Abstract

An innovative approach to enhance volcanogenic massive sulfide (VMS) exploration in regions outside of mining camps is to first use physical volcanology with litho- and chemo-stratigraphy to establish the location of effusive centers in the volcanic units and use pyrite geochemistry in sulfide-bearing stratified intervals with whole-rock geochemistry in the underlying volcanic units to identify hydrothermal upflow zones.

This methodology is illustrated by this study in the Archean Blake River Group within the Abitibi greenstone belt of Quebec and Ontario. The Blake River Group contains numerous VMS deposits, yet large segments remain underexplored, including the Hébécourt Formation which contains four tholeiitic units that range from basalt to rhyolite in composition. Effusive centers are located for three felsic units and subunits: (i) low-Ti (porphyritic) subunit of the main rhyolite, (ii) high-Ti (aphyric) subunit of the main rhyolite, and (iii) the upper rhyolite, and for a basaltic andesite unit. Stringer and disseminated Zn-Cu mineralization occurs within the flank breccia of the low-Ti rhyolite dome. An inferred vent area for an overlying basaltic andesite unit has also been identified in this area, illustrating the coincidence of hydrothermal upflow zones with volcanic vents.

LA-ICP-MS analysis of pyrite grains from several sulfide-bearing stratified intervals indicates two broad areas of higher Cu, Zn, Au and Ag contents. The eastern region corresponds to known volcanic vents and mineralization. The western region also indicates upflow of Cu-bearing hydrothermal fluids, and corresponds to a possible effusive centre for the high-Ti subunit. The western region does not contain known mineralization at lower stratigraphic positions, but it has not been thoroughly explored.

Introduction

Volcanogenic massive sulfide (VMS) deposits typically form polymetallic sulfide lenses at or near the sea floor in submarine volcanic successions (Franklin et al., 2005; Galley et al., 2007). Worldwide, VMS deposits are major sources of Zn, Cu, Pb, Ag, and Au, and significant sources for Co, Sn, Se, Mn, Cd, In, Bi, Te, Ga, and Ge (Galley et al., 2007). At a regional scale, the exploration for VMS deposits uses criteria such as the presence of submarine volcanic rocks, large synvolcanic intrusions (thought to drive hydrothermal convection), and bimodal volcanic sequences (thought to indicate extension). At a more local scale, features such as texturally destructive alteration of volcanic rocks to chlorite and sericite (indicating intense water-rock interaction in greenschist facies terrains), broader Na-depletion haloes (again supporting hydrothermal alteration), synvolcanic faults (to provide fluid conduits), the presence of rhyolite domes and dome alignments, and “exhalites” (indicating a hiatus in volcanism and venting of hydrothermal fluids at the sea
Within a given volcanic succession, VMS deposits tend to be associated with specific stratigraphic levels (e.g., Gibson and Watkinson, 1990; Piché et al., 1993). Therefore relatively detailed geological mapping, core logging and chemical stratigraphy can help VMS exploration, especially in the absence of traceable “exhalites” (e.g., Mercier-Langevin et al., 2009).

Where “exhalites”, iron formations, “tuffites” or metal-rich sediments such as argillites are present, approaches that can be useful in providing a vector to ores in VMS and SEDEX systems include geochemical ratios derived from whole-rock analyses (e.g., Scott et al., 1983; Liaghat and MacLean, 1992; Spry et al., 2000; Peter, 2003; Barrie et al., 2005), analyses of sulfide separates (e.g., Hannington et al., 1999), and elemental analysis of specific minerals such as chlorites or sulfides (e.g., Kalogeropoulos and Scott, 1989; Peter et al., 2003a, b; Chapman et al., 2008). So far the literature describing the use of such techniques seems to be limited to districts where the deposits have already been found (e.g., Liaghat and MacLean, 1992; Peter et al., 2003a, b; Barrie et al., 2005); in other words, they are not applied outside of mining camps (at least not in the literature).

The study area, representing a very small portion of the Archean Abitibi greenstone belt, does not contain a known VMS deposit, and is located outside of a mining camp. However it displays many of the favorable features described within the VMS model: bimodal submarine volcanism including rhyolite domes; Zn-Cu mineralization and hydrothermal alteration zones; and metal-bearing stratified intervals. We have used a combination of techniques to improve the understanding of the volcanological and hydrothermal evolution of this area, and to facilitate future VMS exploration. This combination of field-based and advanced laboratory techniques provides an example of a methodology applicable to other prospective areas, including those outside of established mining camps, in Archean or younger volcanic successions.

The objectives of this paper are: 1) to present a chemical stratigraphy framework for the volcanic rocks in the study area (Figs. 1, 2, 3), integrating data from this study with data obtained in previous regional studies; 2) to document the volcanic facies within each unit including lateral and vertical variations in order to determine the vent areas; 3) to use the trace element geochemistry of pyrite, from sulfide-bearing stratified intervals, in combination with geochemical and mineralogical studies of alteration in the underlying volcanic rocks, in order to identify high temperature, VMS-related hydrothermal upflow zones. We also make preliminary comments on the possible petrogenesis and tectonic settings of the studied rocks using a uniformitarian approach.
In summary, the Hébécourt Formation contains four tholeiitic volcanic units (Rogers, 2010; Rogers et al., 2010a, b; Figs. 2, 3: Table 1). The oldest unit is a voluminous basalt, intercalated with variably variolitic basaltic andesite. The main mafic unit is overlain by a ≤495 m thick rhyolite. This “main rhyolite” is locally overlain by a thin basalt and a ≤210 m thick unit of basaltic andesite in the eastern part only. The 45-75 m thick “upper” rhyolite overlies the basaltic andesite. U-Pb zircon ages for the two rhyolite units are 2703.0 ± 0.9 Ma for the main rhyolite and 2702.0 ± 1.0 Ma for the upper rhyolite (Fig. 2: McNicoll et al, this volume). There are minor intercalations of extrusive calc-alkaline volcanic rocks, occurring above the main rhyolite unit and within the youngest basaltic andesite unit in the Hébécourt Formation (Fig. 3). The mafic to intermediate lavas at the base of the Reneault-Dufresnoy formation conformably overlie the Hébécourt Formation. The chemical stratigraphy and physical volcanology of all these rocks will be described in detail below.

