An overview of petrochemistry in the regional exploration for volcanogenic massive sulphide (VMS) deposits

S.J. Piercey
Department of Earth Sciences, Memorial University of Newfoundland, St. John’s, NL, Canada, A1B 3X3
(e-mail: steve_piercey@me.com)

ABSTRACT: Volcanogenic massive sulphide (VMS) deposits are important global sources of base and precious metals. Igneous geochemistry (petrochemistry) of mafic and felsic rocks associated with VMS deposits is extremely useful in delineating potentially fertile ground for VMS mineralization. In mafic-dominated, juvenile environments (e.g. mafic, bimodal mafic and mafic-siliciclastic VMS-types) VMS deposits are associated with boninite and low-Ti island arc tholeite, mid-ocean ridge basalt, and back-arc basin basalt. These rocks are ultimately sourced from either depleted arc mantle wedge (e.g. boninite, low Ti island arc tholeiite) or upwelling depleted, mid-ocean ridge or back-arc asthenospheric mantle (e.g. MORB and back-arc basin basalt). In evolved environments, those associated with continental crust and typically dominated by felsic magmatism (e.g. bimodal felsic and felsic-siliciclastic VMS-types), VMS-associated mafic rocks have alkaline (ocean island basalt-like) and/or mid-ocean ridge/back-arc basin basalt-like signatures. In these environments felsic rocks are associated with trace element depleted rhyolites with tholeiitic to boninite-like signatures and M-type and FIV affinities on discrimination plots.

Using mafic or felsic rocks in isolation may lead to erroneous assignments of prospectivity for terrains; however, when mafic and felsic rocks are used in tandem with geological context they are powerful tools in outlining potentially prospective regions. Within VMS-hosting environments there are specific petrochemical assemblages of mafic and felsic rocks. Petrochemical assemblages are specific lithogeochemical associations between mafic and felsic rocks that are common to VMS forming environments and are useful in identifying two key ingredients required to form prospective VMS belts: (1) rifting; and (2) high temperature magmatism.

KEYWORDS: Lithogeochemistry, volcanogenic massive sulfide (VMS), petrochemistry, rifting, heat flow, area selection

Volcanogenic massive sulphide (VMS) deposits have been, and continue to be, important contributors to the global economy. These deposits are important global sources of the base metals Zn, Pb, and Cu, and many deposits (e.g. Eskay Creek, Bousquet-LaRonde) are important sources of precious metals. VMS deposits are one of the best understood mineral deposit types due to numerous studies of ancient deposits, as well as those that are currently forming on the modern seafloor.
with few studies aimed at using lithogeochemistry to outline prospective belts on a regional scale (e.g. Lesher et al. 1986; Paradis et al. 1988; Swinden et al. 1989).

With the developments of new analytical technology in the late 1980s and 1990s, however, this situation has changed and the application of high precision lithogeochemical data is becoming commonplace in VMS deposit exploration. One of the key advances was the development of inductively coupled plasma-mass spectrometer (ICP-MS), once primarily a research tool in universities and government laboratories, which has become commonplace in most commercial lab facilities. The ICP-MS system has revolutionized the application of lithogeochemistry to VMS exploration allowing individuals to use a wider array of high precision trace element data, particularly for the HFSE and REE, and this has led to more sophisticated petrological models and major advancements in understanding volcanic and intrusion geochemistry and its application to delineating prospective regions for VMS exploration (e.g. Swinden 1991; Barrie et al. 1993; Syme & Bailes 1993; Syme et al. 1995; Barrett et al. 1996; Swinden 1996; Kerrich & Wyman 1997; Lentz 1998; Syme et al. 1999; Wyman et al. 1999; Piercey et al. 2001a; Piercey et al. 2001b; Dusel-Bacon et al. 2004). On a belt scale, deposits within these rifts are associated with extensional and trans-tensional grabens, calderas, and synvolcanic and synsedimentary faults (e.g. Gibson 1989; Allen 1992; McPhie & Allen 1992; Setterfield et al. 1995; Allen et al. 1996; Gibson et al. 1999; Stix et al. 2003; Gibson 2005). Synvolcanic and synsedimentary structures are commonly associated with felsic and mafic dyke swarms that parallel the axis of the rift corridor (e.g. Gibson & Watkinson 1990; Setterfield et al. 1995; Galley 1996; Galley 2003; Hart et al. 2004).

