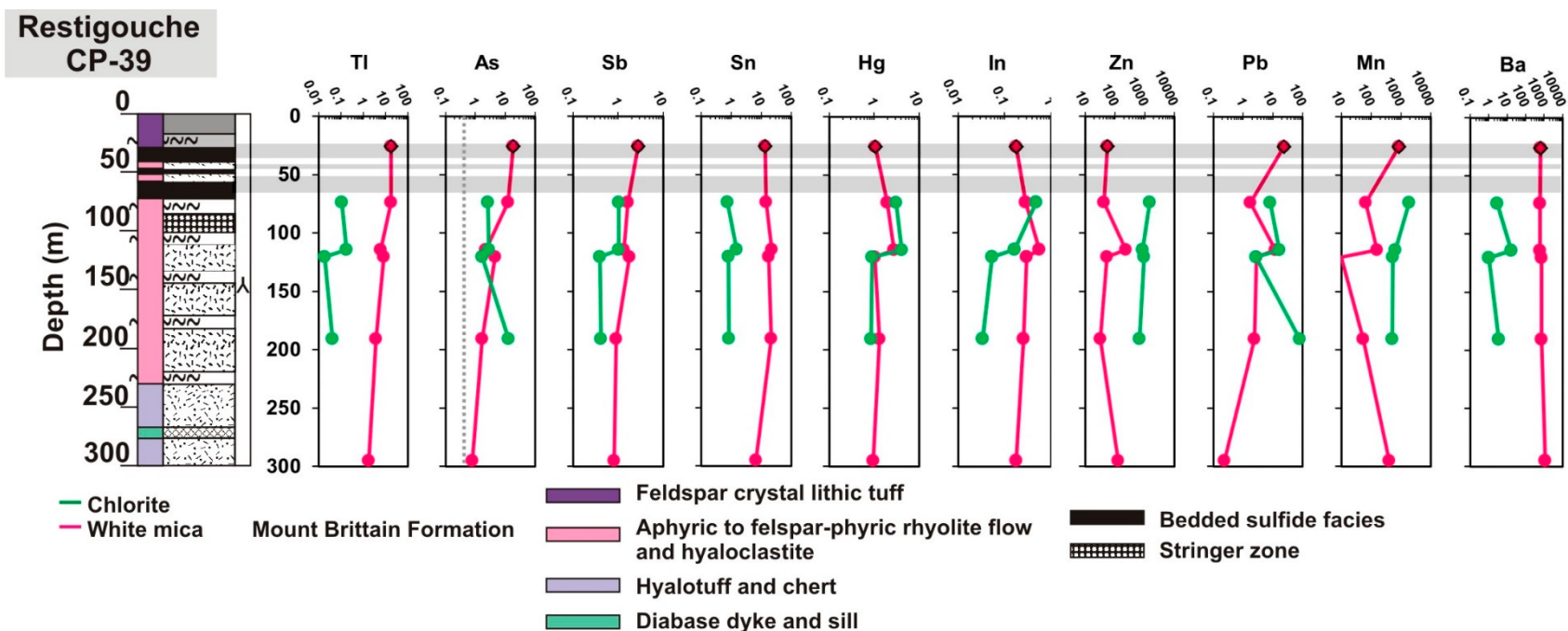


Figure 14. LA-ICP-MS geochemical data profiles illustrating fluid-mobile trace elements, as well as Zn, Pb, Mn, and Ba content (in ppm) of white mica plotted with respect stratigraphy of the Heath Steele B zone deposit intersected by drill hole HSB-3409 (see Supplementary Tables S6 and S7). Black outline symbols denote hanging wall samples.

5. Discussion

5.1. Origin of Phyllosilicates in the BMC

The origin of phyllosilicates in host rocks of VMS-mineralized systems is complicated because of superimposed epigenetic, authigenic, and metamorphic processes [49,50]. The phyllosilicates of VMS deposits of the BMC have been suggested to form by hydrothermal metasomatic processes, such as devitrification [51–55] and hydrolysis, via interaction with heated seawater [8,9,40,41]. The alteration reactions forming phyllosilicates include the replacement of albite by white mica and quartz, alteration of K-feldspar to white mica, development of chlorite at the expense of white mica (de-phengitization), alteration of biotite to chlorite, and also the destruction of iron oxides to chlorite. Furthermore, [56] proposed that a precursor mineral of nontronite or the reaction of primary Fe-bearing phases (i.e., siderite) with chert (now quartz) most likely formed chlorite in the iron formation and related crystal tuff along the Heath Steele Belt.