Nomenclature

In this paper, volcaniclastic nomenclature follows White and Houghton (2006) and references therein. Stratification thickness in bedded rocks (e.g., “thinly laminated”) is after Ingram (1954). For Archean volcanic rocks that have experienced metamorphism and hydrothermal alteration, magmatic affinities cannot be reliably determined using major elements. Therefore, ratios of immobile trace elements such as Zr/Y, La/Yb or Th/Yb are used to assign magmatic affinities (Pearce and Norry, 1979; Barrett and MacLean, 1999; Ross and Bédard, 2009). ‘Transitional’ is employed to describe rocks that plot between tholeiitic and calc-alkaline fields. The term “exhalite” (Ridler, 1971) is commonly used in VMS exploration and research. True exhalites must have an exhalative component (e.g., Knuckey et al., 1982; Kalogeropoulos and Scott, 1989) and this is typically difficult to prove since post-depositional fluid circulation in a sediment or tuff can introduce components such as silica and sulfides. Herein, we use the descriptive expression “sulfide-bearing stratified intervals”, which has no genetic connotation, instead of “exhalites”.

Mafic Tholeiitic Rocks in the Hébécourt Formation

**Description**

In the study area (Fig. 2), the Hébécourt Formation is divided into two intercalated aphyric units: (1) the volumetrically dominant Hébécourt basalt, and (2) the variably variolitic Hébécourt basaltic andesite. The volcanological and geochemical characteristics of these units are summarized in Tables 1 and 2. Figure 4 shows the typical facies, Figure 5 shows the facies variation in one well studied basaltic andesite unit, and geochemistry is presented in Figures 6 and 7. Further details are available from Rogers (2010), and Rogers et al. (2010a, b).

Mapping focused on a 132 m thick basaltic andesite interval located between the main and upper rhyolites (Figs. 4, 5). Based on field and core observations in four separate drill holes, this unit thins westward, from 132 m to 56 m, until it eventually pinches beyond hole HEB-08 (Fig. 5). The pillow facies dominates, with average pillow size decreasing from 90-100 cm in the east (DDHs HEB-01, -02 and -03) to 40 cm in the west (DDH HEB-08). The proportion of volcanoclastic rocks within the unit increases westward, from 0 percent in DDH HEB-03 to 30 percent in DDH HEB-08 (Fig. 5). The massive facies, by contrast, is absent in DDH HEB-08 and is thickest in DDH HEB-03.

**Interpretation**

The Hébécourt basalt and the Hébécourt basaltic andesite consist of submarine mafic lavas displaying the facies typical of such flows (e.g., Dimroth et al., 1978; Gibson et al., 1999). In the equivalent lower Blake River strata of Ontario, the airborne magnetic patterns suggests laterally extensive subunits, which may represent individual flows or packages of flows, possibly with intercalated mafic sills. The Hébécourt Formation has been interpreted a submarine lava plain (Dimroth et al., 1982).

A comparison of our observed facies variations with typical facies variations in mafic to intermediate lavas suggests that the vent area for the uppermost basaltic andesite is located in the eastern part of the unit, near DDH HEB-03. Massive rocks are more abundant in HEB-03 and from here the unit thins westward, pillow size decreases westward, and the proportion of volcanoclastic rocks within the unit increases westward.

Geochronically, data from the Hébécourt basalt and the Hébécourt basaltic andesite plot along the same trends on binary diagrams displaying incompatible elements (e.g., Fig. 6D); further, their extended trace element profiles are very similar (Fig. 7). This geochemical similarity and their...
stratigraphic relationships suggest that the two units are comagmatic where the Hébécourt basaltic andesite may be a slightly differentiated version of the Hébécourt basalt.

The trace elements patterns for the Hébécourt basalt, with depletions of Th, Nb, and Ta relative to the rest of the profiles, are similar to those of modern back-arc basin basalts (BABB, Fig. 7F) or to a lesser extent, normal mid-ocean ridge basalts (N-MORB, Fig. 7E). On a tectonic classification diagram, the Hébécourt basalts and basaltic andesites plot in the MORB field, but not far from the island arc basalt (IAB) field (Fig. 7G). Finally, on the Th/Yb versus Nb/Yb diagram, the samples plot near the present-day MORB-OIB array, indicating only minor contributions of a subduction component or limited crustal contamination (Pearce, 2008: Fig. 7H).

**Felsic Tholeiitic Rocks in the Hébécourt Formation**

**Description**

There are two main tholeiitic felsic units in the Hébécourt Formation within the study area: the main rhyolite (separated into two subunits) and the thinner upper rhyolite. Their volcanological and geochemical characteristics are summarized in Tables 1 and 3. Figure 8 shows the map distribution of facies in the main rhyolite whereas Figure 9 illustrates typical textures in these submarine felsic rocks. Figures 10 and 11 display the geochemistry of our samples compared to previous studies. Figure 12 shows the variations in thickness and facies in the upper rhyolite using drill hole information, since this unit does not crop out well.

**Interpretation**

The main rhyolite can be divided in two subunits based on quartz crystals abundance, Zr/Y ratios and Ti contents. This is important because without the separation into two subunits, the facies variations would have been interpreted differently. Facies variations in the low-Ti (quartz-phyric) subunit suggest that it was emplaced as a dome with a massive core, thick flank breccias, and a thin carapace (e.g., Yamagashi and Dimroth, 1985; McPhie et al., 1993). The low-Ti lava dome was presumably emplaced on a paleo-horizontal surface formed by mafic lavas. The location of the massive core of the dome gives the general location of the effusive centre (volcanic vent), just east of Chemin de la Mine (Fig. 8B).

The high-Ti (aphyric) subunit of the main rhyolite is also interpreted as submarine lava flows or domes. It has more complex facies variations than the low-Ti subunit. Massive facies are not located near the proposed volcanic vent area of the underlying low-Ti rhyolite, suggesting that the two subunits do not share the same vent. Given the location of the massive facies and the thickness variations within the high-Ti subunit, we propose it erupted from two separate vents, one on either side of the Chemin de la Mine (Fig. 8C).