In this paper the current state of knowledge in lithogeochemistry of mafic and felsic igneous rocks associated with VMS deposits and their application to exploration for VMS systems on a regional scale will be reviewed. Regional scale, as defined in this paper, is >1:50,000 scale and the methods put forth are aimed at defining prospective belts and stratigraphic sequences. The paper will first define the attributes of the target and outline key geological and tectonic settings that these deposits occur in. This will be then followed by reviews of the key advances and current state of knowledge in volcanic and intrusion geochemistry and petrochemical assemblages—key chemostratigraphic relationships useful for delineating prospective environments at the belt scale. The paper will conclude with the unresolved questions and anticipated advances in the next ten years.

**THE TARGET: VOLCANOGENIC MASSIVE SULPHIDE DEPOSITS AND THEIR CLASSIFICATION**

Volcanogenic massive sulphide (VMS) deposits have formed throughout Earth history from early Archean to the present. They form within extensional geodynamic regimes, in particular rift environments (Fig. 1). These rift environments include mid-ocean ridges, back-arc basins, intra-oceanic arc rifts, and continental arc rifts (e.g. Swinden 1991; Hannington et al. 1995; Scott 1997; Syme et al. 1999; Barrett et al. 2001; Piercey et al. 2001b; Dusel-Bacon et al. 2004). On a belt scale, deposits within these rifts are associated with extensional and trans-tensional grabens, calderas, and synvolcanic and synsedimentary faults (e.g. Gibson 1989; Allen 1992; McPhie & Allen 1992; Setterfield et al. 1995; Allen et al. 1996; Gibson et al. 1999; Stix et al. 2003; Gibson 2005). Synvolcanic and synsedimentary structures are commonly associated with felsic and mafic dyke swarms that parallel the axis of the rift corridor (e.g. Gibson & Watkinson 1990; Setterfield et al. 1995; Galley 1996; Galley 2003) and are commonly above a coeval synvolcanic intrusive complex (Fig. 1) (e.g. Campbell et al. 1981; Galley 1996; Galley 2003). The dyke swarms and subvolcanic intrusive complexes typically have geochemical signatures identical to the VMS-hosting volcanic sequences; however, many cross-cut and post-date the formation of VMS mineralization (e.g. Galley 1996; Barrett & MacLean 1999; Galley 2003). The subvolcanic intrusive complexes are interpreted to be the manifestation of a geodynamic environment with an elevated geothermal gradient (high heat flow), a key ingredient for driving hydrothermal circulation required to form VMS mineralization (e.g. Campbell et al. 1981; Galley 1996; Large et al. 1996; Galley 2003). Some workers have also suggested that these intrusive complexes also contribute metals to the VMS hydrothermal system (Large et al. 1996; Galley 2003).

A major challenge in VMS exploration is the identification of high heat flow rift environments. Petrochemistry, in conjunction with geological methods, is particularly useful in...
identifying rift sequences as rift-related mafic and felsic rocks that have specific petrochemical signatures (see below). Furthermore, petrochemistry can also provide an indicator of the heat flow of a specific geodynamic environment. In particular, many VMS environments are associated with rocks that have signatures indicative of generation and emplacement at high temperatures; hence, their petrochemical signatures can provide an indicator of the geothermal gradient and heat flow of the environment that these rocks were emplaced into.

Figure 1 illustrates the generalized setting of VMS deposits, but there are significant differences in the style and setting of these deposits (Barrie & Hannington 1999; Franklin et al. 2005). These variations may extend to the lithogeochemical signatures of the VMS-associated rocks, and hence, a brief note on VMS classification is required. Recently VMS deposits have been classified into five groups based on their host-rock assemblages (Barrie & Hannington 1999; Franklin et al. 2005): 1. **Mafic**: these are deposits associated with mafic-dominated assemblages, commonly ophiolitic. The Cyprus, Oman, and ophiolite-hosted deposits in the Newfoundland Appalachians represent classic districts of this group; 2. **Bimodal-mafic**: these are deposits associated with mafic-dominated settings, but with up to 25% felsic rocks, the latter often hosting the deposits. The Noranda, Flin Flon- Snow Lake and Kidd Creek camps would be classic districts of this group; 3. **Mafic-siliciclastic (or pelitic-mafic)**: these are deposits associated with subequal proportions of mafic and siliciclastic rocks; felsic rocks can be a minor component; and mafic (and ultramafic) intrusive rocks are common. The Besshi deposits in Japan, Outokumpu deposits in Finland, and Windy Craggy in Canada represent classic districts of this group; 4. **Felsic-siliciclastic (or siliciclastic-felsic or bimodal siliciclastic)**: these are deposits associated with siliciclastic dominated settings with abundant felsic rocks and less than 10% mafic rocks. These settings are often shale-rich and the Bathurst camp, Iberian Pyrite Belt, and Finlayson Lake areas are classic districts of this group; and 5. **Bimodal-felsic**: these are deposits associated with bimodal sequences where felsic rocks are in greater abundance than mafic rocks with only minor sedimentary rocks. The Kuroko, Buchans, and Skellefteu camps would be classic districts of this group.