Systematic zoning of white mica and chlorite of the hydrothermal conduits of the Brunswick No. 12, and Heath Steele B zone deposits [8,9,39] is interpreted to reflect primary hydrothermal zoning in these fossilized hydrothermal up-flow zones. Moreover, the Ba-rich nature of white mica in the BMC [22,33,55] is interpreted to reflect deposit-related hydrothermal enrichment, similar to white mica from Kristineberg deposit [57]. Herein, two distinct generations of chlorite have been investigated for fluid-mobile element variations, i.e., chlorite fringes formed on the margins of pyrite and massive pyrite (Figure S5). Chlorite on the fringes of pyrite has higher As, Se, and Sb and distinctly higher Cd, In, Sn, and Bi relative to masses of chlorite. In addition, an LA-ICP-MS raster line across sericitic bands and fine-grained sericite in the matrix have a highly variable Ba profile. Zinc and Mn do not show distinctive concentration differences along the same sericite raster line. Results of this study suggest that the distribution of Tl, Hg, Sb, Sn, and Ba among phyllosilicate phases (Figure S7A–D) is, in decreasing order: biotite (primary/secondary) > white mica (distal alteration) > chlorite (proximal alteration). Petrographic evidence shows that chlorite may be the final product of alteration of biotite and white mica. Fluid-mobile element loss (Tl, Hg, Sb, Sn, and Ba) during this process may account for the hierarchy of fluid-mobile element concentrations among these minerals. In contrast, Mn and Zn are distributed among phyllosilicates in the order biotite > chlorite > white mica (Figure S7E,F). Since [58] suggested the mass changes related to deformation do not operate over large distances and are not significant in terms of potential application as a vectoring tool, the signature of fluid-mobile elements is interpretable in the context of a fossilized hydrothermal system. Despite the acceptance of preserved fossilized hydrothermal up-flow zones in most deposits of the BMC, the overlap between the pressure-temperature (*P-T*) condition of hydrothermal and metamorphic events provide complication. White mica and chlorite in the BMC have undergone some degree of recrystallization in response to greenschist facies metamorphic conditions. Recently, [59] presented $^{40}\text{Ar}/^{39}\text{Ar}$ dating of white mica, which refined the timing of *S*₁ white mica growth (and hence *M*₁-*D*₁) (ca. 452–437 Ma) and *S*₂ white mica growth (also *D*₂) to ca. 427–418 Ma in the Bathurst Supergroup. In addition, the Acadian Orogeny *D*₃ and *D*₄ and granite emplacement (370–380 Ma) in the early- to mid- Devonian were distinguished previously. After the metamorphism and deformation of the hydrothermal systems in the BMC, the whole of the fossilized systems did not change significantly [59].

Because all the rocks in the BMC are poly-deformed and metamorphosed to middle- to upper-greenschist facies, it is impossible to unequivocally differentiate phyllosilicate of purely metamorphic origin from those originally of primary hydrothermal origin. Nevertheless, the location of the selected samples with respect to recognizable alteration haloes (sericite and chlorite zones) and stratiform massive sulfide bodies, along with previously published whole rock chemistry from these alteration zones gives the authors confidence that the trace element contents of phyllosilicates examined reflect primary hydrothermal signatures (see [27]). Nevertheless, this is still a subject of matter and needs to be addressed by examining and comparing the elemental dispersion haloes in other massive sulfide deposits.

5.2. Distribution of Fluid-Mobile Elements in Phyllosilicates

Phyllosilicates can accommodate a wide range of elements in their structure. The chemical composition of chlorite is controlled by bulk-rock composition, temperature, and pressure [60,61] (and references therein). Chlorite can accept substituting elements in both the tetrahedral talc layer (2:1 layer $R_6Z_8O_{20}(OH)_4$) and the octahedral brucite ($R_6(OH)_{12}$) layer ($R = Mg, Fe^{2+}, Al$, and Fe^{3+} , occasionally $Cr, Mn, V, Ni, Cu, Zn, Ti, Li$; $Z = Si$, partially replaced by Al , occasionally by $Fe^{3+}, B^{3+}, Zn^{2+}, Be^{2+}$) [62] (and references therein). The Tschermak, dioctahedral and $FeMg_{-1}$ substitution are common substitutional processes in chlorite.

