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

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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 tholeiite, 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 alkalic (ocean island basalt-like) and/or mid-ocean ridge/back-arc basin basalt-like signatures. In these environments alkalic basalt and mid-ocean ridge/back-arc basin basalt-like mafic rocks overlie felsic rocks and mineralization and represent melts derived from lithospheric and asthenospheric mantle sources, respectively.

Felsic rocks in Archean sequences are typically tholeiitic, have elevated high field strength elements (HFSE) and rare earth elements (REE), and FIII affinities (low Zr/Y and La/Yb_n, flat chondrite-normalized rare earth element profiles). In post-Archean evolved environments, felsic rocks associated with VMS deposits have HFSE- and REE-enrichment and within-plate signatures on discrimination diagrams, like their Archean counterparts, but are more calc–alkalic in composition and commonly have FII affinities. Felsic rocks associated with VMS deposits in post-Archean mafic-dominated, juvenile substrates 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.

Lithogeochemistry and petrology have been important tools in our understanding of and exploration for VMS deposits since the 1970s, and continue to be an important tool in our arsenal in exploring for these deposits. Most of the early lithogeochemical work in the in the 1970s and 1980s focused on alteration lithogeochemistry (e.g. Ishikawa *et al.* 1976; Spitz & Darling 1978; Saeki & Date 1980; Date *et al.* 1983; Gibson *et al.* 1983; Campbell *et al.* 1984; Lesher *et al.* 1986*a*; Kranidiotis &
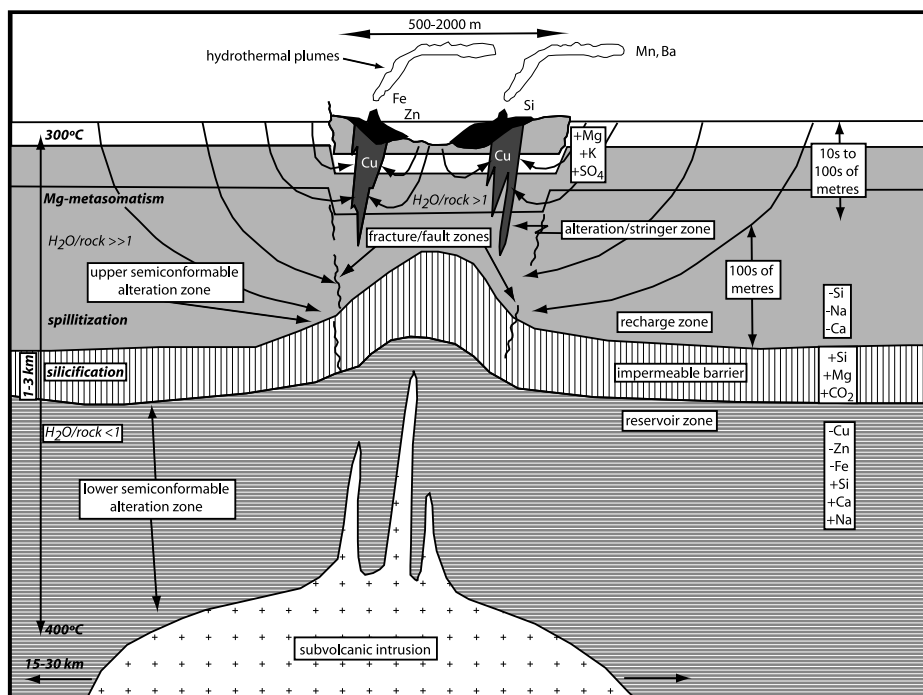
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Fig. 1. Model for the setting and genesis of volcanogenic massive sulphide (VMS) deposits (from Galley 1993; Franklin *et al.* 2005).