The first three groups above are dominated by mafic material and juvenile environments with very little continental crustal influence. Felsic rocks are derived primarily from melting of hydrated mafic crust, and mafic rocks are predominately sourced from asthenospheric mantle. The first three groups are also dominated by deposits enriched in Cu–Zn with very little Pb. The last two groups are associated with evolved environments dominated by continental crust or continental crust-derived sedimentary rocks. Felsic rocks in these environments are derived from melting of continental crust or continental crust-derived rocks, and mafic rocks often are derived from both lithospheric and asthenospheric sources. The deposits of the last two groups are notably Zn–Pb–Cu dominated. As we will see later, whether one is in a juvenile versus evolved environment ultimately controls the felsic and mafic volcanic geochemistry associated with the VMS deposits in a given district.

### REVIEW: VOLCANIC AND INTRUSIVE GEOCHEMISTRY

Volcanic and intrusion geochemical attributes will be discussed together as the composition and textures of both are used primarily to identify regional targets and to identify key regions to undertake detailed exploration (i.e. area selection). In this section, the primary petrological and geochemical signatures in volcanic and intrusive rocks are examined. The primary petrological signatures of rocks are critical to understand because they provide key information on the thermal, tectonic, and petrological history of the mafic and felsic rocks. Thus, it is critical that the freshest, least altered samples (e.g. those having preserved textures, free of veins and secondary minerals) are taken as the geochemical signatures in these rocks will reflect primary tectonic and petrological processes, rather than those associated with secondary alteration (Jennner 1996; Kerrich & Wyman 1997). It is also important that proper analytical techniques and quality control/quality assurance procedures are taken. This is beyond the scope of this paper but readers are referred to the reviews by Jenner (1996) and Kerrich & Wyman (1997).

In the following paragraphs, mafic compositions will be dealt with initially, and will be followed by felsic volcanic compositions. In all the diagrams, immobile major and trace elements are utilized including Al2O3 and TiO2, the HFSE (Zr, Hf, Nb, Ta, Y, Sc, Ti, V), and REE. These elements remain immobile in most altered and metamorphosed rocks, except under very intense alteration (e.g. chloride alteration; Campbell et al. 1984; Whittingford et al. 1988; Bau 1991; Valsami & Cann 1992) and provide us with information on the primary petrogenetic signatures for mafic rocks, even if they are moderately altered. A table of acronyms for geochemistry-related terms and signatures are provided in Table 1.

### Mafic geochemistry

The composition of mafic volcanic and intrusive rocks associated with VMS deposits is, in part, determined by whether they formed in a juvenile or evolved environment. In juvenile environments, deposits are preferentially associated with boninite and low-Ti tholeiite (LTT) or mid-ocean ridge basalt (MORB) of both the normal- (N-MORB) and enriched- (E-MORB) types (e.g. Fig. 2). Boninitic rocks are associated with many ophiolite-hosted (mafic) VMS deposits (e.g. Cyprus, Turner-Albright, Oman, Betts Cove) and bimodal mafic systems (e.g. Kidd Creek, Snow Lake, Rambler), and more rarely in mafic-siliciclastic systems (e.g. Frye Lake). Boninite are characterized by high MgO (Mg#>0.60), Ni and Cr contents, low TiO2 (<0.6%), high Al2O3/TiO2 (often >40), low Ti/Sc and Ti/V ratios, and have distinctive U-shaped REE and primitive mantle-normalized patterns (Figs 2–6) (Crawford et al. 1989; Pearce et al. 1992). Low-Ti tholeiite have somewhat similar geochemical signatures to boninite but can have higher TiO2.
contents and lower Al2O3/TiO2 ratios (Fig. 3), and their REE and primitive mantle-normalized patterns less U-shaped than boninite (Figs 2 and 6) (Brown & Jenner 1989; Kerrich et al. 1998; Wyman et al. 1999). Boninitic rocks are interpreted to have formed from mantle sources that are ultra-depleted in incompatible trace elements and require high temperatures to melt (c. 1200–1500°C) (Crawford et al. 1989; Pearce et al. 1992; van der Laan et al. 1992; Falloon & Danyushevsky 2000). Hence, boninitic melts are typically higher temperature melts than those producing normal arc rocks. Furthermore, most boninite and LOTI are associated with forearc extension and the initiation of subduction (Stern & Bloomer 1992; Bedard et al. 1999) or with the initiation of back-arc basins (Crawford et al. 1981; Piercey et al. 2001a); although some boninite occur in intracratonic settings (e.g. Kemp 2003).