The upper rhyolite, although thinner than the subunits of the main rhyolite, is more complex; it is interpreted to have been produced by two distinct effusive episodes. The oldest episode produced the thickest products and these thin westward, from 70-75 m in DDHs HEB-01 and HEB-03 to 40 m in DDHs HEB-02 and HEB-08 (Fig. 12). The upper rhyolite in DDH HEB-01 consists entirely of the massive facies with increasing amounts of volcanlastic facies in other drill holes. Bedded fragmental rocks with rounded rhyolite clasts are observed in DDH HEB-03, suggesting transport of rhyolitic debris on the flank of a dome or lava. Facies variations suggest that the vent was located near DDH HEB-01 for this episode. Products from the younger episode are only evident in DDH HEB-08 and little can be said about its origin or vent area.

The tholeiitic rhyolites in the Hébécourt Formation have trace element profiles that are similar in form to those of the mafic tholeiitic rocks in the same formation, except for negative Eu and Ti anomalies (relative to the rest of the elements). Rare earth element modeling by Robidoux (2008) suggested that the magma for the main rhyolite can be derived from a magma that produced the Hébécourt basalt lava flows following 70-80 percent plagioclase-dominated fractionation. If this model is correct, then all of the tholeiitic rocks of the Hébécourt Formation may ultimately have been derived from the same magma. However, this interpretation would require that the inferred intermediate differentiation products between the Hébécourt basaltic andesite and the Hébécourt main rhyolite were not erupted on the sea floor, because the Hébécourt Formation is strongly bimodal. The alternative is that the tholeiitic rhyolites were formed by crustal melting of hydrated basalt at shallow crustal depths (e.g., Hart et al., 2004; Leclerc et al., 2011).

The tholeiitic rhyolites in the Hébécourt Formation have an FIIBb-like signature on the diagrams of Lesher et al. (1986) and Hart et al. (2004), although they do not plot entirely within the pre-defined fields (Fig. 11E, F). FIIB rhyolites are associated with VMS deposits at Matagami and Kidd Creek, for example (Hart et al., 2004). This type of rhyolite is formed at shallow crustal depths (<10 km) in the absence of residual garnet or amphibole and the magmas were possibly emplaced in an oceanic rift setting (Hart et al., 2004).

**Calc-alkaline Intercalations in the Hébécourt Formation**

**Description**

Although the Hébécourt Formation is dominantly tholeiitic, minor intercalations of calc-alkaline rocks occur in the easternmost part of the study area (DDH HEB-03 and HEB-01). These mostly felsic intercalations are summarized in Tables 1 and 4, and their geochemistry is shown on Figures 10 and 11. Rogers (2010) provides a more detailed description of the units.
Intervals of calc-alkaline rocks within the Hébécourt Formation were not anticipated. Rocks with transitional to calc-alkaline affinities were previously interpreted to have been restricted to the stratigraphically overlying Reneault-Dufresnoy formation (Goutier, 1997). The possibility that the rhyodacitic calc-alkaline rocks in the Hébécourt Formation are intrusive (as thought by some previous workers) is not consistent with the large proportion of volcaniclastic facies that display multiple graded beds and rounded fragments requiring lateral transport by density currents, and a calc-alkaline andesite facies that consists of pillow breccias (formed on the sea floor). Therefore, near simultaneous extrusion of abundant tholeiitic and minor calc-alkaline magmas is required during Hébécourt Formation volcanism. It is likely that the volcanic vents for each magma type were separate. The vent for calc-alkaline volcanism may have been located to the east of where these rocks were encountered as there is a higher proportion of calc-alkaline rhyodacite towards the east in the observed drill holes. Also, clasts size in the volcaniclastic strata is larger to the east.

**Reneault-Dufresnoy Formation**

The Reneault-Dufresnoy formation is the youngest stratigraphic unit in the study area (Rogers, 2010). It consists mostly of massive to pillowed submarine lavas in the first few hundred meters (Tables 1, 4). The Reneault-Dufresnoy rocks are geochemically variable (Figs. 6, 7), as also noted by Ross et al. (2011a, b) and Goutier et al. (in press). The whole of this formation west of Lake Dufresnoy (including the study area and units further south) was interpreted as a now-tilted submarine shield volcano built on the Hébécourt lava plain (Dimroth et al., 1985; Ross et al., 2011a).

Trace element profiles of Group 2 lavas (Fig. 7D) resemble those of modern oceanic arc magmas (e.g., Fig 7F: medium-K calc-alkaline basalts). On a tectonic discrimination diagram, the Reneault-Dufresnoy lavas straddle the MORB-IAB boundary (Fig. 7G), with most Group 2 samples plotting in the IAB region. Finally, on the Th/Yb versus Nb/Yb diagram (Fig. 7H), Reneault-Dufresnoy samples define a trend away from the MORB-OIB array, suggesting significant involvement of a subduction component or crustal contamination.

The calc-alkaline andesite intercalated in the Hébécourt Formation plots with Group 2 samples from the Reneault-Dufresnoy formation on all geochemical diagrams shown. Figure 3 illustrates that the thin calc-alkaline intercalations (andesite and rhyodacite) occur at several stratigraphic levels. The Hébécourt Formation is a product of near contemporaneous tholeiitic and minor calc-alkaline volcanism with magmas erupted erupted from different vents located in the same general area. This spatial and temporal coincidence favors crustal contamination of the tholeiitic magma – not variable degrees of subduction involvement – as the easiest mechanism to produce arc-like calc-alkaline trace element signatures in the Reneault-Dufresnoy formation (and in the calc-alkaline intercalations in the Hébécourt Formation). This conclusion may extend to most of the Blake River Group, for which many samples plot between the MORB-OIB array and the pole for Archean crust on Figure 7H.

**Mineralization and Alteration**

The top of the Hébécourt Formation in the area between the Ontario-Quebec border and Lake Hébécourt, including the two tholeiitic rhyolites described above, has historically been recognized as a prospective area for VMS-type mineralization since the discovery of Zn in this area in the 1970s (Cloutier, 1975; Cashin and Fraser, 1992). Since then, exploration has focused mainly on the main rhyolite east of the Chemin de la Mine (Fig. 2).