MacLean 1987; MacLean & Kranidiotis 1987; MacLean 1988) with few studies aimed at using lithogeochemistry to outline prospective belts on a regional scale (e.g. Lesher *et al.* 1986*b*; 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 lithogeo-chemistry 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 lithogeochemistry and its application to delineating prospective regions for VMS exploration (e.g. Swinden 1991; Barrie *et al.* 1993; Syme & Bailes 1993; Barrett & Sherlock 1996; Swinden 1996; Kerrich & Wyman 1997; Lentz 1998; Syme 1998; Syme *et al.* 1999; Wyman *et al.* 1999; Piercey *et al.* 2001*a*; Piercey *et al.* 2001*b*; Galley 2003; Hart *et al.* 2004).

In this paper the current state of knowledge in lithogeo-chemistry 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.* 2001*b*; 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; Gibson *et al.* 1999) 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 con-junction with geological methods, is particularly useful in

Table 1. *Definitions for acronyms presented within this paper.*

Acronym	Definition
VMS	Volcanogenic massive sulphide
ICP-MS	inductively coupled plasma mass spectrometer
HFSE	high field strength elements
REE	rare earth elements
LREE	light rare earth elements
LOTI	low Ti island arc tholeiites (or low Ti tholeiites)
MORB	mid-ocean ridge basalt
N-MORB	normal mid-ocean ridge basalt
E-MORB	enriched mid-ocean ridge basalt
OIB	ocean island basalt
BABB	back-arc basin basalt