Mid-ocean ridge basalts (MORB) are associated with many mafic-hosted VMS deposits in ophiolites and modern mid-ocean ridges (e.g. TAG, East Pacific Rise). MORB-type rocks are characterized by smooth REE and trace element patterns that are either depleted in light-REE (LREE) in the case of N-MORB, or are flat to weakly enriched in LREE in the case of E-MORB (Fig. 2). MORB and MORB-like rocks with weak negative Nb anomalies on primitive mantle-normalized plots are called back-arc basin basalt (BABB) and are present in many mafic-type VMS environments in modern and ancient back-arc basins (e.g. Lau Basin, Manus Basin, Semail) (Figs 3–7). In mafic and bimodal-mafic systems (e.g. forearc or back-arc settings) the MORB-type rocks often show an intimate relationship with boninitic and arc-tholeiitic rocks, with MORB either underlying boninite (e.g. Semail), or overlying and/or cross-cutting the boninite (e.g. Troodos, Rambler, Turner-Albright). In some modern back-arcs island arc tholeiite (IAT) are interlayered with BABB and MORB (Figs 2 and 7). MORB-type rocks are also associated with mafic-siliciclastic deposits in the ancient record (e.g. Greens Creek) and at modern sedimented ridges (e.g. Middle Valley, Guaymas, and Escanaba Trough) (Figs 3–7). MORB-type rocks are interpreted to have formed from incompatible element-depleted mantle with liquidus temperatures c. 1200°C (e.g. McKenzie & Bickle 1988; McKenzie & O’Nions 1991; Langmuir et al. 1992) and represent extension either at mid-ocean ridges or within back-arc basins (e.g. Langmuir et al. 1992; Hawkins 1995).

In evolved environments, deposits are preferentially associated with mafic rocks that have MORB and alkalic signatures (or within-plate or ocean island basalt (OIB)) signatures (Figs 2, 5 and 8). The MORB present in the evolved environments is often of E-MORB affinity and in some areas there is a complete spectrum of mafic rocks from incompatible element-depleted MORB, to weakly incompatible element-enriched E-MORB, to incompatible element-enriched OIB (e.g. Fig. 8). MORB-type rocks in evolved environments are interpreted to represent depleted asthenospheric mantle that upwells beneath a rift and likely reflects the onset of seafloor spreading within a new ocean basin or back-arc basin (e.g. Barrett & Sherlock 1996; Almodovar et al. 1997; Piercey et al. 2002b; Rogers & van Staal 2003). Commonly, the MORB-type rocks occur as sills and
Fig. 3. $\text{Al}_2\text{O}_3/\text{TiO}_2$ versus $\text{Zr}/\text{Y}$ and $\text{Nb}/\text{Y}$ for VMS associated mafic rocks from mafic-dominated environments (A, D), modern environments (B, E), and continental–crust associated settings (C, F). Data sources are listed in Appendix 1.
dykes that cross-cut mineralization or as flows that overlie felsic rocks and the associated mineralization (i.e. they typically post-date the main mineralization event). Alkalic (OIB-like) mafic rocks are characterized by high HFSE contents (e.g. Nb, Zr), Nb/Y>0.7, elevated TiO₂ (usually >1%), low Al₂O₃/TiO₂, high Ti/V, and LREE-enriched primitive mantle-normalized plots that have a positive Nb anomaly relative to Th and La (Figs 2, 3, 5 and 8). These types of rocks are often associated with mantle plumes but are also common of continental lithospheric mantle-derived magmas associated with continental- and continental arc-rifting (e.g. van Staal et al. 1991; Goodfellow et al. 1993; Shinjo et al. 1999; Colpron et al. 2002; Piercey et al. 2002a). In these evolved environments, alkalic basalt typically cross-cut and overlie the main VMS hosting horizon, and typically show a stratigraphically upward progression above the VMS hosting horizon from alkalic basalt to MORB; this progression is often interpreted to reflect a shift from rifting (alkalic basalt) to true spreading (MORB) (e.g. Rogers & van Staal 2001; Piercey et al. 2004). Alkalic and MORB-type basalt are associated with many bimodal-felsic and felsic-siliciclastic settings from both the modern (e.g. Bransfield Strait, Okinawa Trough) and ancient (e.g. Bathurst, Iberian Pyrite Belt, Finlayson Lake, Eskay Creek) records (Fig. 8).

**Felsic geochemistry**

Considerable research has been undertaken on the geochemistry of felsic rocks associated with VMS systems (e.g. Lesher et al. 1986b; Barrie et al. 1993; Lentz 1998; Hart et al. 2004). Felsic rocks formed via melting or interaction with continental crust are fundamentally different than those associated with melting a more mafic substrate, thus leading to different signatures for strata in each of these VMS environments. Furthermore, Archean felsic rocks, although similar in some cases to their younger counterparts, have signatures that are somewhat unique and must be dealt with separately from VMS-associated Proterozoic and Phanerozoic felsic rocks.