**Alteration**

The Ishikawa alteration index (AI: Ishikawa et al., 1976) is a good indicator of chloride and sericite alteration commonly associated with metamorphosed VMS deposits (e.g., Paulick et al., 2001; van Ruitenbeek et al., 2011). Values below 20 are indicative of diagenetic trends, fresh rocks have AI values between 20 and 60-65, and rocks with higher values are more altered (e.g., Large et al., 2001; Gifkins et al., 2005). AI values were calculated for compiled datasets of historical and new surface samples (Fig. 13A) and drill core samples (Fig. 13B). Figure 13A shows that the low-Ti rhyolite is much more altered than the overlying high-Ti rhyolite near the Chemin de la Mine. Differing degrees of alteration of the main rhyolite subunits was also observed in drill cores further east (Fraser, 1991; Martin, 1994; Bambic, 1998), as shown on Figure 13B. The low AI values for the high-Ti rhyolite are indicative of diagenetic trends, as shown by the alteration box plot for felsic volcanic rocks (Fig. 13D). However, many samples of felsic volcanic rocks show evidence of VMS-related hydrothermal alteration as defined by chloride±pyrite±sericite and sericite±chlorite±pyrite trends in Figure 13D. The alteration box plot indicates that the mafic volcanic rocks are predominantly unaltered (Fig. 13C), perhaps with some carbonate alteration and minor chloride alteration.

**Mineralization in the main rhyolite**

Assay data (compiled by Cogitore Ressources Inc.) indicates that sulfide mineralization and anomalously high metal concentrations define two zones, informally called zone A (Fig. 14A) and zone B (Fig. 14B). Zone A is located in the central region of the main rhyolite (mostly within the high-Ti subunit) and is characterized by anomalously high Zn, with almost no Cu. The highest assays for Zn (e.g., 6.17 wt % over 0.1 m) are in DDH SC-13 and are represented by semimassive bands or stringers of pyrite and sphalerite (Cloutier, 1975; Martin, 1994; Bambic 1998). Lesser Zn values occur to the east and west. To the west, in DDH 77738, Zn occurs in pyrite-rich sulfide disseminations and thin, fracture-controlled stringers. In DDH SC-14 to the east, the mineralization
consists of pyrite and sphalerite stringers associated with quartz.

Zone B, with higher Cu and Zn values than zone A, is located in the north-east corner of the study area (Fig. 14B). It consists of up to 40 m long mineralized DDH intersections within a chlorite and sericite alteration (Cloutier, 1975; Bambic, 1998), with both disseminated and stringer sulfide mineralization (Cloutier, 1975). Disseminated pyrite, sphalerite and chalcopyrite occur mostly in the westernmost part of zone B, whereas pyrite-dominated stringers occur in the eastern part (Cloutier, 1975). The highest Cu grades (0.19 wt % Cu over 1.9 m) and the most altered rocks (Al = 80 to 95) occur in DDH 753-07, where mineralization occupies the matrix of a low-Ti rhyolite breccia containing angular fragments with an average size of 3-4 cm (Cloutier, 1975). This breccia is part of the east flank of the low-Ti rhyolite dome. Much lower Cu and Zn values occur higher up in the high-Ti rhyolite. The highest Zn intersection in zone B is 11.6 wt percent Zn over 1.1 m in DDH 753-01 (Cloutier, 1975).

Interpretation
Known alteration and mineralization in the study area is typical of Cu-Zn VMS systems, but an economic deposit is yet to be discovered. Mineralization occurs as sulfide stringers and disseminations within chlorite and/or sericite altered rocks, consistent with formation below the sea floor by replacement processes (Doyle and Allen, 2003), for example in permeable breccias along the flanks of rhyolite domes. Large portions of the study area remain underexplored. In the following section, we discuss the use of sulfide-bearing stratified intervals, in particular the mineral chemistry of pyrite from these intervals, as an aid for VMS exploration.

Sulfide-Bearing Stratified Intervals, and their Use in Targeting Hydrothermal Upflow Zones
Two sulfide-bearing stratified intervals, historically termed “exhalites”, were previously identified at the contact between the main rhyolite and the youngest basaltic andesite in the Hébécourt Formation, and at the contact between the Hébécourt upper rhyolite and the Reneault-Dufresnoy formation (Fraser, 1991; Carignan and Lafrance, 2008). Cogitore Resources Inc. intersected Zn values up to 1.2 wt percent over core lengths of several dm within these intervals (Carignan and Lafrance, 2008). During the examination and sampling of these intervals it was noted that they did not always occur at the contacts mentioned above (see Fig. 3B), and that the number of these intervals in a DDH could range from one to three. In addition, a few sulfide stratified intervals were found in the Reneault-Dufresnoy formation, especially in the western portion of the study area (Rogers, 2010).

General description of sulfide-bearing stratified intervals
Sulfide-bearing stratified intervals include: (1) thinly laminated to thinly bedded intervals, 20 cm thick on average (locally up to 50-60 cm thick) consisting of alternating fine-grained tuff, chlorite, argillite and very fine-grained pyrite (Fig. 15A, B), and (2) generally thicker tuffaceous intervals, 60-70 cm thick on average, which typically lack internal stratification. In the thinly laminated to thinly bedded portions, individual layers range from 1-2 mm to 3-4 cm in thickness. Laminae containing fine-grained (≤1 mm) pyrite are commonly the thinnest, <1 mm to 2 mm in thickness, and in many cases the pyrite is hosted by argillite. Chalcopyrite stringers were also observed. The thicker tuffaceous portions consist of tuff and lapilli-tuff. The larger clasts in these units are typically 2-3 cm in size and are mostly angular. Grading is not commonly observed. Microscopic grains of chalcopyrite and sphalerite are minor to trace phases in the sulfide-bearing stratified intervals, but the dominant sulfide mineral that occurs in all samples is pyrite.

Pyrite occurrences and textures in the thinly laminated to thinly bedded portions
Pyrite is most common in the thinly laminated to thinly bedded portions. Pyrite is typically fine-grained (<2 mm) and is associated with specific laminations (Fig. 15C). In some examples the abundance of pyrite is high enough to produce apparent massive sulfide laminations. Disseminations of pyrite dispersed evenly through several laminations are rare. Locally pyrite forms coarse blebs within a lamination or at the contact between laminations.

Discordant pyrite veinlets were observed in most of the samples (e.g., Fig. 15A). In these veinlets, pyrite is typically associated with quartz, although in some cases the veinlets are entirely pyrite. The pyrite grains are typically coarser (Fig. 15D) than those within laminations, and better formed. Veinlets cut the laminations or connect with them, suggesting that at least some of the discordant pyrite may have been introduced after sediment deposition.