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 Skellefte 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 predominantly 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 INTRUSION 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 (Jenner 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 Al_2O_3 and TiO_2, 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. chlorite alteration; Campbell *et al.* 1984; Whitford *et al.* 1988; Bau 1991; Valsami & Cann 1992) and provide us with information on the primary petrogenetic signatures for magmatic 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 (LOTI) 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. Fyre Lake). Boninite are characterized by high MgO (Mg#>0.60), Ni and Cr contents, low TiO_2 (<0.6%), high Al_2O_3/TiO_2 (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 TiO_2
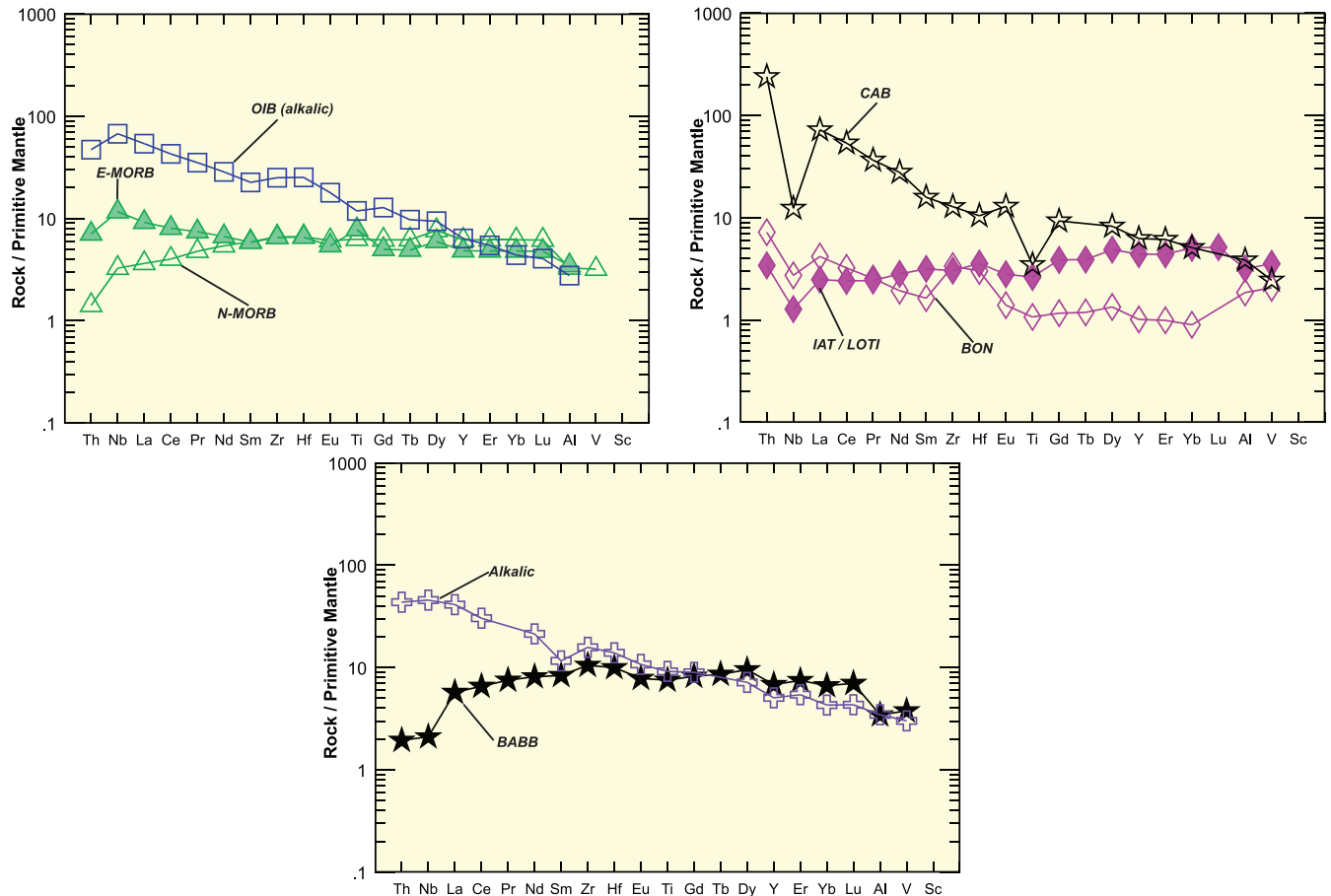
Fig. 2. Primitive mantle-normalized plots for: (**A**) non-arc basalt; (**B**) arc basalt; and (**C**) transitional (back-arc and arc rift-related basalt). Data from Sun & McDonough (1989), Stoltz *et al.* (1990), Jenner (1981), Piercey *et al.* (2004), Ewart *et al.* (1994), and Kepezhinskas *et al.* (1997). Abbreviations: OIB, ocean island basalt; N-MORB, normal mid-ocean ridge basalt; E-MORB, enriched mid-ocean ridge basalt; CAB, calc-alkaline basalt; IAT, island arc tholeiite; LOTI, low-Ti island arc tholeiite; BON, boninite; and BABB, back-arc basin basalt. Primitive mantle values for this diagram and all others in this paper from Sun & McDonough (1989).