In Archean terrains considerable work has been undertaken on felsic volcanic geochemistry, particularly in the Superior Province of Canada (e.g. Lesher et al. 1986a; Barrie et al. 1993; Prior et al. 1999; Hart et al. 2004). In these belts, previous workers have outlined a tripartite subdivision of rocks, the FI

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**Fig. 4.** Diagrams for mafic rocks from mafic-dominated VMS environments. (A) Al₂O₃/TiO₂ versus Ni (A) and Cr (B), Ti/V–Ti/Sc (from Hickey & Frey 1982); and (D) La/Sr–TiO₂ (from Brown & Jenner 1989; LOTI data from Meffre et al. 1996 and Wyman et al. 1999). Data sources can be found in Appendix 1.
to FIII suites of rhyolites (Lesher et al. 1986b). This classification has been recently modified by Hart et al. (2004) to include a fourth suite, FIV, but FIV felsic rocks are largely restricted to juvenile terranes in the post-Archean. The FIII suite of felsic rocks have low Zr/Y and La/Yb ratios, high HFSE contents (e.g. Zr>200 ppm), and have flat, tholeiitic chondrite-normalized REE patterns (Figs 9 and 10). The FI have high Zr/Y and La/Yb ratios, lower HFSE contents, and LREE-enriched, calc-alkalic chondrite-normalized REE patterns (Figs 9 and 10). The FII have signatures intermediate between the two groups (Figs 9 and 10). The majority of Archean VMS deposits are hosted by FIII and FII felsic rocks, which are interpreted to have formed within Archean rift sequences from high temperature melts (T>900°C) derived from melting of hydrated basaltic crust at shallow levels in the crust (e.g. Lesher et al. 1986b; Barrie 1995; Hart et al. 2004). The formation at shallow depths (i.e. <10 km) allowed these melts to rise to the surficial environment without losing their heat of fusion (T>900°C), thus, giving them greater ability to drive long-lived hydrothermal systems (e.g. Barrie et al. 1999). In contrast, the other suites are interpreted to have formed from lower temperature melts (<900°C) at deeper levels in the crust (>10 km) (e.g. Lesher et al. 1986b; Barrie 1995; Hart et al. 2004). These melts have less potential to drive hydrothermal systems due to their lower temperatures of fusion and loss of heat upon transport to the surface of the Earth from depth.

In Proterozoic and Phanerozoic terrains, the behaviour of felsic magmatism is dependent on whether it is associated with juvenile or evolved environments. In post-Archean evolved environments, felsic rocks have a range of signatures, but

Fig. 5. Ti-V discrimination diagram for (A) mafic-dominated VMS environments, (B) modern environments, and (C) continental-crust associated settings. Data sources are listed in Appendix 1. Diagram from Shervais (1982).
most VMS deposits are associated with rhyolites that have elevated HFSE and REE contents (Figs 11–13). These rhyolites are typically FIII to FII rhyolites (Fig. 11), but some deposits have FI rhyolites (e.g. Wolverine). These rocks typically have calc-alkalic chondrite-normalized trace element patterns and there is a tendency for rocks in these settings to have FII affinities (Figs 11 and 14) (e.g. Lentz 1998; Piercey et al. 2001b; Hart et al. 2004; Piercey et al. 2008). Some rocks in these evolved settings, particularly those associated with continental rift or continental back-arc rifts (e.g. Delta-Bonnifield, Avoca), have rhyolites with extremely elevated HFSE contents (e.g. Zr>500 ppm; Fig. 13) (e.g. Mortensen & Godwin 1982; McConnell et al. 1991; Dusel-Bacon et al. 2004). Rocks of these evolved environments typically have within-plate (A-type) affinities on discrimination diagrams (Fig. 12). Like their Archean equivalents, felsic rocks associated with evolved settings represent high temperature (>900°C) melting of crust within rift environments (e.g.
In post-Archean juvenile environments, felsic rocks are unlike both Archean and evolved post-Archean settings. The rhyolites in juvenile environments mirror the petrology of the mafic rocks and have tholeiitic to boninite-like affinities (Figs 15–17). Tholeiitic rhyolites have low Zr/Y (<4), flat REE and primitive mantle-normalized patterns, commonly with negative Nb.