Small inclusions of other sulfide and silicate minerals within the pyrite are very common. However, euhedral coarser-grained pyrite (>2 mm) contain far fewer inclusions, probably as a result of metamorphic recrystallization (Tomkins et al., 2007).

LA-ICP-MS analyses of pyrite
Samples. Thick sections (~100 µm thickness) were prepared for 19 representative samples of the thinly laminated to thinly bedded intervals within the sulfide-bearing stratified intervals. Each sulfide-bearing stratified interval is represented by one or two thick sections. Sections were made in areas of abundant pyrite, irrespective of the type of occurrence (e.g., pyrite veinlets versus pyrite-rich laminations, fine or coarse grains, etc.).

Methods. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) spot analyses were performed on pyrite grains at Laurentian University in Sudbury, Ontario, using an ultra-violet laser beam from a
NewWave Research 213 nm probe coupled with a Thermo-Fisher XSeries 2 ICP-MS. Spots to be analyzed were first cleaned of possible surface impurities using a 2 s pre-ablation with a 55 µm wide beam, and the actual analysis used a stationary 40 µm wide beam for 25 seconds. In five of the thick sections, the pyrite grains were too small and a 25 µm wide beam had to be used (same ablation time, following cleaning with a 2 seconds pre-ablation using a 30 µm wide beam).

Between 10 and 20 spots were analyzed per thick section. Most pyrite grains are represented by one spot, although in larger grains there may be two or more points to detect possible metal zonation. Analyzed spots were chosen to obtain information on all pyrite types within the samples (concordant versus discordant pyrite, with or without inclusions, etc.).

When selecting the integration interval for trace element calculations from the raw spectra, inclusions of other minerals in the pyrite grains, visible by spikes of elements such as Cu, Au and Zn in the spectra, could not be avoided due to their small size, their relative abundance and their presence at depth within the analyzed grains. Due to the metamorphic recrystallization, inclusions in the pyrite contain the bulk of the trace metals of interest. As these metals do not reside in the pyrite lattice they are interpreted to have been derived from primary, trace metal-enriched pyrite during regional metamorphism as this is common for metamorphosed sulfides (Huston et al., 1995; Abraitis et al., 2004). Thus, the trace elements values reported were obtained from mixtures of pyrite and tiny inclusions of other minerals within the pyrite grains. The external standards used were the MASS1 synthetic polymetallic sulfide standard from the U.S. Geological Survey for most trace elements (Ag, As, Au, Bi, Cd, Co, Cr, Cu, Hg, Mn, Mo, Sb, Sn, V, Zn) and Standard Reference Material 612, a glass from the U.S. National Institute of Standards and Technology (NIST), for Ni, Pb, Sc, Ti, Tl, Th and U.

**Results.** The determined trace element content of pyrite is extremely variable between samples and within samples, as found in similar studies (e.g., Peter et al., 2003a, b using electron microprobe; Chenery et al., 1995; Chapman et al., 2008; Maslennikov et al., 2009, using LA-ICP-MS). The spatial distribution of Cu and Zn values are shown as thematic maps on Figure 14C, D.

The distribution of values for four economically significant elements within pyrite grains is portrayed on a graph of metal content versus DDH lateral position (Fig. 16). Based on variations in the median and 90th percentile curves for Cu, two peaks are observed: a western one centered on HEB-04, and an eastern one in the region of HEB-02 to HEB-03, with an intervening gap clearly illustrated by a sharp decrease in the median and 90th percentile curves (Fig. 16A). A similar pattern was observed for Zn, although the western peak is only distinguished on the median curve and the eastern Zn peak contains a sharp decrease at HEB-01 (Fig. 16B). Gold and Ag values also display eastern and western peaks that coincide with those for Cu and Zn, and a gap illustrated by a sharp decrease in the median and 90th percentile curves for Au and Ag relative to neighboring drill holes at HEB-08 (Fig. 16C, D). Similar patterns exist for As, Bi, Cd, Hg, Mn, Pb, Sb and Tl (not shown).

**Interpretation**

Sulfide-bearing stratified intervals consist of tuff, argillite, chlorite, and sulfides. The tuff and argillite component in these intervals represent a hiatus in effusive volcanic activity and these hiatuses may indicate favorable periods for VMS formation. The presence of chlorite veinlets suggests that the chloride laminations were formed by replacement of tuff laminations; in the same way, discordant sulfide veinlets connected to sulfide laminations indicate that at least a portion of the sulfides were introduced post-deposition. Therefore the sulfide-bearing stratified intervals are not true ‘exhalites’, as the sulfides were not exclusively deposited by precipitation and sedimentation from a hydrothermal plume in the water column. However, these intervals can still be used to identify possible hydrothermal upflow zones. High metal values in the sulfide-bearing stratified intervals may indicate mineralized zones at deeper (or even possibly higher) stratigraphic levels, as the metal-bearing fluids which introduced the sulfides were likely moving in a mostly vertical direction as is generally the case for flow-dominated VMS systems (Franklin et al., 2005).

Lateral, spatial variations of precious and base metals in pyrite from sulfide-bearing stratified intervals suggest the existence of two distinct broad hydrothermal upflow zones in the upper part of the Hébécourt Formation: a western one in the HEB-09 to HEB-04 region, and an eastern one in the HEB-02 to HEB-03 region. These findings have implications for exploration as discussed in the next section. Hydrothermal fluids also likely traversed the lower levels of the Reneaul-Dufresnoy formation, as shown by high Cu and Zn values in this formation within DDH HEB-09 (Fig. 14C, D).