The common substitution process of white mica is Tschermak substitution (coupled octahedral and tetrahedral cation substitutions: $[Fe^{2+}, Mg^{2+}]_{VI} + Si^{4+} \leftrightarrow (Al^{3+})_{VI} + (Al^{3+})_{IV}$) [63–66]. Tschermak substitution results in white mica with compositions transitional from muscovite to celadonite (phengite). In the octahedral site, Al^{3+} is commonly replaced by Mg^{2+} and Fe^{2+} . In addition, $Fe^{3+}, Mn^{2+}, Cr^{3+}, Ti^{4+}, Li^+$, and V^{5+} can be accommodated in octahedral sites. In addition to octahedral and tetrahedral site replacements described above, it has interlayer cations that can accommodate large ion lithophile elements substitution (i.e., Ba, Sr , and REE). Interlayer K^+ in muscovite can be replaced by large ion lithophile elements (e.g., Rb^+, Cs^+, Ca^{2+} , and Ba^{2+}); however, their inclusion may result in low occupancy in the interlayer space [65,66]. The occurrence of Tl and Hg in the white mica most likely follows the same process [67]. Chlorite is unlikely to incorporate significant Tl , due to the lack of suitable lattice sites that can accommodate the large Tl^+ ion. The volume of published material pertaining to the investigation of fluid-mobile element substitution in chlorite and white mica is quite limited; however, it is likely that Tschermak substitution is the main process.

A thermally-controlled processes such as circulation of VMS deposit-forming hydrothermal fluids containing multiple cations and possibly anions controls the substitution of fluid-mobile elements in phyllosilicates. This can be accomplished in a manner similar to the incorporation of Ti (immobile element) into the octahedral site of chlorite and biotite via coupled substitution. In the case of Ti , biotite and white mica host the bulk Ti budget of the host rocks in the BMC (see [22] and this study), and Ti -bearing oxides are expected to form during the alteration of biotite to chlorite (see [22]). The lower budget of Ti of chlorite may reflect the high levels of octahedral Al unique to the chlorite structure [68]. The titanium content of chlorite generally increases trend with proximity to the ore horizon, a trend related to higher temperature up-flow zone (see Supplementary Table S6). By analogy, Tl, Sn, Sb, Hg , and In substitution in the structure of phyllosilicates can be a result of high-temperature fluid interaction with host rocks. In addition to temperature, the composition of protolith, mineral assemblages, oxidation state, the pH of the hydrothermal fluids, and element endowment of the system are other factors to be considered. Herein time-resolved LA-ICP-MS profiles of chlorite and white mica from the BMC show that both can contain high concentrations of regularly distributed fluid-mobile elements, e.g., In and Sn in chlorite and Tl, Sb , and Sn in white mica, indicating structural substitution of these elements (see Figure 2); however, the presence of nano-scale inclusions of other mineral phases cannot be completely ruled out. Further research needs to be done for the occurrence of fluid-mobile elements within phyllosilicates in nano-scale.

5.3. Fluid-Mobile Element Distribution Patterns at Deposit Scale

Here, we show systematic fluid-mobile element dispersion patterns in phyllosilicates related to known massive sulfides of various deposits of the BMC. Using various minerals in alteration haloes allows validation of the observed signatures (see [28,69]). In particular, the link between the low-temperature outboard hydrothermal zones and the high-temperature central zones can be shown by the chlorite and white mica pairs.

In both proximal footwall and hanging wall of the deposits (i.e., from <20 m of the sulfide horizons up to 100 m) chlorite and white mica have elevated fluid-mobile element contents (Tl, Sn, Sb , and Hg), which generally increase with proximity to the sulfide horizon (see Figures 7 and 9–14). In more distal parts of these systems, fluid-mobile element contents are highly variable and in line with the variable

bulk composition of the protolith as determined from whole rock analysis (e.g., [8]). The occurrence of chlorite becomes prevalent with proximity to the sulfide horizon; however, the fluid-mobile element concentrations (e.g., Tl, Sb, Sn, and Hg) within chlorite, though detectable, are several times lower than coexisting white mica (see Supplementary Tables S6 and S7). White mica is ubiquitous in distal zones (up to several hundred meters). The Tl and As (also Pb) concentrations of white mica increase in excess of 15 times from distal parts of the hydrothermal system to areas more proximal to sulfide horizon, whereas the concentrations of Sn, Sb, Hg, and In increase two times over the same interval. Furthermore, [28] showed that summation of the most important vectoring elements (Tl, Sb, Sn, and Hg) of white mica is a more effective vectoring tool in more distal parts of the hydrothermal systems. In addition, the budget of some fluid-mobile elements within phyllosilicates is compared to that of coexisting pyrite (see [27,28]). For example, white mica is highly enriched in Tl, Sn, Hg, and In relative to coexisting pyrite from the same sample. The same pattern, except for Tl, is evident in chlorite. This work has shown that phyllosilicate chemistry may be a useful means to fingerprint of VMS deposits of the BMC but requires further research and testing in the prospecting regions in the BMC as well as other mining camps. Moreover, protocols for distinguishing barren regional metamorphic phyllosilicate assemblages from those related to VMS-related assemblages must be established to develop a vectoring tool. To do so, it is critical to establish the background of the elements of interest as well as variations in enrichment and/or depletion of the elements in the context of metamorphic and structure factors. The mineral geochemical vectoring tools can be an effective discriminator of mineralized and barren environments, locating hydrothermal centers within a broader zone, and recognizing the peripheries of ore systems not only in VMS systems but also in other hydrothermal mineralization systems (see [26,70]).