**Fig. 8.** Primitive mantle-normalized plots for mafic rocks associated with VMS deposits associated with continental crust including: (A) mid-ocean ridge basalt (MORB) (note the enrichment in incompatible elements, typical of enriched-MORB); and (B) alkalic, ocean island basalt-like mafic rocks. Data sources in Appendix 1. Symbols as in Figure 5.

**Fig. 9.** Key diagrams for felsic rocks associated with Archean VMS deposits. (A) Zr/Y–Y diagram with FI to FIII affinities (from Lesher et al. 1986b); (B) La/Yb–Yb, with FI-FIII affinities (from Lesher et al. 1986b; Hart et al. 2004); (C) Zr–Nb plot (from Leat et al. 1986); and (D) frequency histogram of Zr for Archean rhyolites associated with VMS deposits. Note that in both (C) and (D) that most Archean VMS have felsic rocks with Zr>200 ppm. Data sources in Appendix 1.
anomalies (not shown), are depleted in HFSE and REE (e.g. 
Zr<50–100 ppm), and M-type affinities on discrimination plots
(Figs 15–17). Boninite-like rhyolites are similar to tholeiitic
rhyolites but are more depleted in HFSE and REE with
U-shaped REE patterns (Fig. 17). Rhyolites from these juvenile
environments have FIV affinities (Fig. 15). These rhyolites
typically form from melting of mafic (to andesitic) substrates
often associated with forearc rifting, intra-arc rifting, or rifting
during the initiation of back-arc basin activity (e.g. Shukuno
et al. 2006).

Fig. 10. Chondrite-normalized REE plots for averages of: (A) Archean FIII rhyolites; (B) Archean FII rhyolites; and (C) Archean FI rhyolite. Data sources in Appendix 1.

Fig. 11. Rhyolite discrimination diagrams for average values for post- Archean continental crust-associated rhyolites. (A) Zr/Y–Y diagram with FI to FIII affinities (from Lesher et al. 1986b); and (B) La/Ybub–Ybub with FI–FIII affinities (from Lesher et al. 1986b; Hart et al. 2004). Data sources in Appendix 1.
PETROCHEMICAL ASSEMBLAGES

Very few past studies have considered coincidently the geochemical attributes of both felsic and mafic rocks; most studies focus on felsic (e.g. Lesher et al. 1986b; Lentz 1998; Hart et al. 2004) or mafic (e.g. Swinden et al. 1989; Swinden 1991) rocks. In most VMS camps, however, there are specific lithochemical associations between mafic units in mafic-dominated settings and between mafic and felsic rocks in bimodal and felsic-dominated settings (Fig. 18; Table 2). The groups of
lithogeochemical signatures associated with different rock assemblages and deposit classifications are termed petrochemical assemblages (Fig. 18; Table 2).

In mafic-dominated VMS environments, boninite and/or LOTI are commonly hosting the VMS deposits, but are often overlain (or underlain) by MORB- or BABB-type rocks, indicative of forearc rifting or initiation of back-arc spreading (Fig. 18; Table 1) (e.g. Swinden 1991; Piercey et al. 1997; Bedard et al. 1999). In mafic-siliciclastic environments, the deposits are commonly associated with MORB (e.g. Escanaba Trough, Guaymas, Middle Valley), or more rarely OIB (e.g. Windy Craggy) or boninite (e.g. Fyre Lake), indicative of...
formation within sedimented rifts or sedimented-back-arc rifts (Fig. 18; Table 1) (Saunders et al. 1982; Davis et al. 1994; Stakes & Franklin 1994; Peter & Scott 1999; Piercey et al. 2001a). Plumes may have been significant in the case of the OIB-type rocks at Windy Craggy (Peter & Scott 1999).

In bimodal-mafic environments, boninite and LOTI are commonly spatially associated with depleted, boninite-like or tholeiitic rhyolites with the rhyolites hosting the ores (Fig. 18; Table 1) (e.g. Kerrich et al. 1998; Syme 1998; Bailes & Galley 1999; Syme et al. 1999; Wyman et al. 1999; Bailey 2002). These...
are overlain by MORB-type basaltic rocks (Fig. 18; Table 1) (Piercey et al. 1997; Bailes & Galley 1999; Syme et al. 1999; Wyman et al. 1999; Bailey 2002). For example, in the Rambler Camp in the Newfoundland Appalachians, boninite forms the footwall to the deposits, which are hosted by boninite-like rhyolites, and cross-cut by MORB dykes (e.g. Piercey et al. 1997; Bailey 2002). Similarly, in the Flin Flon camp, the deposits are hosted by tholeiitic rhyolites, yet are spatially associated with LOTI, and are cross-cut and regionally associated with MORB-type rocks (Syme 1998; Syme et al. 1999). In other bimodal mafic environments, the deposits are hosted by rhyolites yet the underlying mafic rocks are MORB in affinity (Fig. 18; Table 1). For example, in the Noranda camp most of the deposits are spatially associated with FIII felsic rocks, yet the bulk of the underlying stratigraphy is MORB (e.g. Laliberte et al. 1992a, Laliberte et al. 1992b; Hart et al. 2004). In all these cases, the stratigraphic sequences are indicative of formation within rift environments, either via true spreading centres (e.g. Noranda), or via a transition from normal arc volcanism to back-arc related magmatic activity (e.g. Rambler, Flin Flon). In most cases, the felsic rocks that occur within these mafic-dominated environments mark the rift episode and reflect melting of the preexisting mafic-dominated substrate via mantle upwelling during the rift event (e.g. Barrie et al. 1993).