**Discussion and Conclusions**

**Chemical stratigraphy and identification of volcanic vents**

The Hébécourt Formation has been divided into four tholeiitic volcanic units: basalt; basaltic andesite; main rhyolite (comprising a low-Ti subunit and a high-Ti subunit); and the upper rhyolite. As shown in Figure 2, the bimodal Hébécourt Formation consists of two tholeiitic mafic-felsic cycles, the second being significantly thinner than the first. The low-Ti main rhyolite subunit was initially erupted from a vent located just east of the Chemin de la Mine (Fig. 17A). For the high-Ti subunit two distinct felsic volcanic vents were probably active, one on each side of the low-Ti dome (Fig. 17B). The overlying basaltic andesite was extruded from the east, and flowed westward (Fig. 17C). Utilization of the eastern effusive...
centre by both felsic and mafic magmas suggests a control
by synvolcanic structure (e.g., Setterfield et al., 1995;
DeWolfe et al., 2009). The effusive centre probably shifted
slightly westward (towards HEB-01) to produce the main
part of the upper rhyolite (Fig. 17D). Facies variations
allow reconstruction of the volcanic vent systems for the
various units, but this is only a two dimensional image of a
three dimensional system. Feeder dikes were not observed
in this study, thus the exact position of the vents in the
third dimension are unknown.

Possible tectonic setting and rhyolite fertility
Regionally, the Hébécourt Formation consists largely of
monotonous tholeiitic basaltic lavas that were interpreted
as a lava plain by Dimroth et al. (1982). Trace element
patterns determined in this study are compatible with a
back-arc basin tectonic setting for these basalts (and
basaltic andesites). Felsic complexes within the Hébécourt
Formation are uncommon regionally, and calc-alkaline
intercalations have not been reported outside of the study
area. There is no obvious explanation in our data to
account for the greater volume of rhyolite in the study
area; perhaps it may be related to the development of a
local, high-level magma chamber, and/or to local crustal
extension generating a thermal anomaly (Franklin et al.,
2005; Galley et al., 2007). Regardless of the mechanism of
formation (e.g., differentiation from a tholeiitic basaltic
magma or partial melting of a mafic source), the tholeiitic
rhyolites must have been generated at relatively shallow
crustal depth based on their flat REE patterns (Hart et al.,
2004), which would have created enhanced heat flow and
favored hydrothermal activity. FIII rhyolites, like those of
the Hébécourt Formation, are commonly associated with
VMS deposits in the Archean (Lesher et al., 1986; Hart et
al., 2004).

Following the emplacement of the Hébécourt Formation,
magmas were repeatedly extruded from the same general
areas and this led to the construction of a large shield
volcano now exposed further south in the Reneaulf-
Dufresnoy formation (Ross et al., 2011a). The tholeiitic to
calc-alkaline magmas that produced the Reneaulf-
Dufresnoy formation had a greater influence from a
subduction component relative to those that created the
Hébécourt Formation, or else they were more contaminates by existing crust.

Mineralization and hydrothermal upflow
In the study area, there is a spatial coincidence between the
identified effusive centers, hydrothermal alteration zones,
base metal mineralization, and metal concentrations in
pyrite from the sulfide-bearing stratified intervals (Fig.
17). Specifically, the proposed effusive centre for the
Hébécourt basaltic andesite is located immediately south
of the zone B stringer-type mineralization; an area of most
intense sericite-chlorite alteration within breccias of the
main rhyolite that is located lower in the stratigraphic
succession. This suggests that the basaltic andesite
magmas used the same or nearby synvolcanic structures as
the hydrothermal fluids which altered and mineralized the
main rhyolite. This implies the continued existence of
synvolcanic extension, which is critically important to
provide access to the near-surface environment for
mineralizing fluids. Synvolcanic faults are likely to have
been active elsewhere in the area and to have controlled
pathways for both magmas and hydrothermal fluids,
although such faults are difficult to locate precisely. Other
studies in VMS-hosting volcanic successions, including in
the Noranda mining camp, have showed the importance of
long-lived and reactivated synvolcanic structures, which
are responsible for the observed coincidence between
volcanic and hydrothermal vents (Gibson et al., 1999, and
references therein; Galley et al., 2007).

Pyrites in sulfide-bearing stratified intervals from multiple
stratigraphic levels in the study area contain appreciable
Ag, Au, Cu and Zn, among other elements. The interest
here is not necessarily the high trace element values
themselves (this is typical of VMS settings: Huston et al.,
1995) but rather their spatial distribution. The high metal
values define a broad zone east of the Chemin de la Mine
(Figs. 14, 17) and therefore correspond to an area also
containing the effusive centre for the low-Ti dome, the
main volcanic vent for the upper rhyolite, and one of the
vents for the high-Ti rhyolite, as well as the weak Zn
mineralization in Zone A.

The high metal contents of pyrite from sulfide-bearing
stratified intervals located west of the Chemin de la Mine –
metal values comparable to those in east – are not
explained by known base metal mineralization and
hydrothermal alteration within the underlying strata. This
may be the result of the limited exploration in this area as
compared to the area further to the east, especially in the
main rhyolite, rather than to a lack of alteration and
mineralization. The western metal anomaly indicated by
elevated pyrite metal contents could potentially be
associated with a proposed high-Ti rhyolite western
effusive centre (centered on DDH HEB-04, see Figs. 8, 14,
15, 17), or with other undefined volcanic vents and
associated hydrothermal upflow zones. This proposition
has obvious implications for exploration and demonstrates
the usefulness of field mapping of volcanic facies and
chemical stratigraphy in parallel with the trace element
analysis of pyrite within stratified intervals to define new
mineralized areas within volcanic terrains.

Implications for VMS exploration elsewhere
The combination of techniques used in this study
represents a new approach outside VMS mining camps,
and could be applied elsewhere. Previous published
investigations of sulfide-bearing stratified intervals, iron
formations, etc., were done in established mining camps,
with a known stratigraphy and structure, and the VMS
deposits had already been found. If “exhalite” studies are
to be applied outside of VMS camps however, it is of
prime importance to combine them with an understanding
of the volcanic architecture of the investigated area. This
requires establishing a litho- and chemo-stratigraphy to constrain volcanic facies mapping and facies analysis in order to locate coincident effusive and hydrothermal centers (Gibson et al., 1999). For example, our interpretation of the facies variations in the main rhyolite would have been very different without its division into two subunits. Further, combining these data with trace element variations in sulfides from laminated intervals may help to identify hydrothermal upflow zones, which can correspond to volcanic effusive centers. In many ancient volcanic sequences, deformation and metamorphism may strongly hinder recognition of primary features, and the use of combined approaches in defining a VMS-prospective environment becomes critical.