6. Conclusions and Implication for VMS Exploration

This study documents the concentrations of fluid-mobile elements within phyllosilicates from the alteration zones of several VMS deposits of the Bathurst Mining Camp, Canada.

The fluid-mobile elements can reside in phyllosilicates as either structural substitution or as micro- to nano-inclusion of other phases. The latter cannot be resolved due to the limitations of the LA-ICP-MS system employed during this study. It is most likely that the high concentration of Tl, Sn, Sb, and As identified in white mica, In in chlorite, and Tl in biotite occur via structural substitution.

Compositional variations in the fluid-mobile element content of chlorite and white mica in the host rocks offer a potential deposit-vectoring tool. Specifically, proximal footwall and hanging wall rocks (up to 100 m from the sulfide horizon) contain white mica and chlorite that are significantly enriched in fluid-mobile elements. Distal to the sulfide horizon (several hundred meters) subtle enrichments in fluid-mobile elements is probably related to massive sulfide occurrences at depth. As previously presented by [28], the fluid-mobile element footprint of white mica is a useful tool in distal zones of the massive sulfides. Herein, coupling chlorite with white mica enhances the identification of proximal alteration zones, which offers a more reliable tool in identifying the geochemical fingerprints related to a mineralized system.

The application of fluid-mobile element contents of white mica and chlorite as an indicator of VMS mineralization is in its infancy. This is an open avenue of research to establish our understanding of the effect of metamorphism in the mobility of elements in micro- to mega-scale. In addition, the complexity of the host rocks of the VMS system leads to multi-component systems, which is a required examination of the other phases and to address the full TE budget of the system. Furthermore, the LA-ICP-MS technique is still an expensive method to be used at the industrial level, and considering this limitation will possibly lead to generating unconventional approaches using laser technology. Finally, the proposed approach requires further work including testing in other mining camps, in particular, those that are less deformed and metamorphosed than the BMC. The approaches proposed here should be considered as complementary techniques to other exploration tools.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/9/2/125/s1>, Figure S1: Assessment of the accuracy of NIST612 standard analyzed by LA-ICP-MS, Figure S2: Assessment of the accuracy of BCR-2G standard analyzed by LA-ICP-MS, Figure S3: Raster LA-ICP-MS spectra for selected elements in white mica from, Figure S4: Raster LA-ICP-MS spectra for selected elements in chlorite from Brunswick No. 12, and Halfmile Lake Deep zone deposits, Figure S5: Bivariate plots of selected trace and major elements exhibiting Spearman Rank correlations for 68 electron-microprobe analyses of chlorite, Figure S6: Variation in the fluid-mobile element content (ppm) between two generations of chlorite from the Heath Steele B zone deposit, Figure S7: Bivariate plots of selected trace and major elements exhibiting Spearman Rank correlations for 13 electron-microprobe analyses of muscovite from the BMC, Figure S8: Binary discrimination diagrams showing Tl versus Sb, Hg, Sn, Ba, Zn and Mn, Table S1: Integration time/point (s) setting for LA-ICP-MS analysis on phyllosilicates in the current study, Table S2: Summary of obtained compositional variations of NIST612 and BCR-2G in this study (in ppm), Table S3: Comparison of Tl and Sb data, using different values for K as internal standard, Table S4: Average microprobe data and mineral formula of chlorite for representative samples of the BMC deposits, Canada, Table S5: Average microprobe data and mineral formula of muscovite for representative samples of the BMC deposits, Canada, Table S6: Compositional variation of chlorite (LA-ICP-MS) for representative samples of the BMC deposits, Canada (in ppm), Table S7: Compositional variation of white mica (LA-ICP-MS) for representative samples of the BMC deposits, Canada (in ppm), Table S8: Compositional variation of biotite (LA-ICP-MS) for representative samples of the BMC deposits, Canada (in ppm).

Author Contributions: A.S.D. did sample selection and microscopic studies, designed and carried out the LA-ICP-MS analysis, data correction and development of methodology, wrote the paper and handle the submission procedure. C.R.M.M. supervised the LA-ICP-MS data obtaining and contributed to data interpretation, writing, and editing the manuscript. D.R.L. provided samples and contributed to interpretation, writing, and editing of the manuscript. S.H.M. provided the electron microprobe data and contributed to data interpretation. J.A.W. helped in sampling and data interpretation as well as editing the drafts of the paper.

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