In bimodal felsic and felsic-siliciclastic environments, felsic rocks predominate over mafic rocks with felsic rocks typically being calc-alkalic with within-plate (A-type) to peralkalic affinities (Fig. 18; Table 1) (e.g. McConnell et al. 1991; Lentz 1999; Piercey et al. 2001b; Dusel-Bacon et al. 2004). These rocks are typically spatially associated, cross-cut, and overlain by OIB-like, alkalic basalt and/or MORB-type basalt (Fig. 18; Table 1) (e.g. van Staal et al. 1991; Almodóvar et al. 1997; Piercey et al. 2002a; Piercey et al. 2002b; Rogers & van Staal 2003). For example, in the Bathurst camp the deposits are hosted by HFSE-enriched felsic rocks (Flat Lake Brooking and Nepisiguit Falls formations) and cross-cut and overlap by alkalic basalt (Brickwall alkali basalt), which are overlain by MORB-type basalt (Boucher Brook formation) (Rogers & van Staal 2003). Similarly, in the Finlayson Lake district the Wolverine deposit is hosted by HFSE-enriched footwall rhyolitic tuffs and porphyrites which are overlain by the MORB-type basalt (Wolverine basalt) (Piercey et al. 2002a); a similar situation exists at Eskay Creek (Barrett & Sherlock 1996). In other cases, like Avoca and the Delta-Bonnifield districts, the deposits are associated with calc-alkalic and peralkalic rhyolites that are cross-cut and spatially associated with OIB-like, alkalic basalt (Fig. 18; Table 1) (e.g. McConnell et al. 1991; Dusel-Bacon et al. 2004). In some cases, HFSE- and REE-enriched rhyolites are absent and the rhyolites have normal, calc-alkalic affinities (i.e. Zr/Y > 7 but with Zr < 200 ppm and volcanic-arc affinities on discrimination plots), but these rocks are cross-cut and/or overlain by OIB and/or MORB-type mafic rocks (Fig. 18; Table 1) (Stolz 1995; Dusel-Bacon et al. 2004). The occurrence of MORB and alkalic basalt in any felsic domed setting is indicative of rifting and the upwelling of mantle beneath a continental crust-dominated substrate.

FUTURE DIRECTIONS

In the last ten years significant knowledge has been gained in understanding volcanic and intrusion geochemistry related to VMS mineralization. Many of the major advances in the 1990s and 2000s have come due to advances in analytical technology and these will continue into the future. Instruments such as the multi-collector ICP-MS will make radiogenic isotopes such as Nd, Sr, Pb, and Hf more readily available to the explorationist providing an even greater understanding of the petrogenetic histories of VMS-associated and VMS-barron rocks. Better understanding of the petrogenesis of these rocks may further enhance our ability to predict prospective versus barren VMS environments. Similarly, techniques such as laser ablation ICP-MS and laser ablation multi-collector ICP-MS may allow researchers to use the geochemical and isotopic signatures of resistant minerals, such as zircon, and trapped melt inclusions in igneous rocks, to predict the prospectivity of igneous rocks and their host settings. The latter is in its infancy, but may become more applicable in the next ten years.