**Exhalites**

The term “exhalite” is sometimes overused in mineral exploration, with laminated sulfide-bearing intervals automatically assumed to represent laterally extensive markers formed by sulfide precipitation and sedimentation in seawater, following venting of a hydrothermal fluid into the water column (e.g., Kalogeropoulos and Scott, 1989; Liaghat and MacLean, 1992; Peter et al., 2003a, b; Chapman et al., 2008). While true exhalites undoubtedly exist in many VMS camps, explorationists have to be careful about using the term “exhalite” too quickly.

This study has shown that careful examination of laminated sulfide-bearing intervals indicates that they do not always form one or several laterally extensive units, but can instead form several discontinuous and unconnected units (Fig. 3B). In such units, the sulfides can be truly exhalative and deposited with the enclosing sediment, or they can also be introduced later by replacement, from hydrothermal fluids moving mostly upward in the crust (e.g., Knuckey and Watkins, 1982, show chalcopyrite veinlets cross-cutting laminated sulfide-bearing intervals at the Corbet mine). Nevertheless, even if they are not classic exhalites, the sulfide minerals within these intervals can still contain useful information on the location of hydrothermal upflow zones that can aid in VMS exploration.

**Conclusions**

Detailed physical volcanology, mapping, and chemical-stratigraphy in the Hébécourt Formation and the overlying Rencault-Dufresnoy formation in the northern part of the Archean Blake River Group was instrumental in locating effusive centers (volcanic vent areas). In addition, LA-ICP-MS analyses of pyrite from sulfide-bearing stratified intervals intercalated with the volcanic units, combined with the mapping of hydrothermal alteration zones using lithogeochemistry, allowed us to locate hydrothermal upflow zones associated in some cases with areas of known mineralization. This approach helped to define areas with potential to host VMS mineralization.

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Figures

Fig. 1. Location maps showing (A) the location of the Abitibi greenstone belt within eastern Canada, (B) the location of the Blake River Group on a map of the Abitibi greenstone belt (courtesy of Marc Legault) and (C) a simplified geological map of the Blake River Group showing the location of the study area.

Fig. 2. Map of the top of the Hébécourt Formation and the base of the Reneault-Dufresnoy formation west of Lake Hébécourt. The geology is based on Ministère des Ressources naturelles et de la Faune (Québec) 1:20 000 scale maps, an unpublished compilation by Cogitore Resources Inc., and new mapping by the first author. Outcrop locations and some drill hole traces are omitted for clarity, but these are available on maps provided by the Ministère des Ressources naturelles et de la Faune (Québec).

Fig. 3. A. Vertical cross-section looking WSW, though the trace of diamond drill hole HEB-02. B. Stratigraphic correlation panel showing most of the diamond drill holes studied. The location of sulfide-bearing stratified intervals is highlighted. A and A’ are two intervals found approximately at the top of the Hébécourt Formation.

Fig. 4. The uppermost occurrence of the Hébécourt basaltic andesite. A. Massive facies displaying a high concentration of varioles. Scale is graduated centimeters. B. Triple junction in the pillow facies with interstitial hyaloclastite (Hy). Varioles (Var) are abundant in the pillow margins. C. A complete pillow with an increase in concentration of varioles and vesicles towards the margin. D. Pillow breccia facies in drill core, comprising in situ fragmented hyaloclastite and larger clasts most likely representing pillow fragments. The ruler is graduated in centimeters and millimeters. E and F. Hyaloclastite facies in drill core, displaying in situ fragmentation and small, chloritized clasts. In both cases the scale is a 15 cm plastic ruler.
are shown on the figure. C. Map showing the distribution of facies in the high-Ti subunit, based on the same data sources.

Distribution of facies in the low-Ti subunit based on our drill core and surface observations, plus historical drill core logs above the central massive region is schematic as it is defined from drill core and three outcrops. Only the compiled DDHs from the Ministère des Ressources naturelles et de la Faune (Québec) mining exploration files. The shape of the breccia units. (E) Plot of TiO₂ (2009): (C) for the two sub-units of the main rhyolite; (D) for the upper rhyolite and the calc-alkaline rhyodacite; (F) for all diagrams from Winchester and Floyd (1977): average of ten chondrites.

Fig. 8. A. Map of the main rhyolite in the Hébécourt Formation showing the subunits distinguished by the high- and low-Ti content, and the observations of porphyritic and aphyric rocks. Where samples and observations are from drill core, they have been projected to the surface using the regional dip of 72°S and a strike perpendicular to S₀. B. Map showing the distribution of facies in the low-Ti subunit based on our drill core and surface observations, plus historical drill core logs from the Ministère des Ressources naturelles et de la Faune (Québec) mining exploration files. The shape of the breccia above the central massive region is schematic as it is defined from drill core and three outcrops. Only the compiled DDHs are shown on the figure. C. Map showing the distribution of facies in the high-Ti subunit, based on the same data sources.

Fig. 9. Felsic rocks in the Hébécourt Formation. A. Massive facies in the low-Ti subunit in the main rhyolite, with hairline sericite veins and 1-2 mm “quartz eye” phenocrysts. B. Volcaniclastic facies of the low-Ti rhyolite, clearly matrix-supported with large clasts. C. Volcaniclastic facies of the high-Ti rhyolite. D. Massive facies of the upper rhyolite, with impinging, irregularly shaped spherules. E. Lapilli-tuff facies of the upper rhyolite, with angular fragments. The smaller clasts are epidote-altered and the larger clasts display a micro-spherulitic texture. F. Interbedded finely laminated tuff and argillite from the boundary between the first and second volcanic episodes of the upper rhyolite.

Fig. 10. Geochemistry of felsic volcanic rocks from the Hébécourt Formation in the study area. A and B. Classification diagrams from Winchester and Floyd (1977) for all units. C, D and F. Magmatic affinity diagrams from Ross and Bédard (2009): (C) for the two sub-units of the main rhyolite; (D) for the upper rhyolite and the calc-alkaline rhyodacite; (F) for all units. (E) Plot of TiO₂ versus Zr for all units.

Fig. 11. Geochemistry of felsic volcanic rocks from the Hébécourt Formation in the study area. A to D. Extended multi-element plots. Primitive mantle normalization values are from Sun and McDonough (1989). E and F. Rhyolite classification diagrams after Lesher et al. (1986) and Hart et al. (2004). FI to FIII fields in (E) after Piercey (2010). Normalization values in (F) from Nakamura (1974): average of ten chondrites.