SUMMARY

Volcanic geochemistry has been and will remain a key tool in the delineation of prospective belts for VMS mineralization on a regional scale. It is a tool for area selection to outline prospective regions that could host VMS hydrothermal systems. In different VMS-hosting environments different groups of hydrochemical assemblages are found. In mafic (e.g. ophiolitic or Cyprus-type) VMS environments, mafic rocks that host deposits are typically boninite and low-Ti island are tholeiite, which are commonly overlain or underlain by basalt of mid-ocean ridge basalt or back-arc basin basalt affinities. In bimodal-mafic environments (e.g. Noranda-type), similar mafic rock assemblages exist, but deposits are often hosted by depleted tholeitic to boninitic rhyolites, except for in Archean environments where they are typically high field strength element-enriched rhyolites. In mafic-siliciclastic (pelitic-mafic) environments (e.g. Besshi-type), mafic rocks typically have mid-ocean ridge basalt affinities and to a lesser extent alkalic/ocean-island basalt-like (e.g. Windy Craggy) or boninitic (e.g. Fyke Lake) signatures. In bimodal-felsic environments (e.g. Kuroko-type) felsic rocks are calc-alkalic to HFSE- and REE-enriched with within-plate (A-type) to peralkalic affinities. These felsic rocks are typically cross-cut and/or overlain by mafic rocks with mid-ocean ridge basalt to alkalic/ocean-island basalt-like affinities. In felsic-siliciclastic environments (e.g. Bathurst-type or Iberian Pyrite Belt-type) felsic rocks are predominantly HFSE- and REE-enriched with within-plate (A-type) to peralkalic affinities. These felsic rocks are typically cross-cut and/or overlain by mafic rocks mid-ocean ridge basalt to alkalic/ocean-island basalt-like affinities. In all of these environments, regardless of setting or style, there are two common themes: (1) rifting and formation within an extensional geodynamic regime; and (2) the presence of high temperature magmatism. These two ingredients are critical in the identification of prospective environments that: (1) have the correct ground preparation to focus hydrothermal fluid flow; and (2) have sufficiently elevated geothermal gradients to drive robust and sustained hydrothermal systems. The concept of petrochemical assemblages, combined with geology and lithogeochemical data well constrained by field relationships, provides a powerful tool in the delineation of potentially fertile belts for VMS mineralization.

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APPENDIX 1: DATA SOURCES

**Mafic rocks**

*Mafic-dominated VMS settings*

Snow Lake and Flin Flon: Stern et al. (1995); Kamiskotia: Hocker et al. (2005); Kidd Creek: Kerrich et al. (1998) and Wyman et al. (1999); Kutcho: Barrett et al. (1996); Rambler/Ming: Piercey et al. (1997) and Bailey (2002); Lake River Group (Noranda): Lafleche et al. (1992a, b); West Shasta: Brouixel et al. (1988), Bence & Taylor (1985), and Lapierre et al. (1985); Bett's Cove: Bedard (1999); Troodos: Cameron (1985) and Rogers et al. (1989); Ic che Deposit: Piercey (unpublished data); Josephine (Turner Albright): Harper (2003); Frye Lake: Piercey et al. (2001a, 2004); and windy Craggy: Peter & Scott (1999).

**Modern VMS environments**

Bransfield Strait: Keller et al. (2002); Okinawa Trough: Shinjo et al. (1999); Manus Basin: Sinton et al. (2003); Juan de Fuca (Axial Seamount): Rhodes et al. (1990); East Pacific Rise: Allan et al. (1987); Middle Valley: Stakes & Franklin (1994); Lau Basin: Ewart et al. (1994); TAG hydrothermal field (Mid-Atlantic): Smith & Humphris (1998); Escanaba Trough: Saunders et al. (1982); Guaymas: Davis & Clague (1987).

**Continental crust-associated VMS settings**

Avoca: Leat et al. (1986) and McConnell et al. (1991); Eskay Creek: Barrett & Sherlock (1996); Kidz Ke Kayah (Finlayson Lake): Piercey et al. (2002a); Parys Mountain: Barrett et al. (2001); Tulsebaq: Sebert & Barrett (1996); Bathurst: Rogers & van Staal (2003); Delta-Bonnefield: Dusel-Bacon et al. (2004); Iberian Pyrite Belt: Almodóvar et al. (1997) and Mitjavila et al. (1997).

**Felsic rocks**

*Archean felsic rocks*

Pilbara: Vearncombe & Kerrich (1999); Kidd Creek: Prior et al. (1999); Sturgeon Lake: Lesher et al. (1986d); Noranda: Lesher et al. (1986b) and Peloquin (1999) (regional); South Bay: Lesher et al. (1986d); Kamiskotia: Hart (1984), Barrie & Pattison (1999); and High Lake: Petch (2004).

*Post-Archean felsic rocks from mafic-dominated settings*


*Post-Archean felsic rocks from continental crust-dominated settings*

Eskay Creek: Barrett & Sherlock (1996); Delta-Bonnefield: Dusel-Bacon et al. (2004); Finlayson Lake: Piercey et al. (2001b); Iberian Pyrite Belt: Almodóvar et al. (1997); Bransfield Strait: Peterson et al. (2004); Okinawa Trough: Shinjo & Kato (2000); Mount Read: Crawford et al. (1992); Parys Mountain: Barrett et al. (2001); Avoca: Leat et al. (1986) and McConnell et al. (1991); and Bathurst: Rogers et al. (2003).

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