Fig. 12. Thickness and volcanic facies variations in the Hébécourt upper rhyolite, shown by graphic logs from DDH HEB-03, -01, -02 and -08, all plotted at the same vertical scale. The horizontal axis is a grain-size scale. The red line is interpreted to represent the boundary between two volcanic episodes in the Hébécourt upper rhyolite, marked by finely laminated tuff and argillite, and in HEB-08 by a thicker unit of mafic felsic.
Fig. 13. Hydrothermal alteration in the study area. A and B. Maps of the Ishikawa alteration index (AI: Ishikawa et al., 1976) for surface and drill core samples, respectively. Geological boundaries are provided for reference. Note that for simplicity, core samples are projected vertically from variable depths and likely do not project to the correct geological unit at surface (recall the 72°S dip of strata). The 10 m AI grids were produced by interpolation between samples with a search radius of 100 m and a minimum of two samples per grid point. C and D. Alteration box plots of AI versus chlorite-carbonate-pyrite index (CCPI: Large et al., 2001) for mafic and felsic samples, respectively. The geochemical analyses used are from this study and a compiled data set supplied by Cogitore Resources Inc. The box of unaltered basalts from young submarine ridges has been compiled from the GEOROC database (http://georoc.mpch-mainz.gwdg.de/georoc/, 274 samples with outliers excluded), whereas the four other boxes for unaltered young arc rocks are taken from Gifkins et al. (2005).

Fig. 14. Base metal mineralization and pyrite geochemistry for samples in the study area. A and B. Copper and zinc contours representing mineralized zones A and B, respectively (see text for descriptions), superimposed on a grid of the Ishikawa alteration index (AI: Ishikawa et al., 1976) for drill core samples, prepared as in Figure 13. The Cu and Zn contours are based on 5 m grids of drill core assays using interpolation between samples with a search radius of 50 m and a minimum of two samples per grid point. Samples were projected vertically from various depths to the surface for both alteration and assays, so the geological boundaries are provided for reference only. C and D. Thematic maps for Cu and Zn values in pyrite from sulfide-bearing stratified intervals in drill core, based on LA-ICP-MS measurements. The samples are projected to the surface using the regional dip of 72°S, so they plot at the correct stratigraphic position.

Fig. 15. Photographs (A, B) and reflected light photomicrographs (C, D) of the sulfide-bearing stratified intervals. A. Thinly laminated to very thinly bedded interval containing tuff and argillite. Pyrite is present in veinlets and in blebs between and within layers. B. Thinly to thickly laminated tuffaceous interval showing syn-sedimentary deformation. Fine-grained concordant pyrite is associated with some laminations. C. Fine-grained concordant pyrite. D. Coarser veinlet-associated pyrite. Pits in the surface resulting from laser ablation are circled in red.

Fig. 16. Geochemical variations in pyrite from sulfide-bearing stratified intervals based on LA-ICM-MS analyses. Metal contents for individual analyses are plotted against the DDH in which the samples were taken, as a representation of lateral variations: A. copper, B. zinc, C. gold and D. silver.

Fig. 17. Geological history of the study area, focusing on the top part of the Hébécourt Formation, illustrated by pre-tilting schematic sections (not to scale). Hydrothermal upflow within volcanic units probably occurred more or less continuously during the time period shown. A. Deposition of the low-Ti subunit of the main rhyolite. Triangles represent the volcaniclastic facies and randomly orientated dashes represent the massive facies. B. Eruption of the high-Ti subunit of the main rhyolite, from two separate vents. Also shown are the Zone A and Zone B alteration and mineralization. Thick red lines represent the location of known sulfide bearing laminated intervals (some may be more continuous than shown). C. Eruption of the youngest interval of the Hébécourt basaltic andesite. Filled triangles represent hyaloclastite and the pillows decrease in size to the west. D. Eruption of the upper rhyolite from the easternmost vent, as the western vent is unknown. Calc-alkaline intercalations in the Hébécourt Formation and eruption of the Reneault-Dufresnoy formation not shown.
Overburden

HEB-02

100 m

200 m

300 m

400 m

500 m

600 m

640 m

NNW

SSE

Reneauld-Dufresnoy formation

Intrusions

Field station

Legend

Elevation (m, a.s.l.)

HEB-02

HEB-04

HEB-08

HEB-09

HEB-01

HEB-03

Field station

Rogers et al., Econ. Geol., Fig. 3
Stratigraphic columns from drill core observations

Top of basaltic andesite

True thickness including intrusions

Base of basaltic andesite

Map projection

Rogers et al., Econ. Geol., Fig. 5
Hébécourt Formation

- Hébécourt basalt
- Basalt previous data
- Hébécourt basaltic andesite
- Basaltic andesite previous data
- Calc-alkaline andesite

Reneault-Dufresnoy formation

- Group 1
- Group 2
- previous data

Rogers et al., Econ. Geol., Fig. 6
Hébecourt formation
Reneault-Dufresnoy formation
- Basalt
- Basalt, previous data
- Basaltic andesite
- Calc-alkaline andesite

Rogers et al., Econ. Geol., Fig. 7
Chemin de la Mine
SC-14
HEB-03
HEB-01
HEB-02
HEB-08
HEB-04
HB□97-03
HB-94-02
HB□97-01
HB-94-01
77745-0
SC-16
SC-15
SC-11
HEB-05
HB□97-02
SC-12
SC□13
77738-0
77739-0
77740-0
77746-0

Low-Ti subunit

Legend
- Porphyritic
- Aphyric
- Massive
- Fragmental
- High Ti subunit
- Low Ti subunit
- Other rocks
- Fault
- Diamond drill hole

Field and projected DDH observations
- Massive
- Fragmental

Low-Ti subunit

High-Ti subunit

Rogers et al., Econ. Geol., Fig. 8
True thickness (excluding intrusions): 70 m
43% Fragmental

True thickness (excluding intrusions): 45 m
67% Fragmental

True thickness (excluding intrusions): 70 m
0% Fragmental

True thickness (excluding intrusions): 75 m
49% Fragmental
Rogers et al., Econ. Geol., Fig. 13