contents and lower Al_2O_3/TiO_2 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.* 2001*a*); 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 inti-
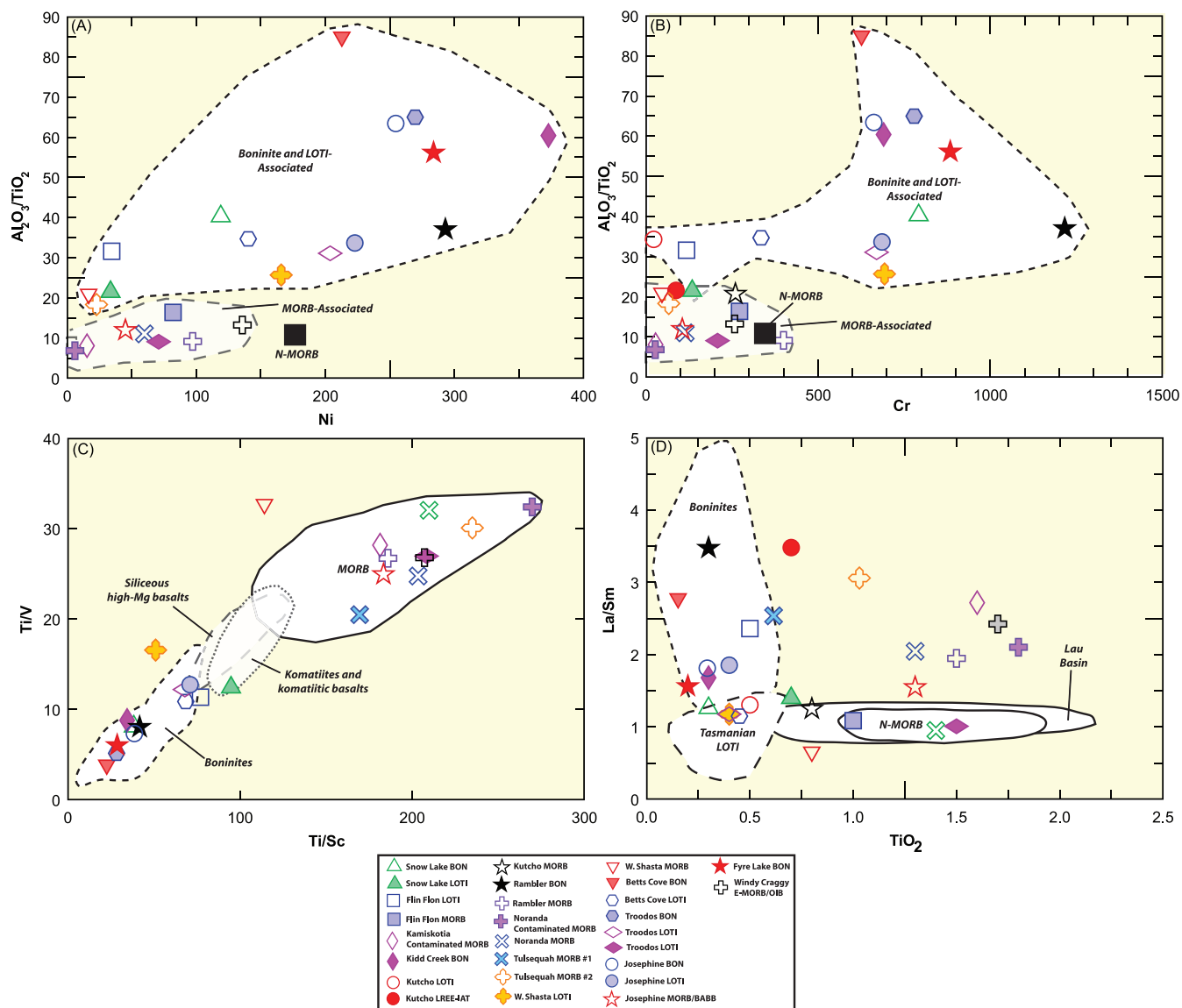
mate relationship with boninitic and arc-tholeiitic rocks, with MORB either underlying boninite (e.g. Semail), or overlying and/or cross-cutting the boninite (e.g. Troodos, Rambler, Turner-Albright). In some modern back-arcs island arc tholeiite (IAT) are interlayered with BABB and MORB (Figs 2 and 7).

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; Almodóvar *et al.* 1997; Piercey *et al.* 2002*b*; Rogers & van Staal 2003). Commonly, the MORB-type rocks occur as sills and

Fig. 3. Al_2O_3/TiO_2 versus Zr/Y and Nb/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.

Fig. 4. Diagrams for mafic rocks from mafic-dominated VMS environments. (**A**) Al_2O_3/TiO_2 versus Ni (**A**) and Cr (**B**), Ti/V–Ti/Sc (from Hickey & Frey 1982); and (**D**) La/Sm-TiO_2 (from Brown & Jenner 1989; LOTI data from Meffre *et al.* 1996 and Wyman *et al.* 1999). Data sources can be found 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 TiO_2 (usually >1%), low Al_2O_3/TiO_2, 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). Theses 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.* 1995; Shinjo *et al.* 1999; Colpron *et al.* 2002; Piercey *et al.* 2002*a*). 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 2003*b*; 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.* 1986*b*; 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.* 1986*b*; 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
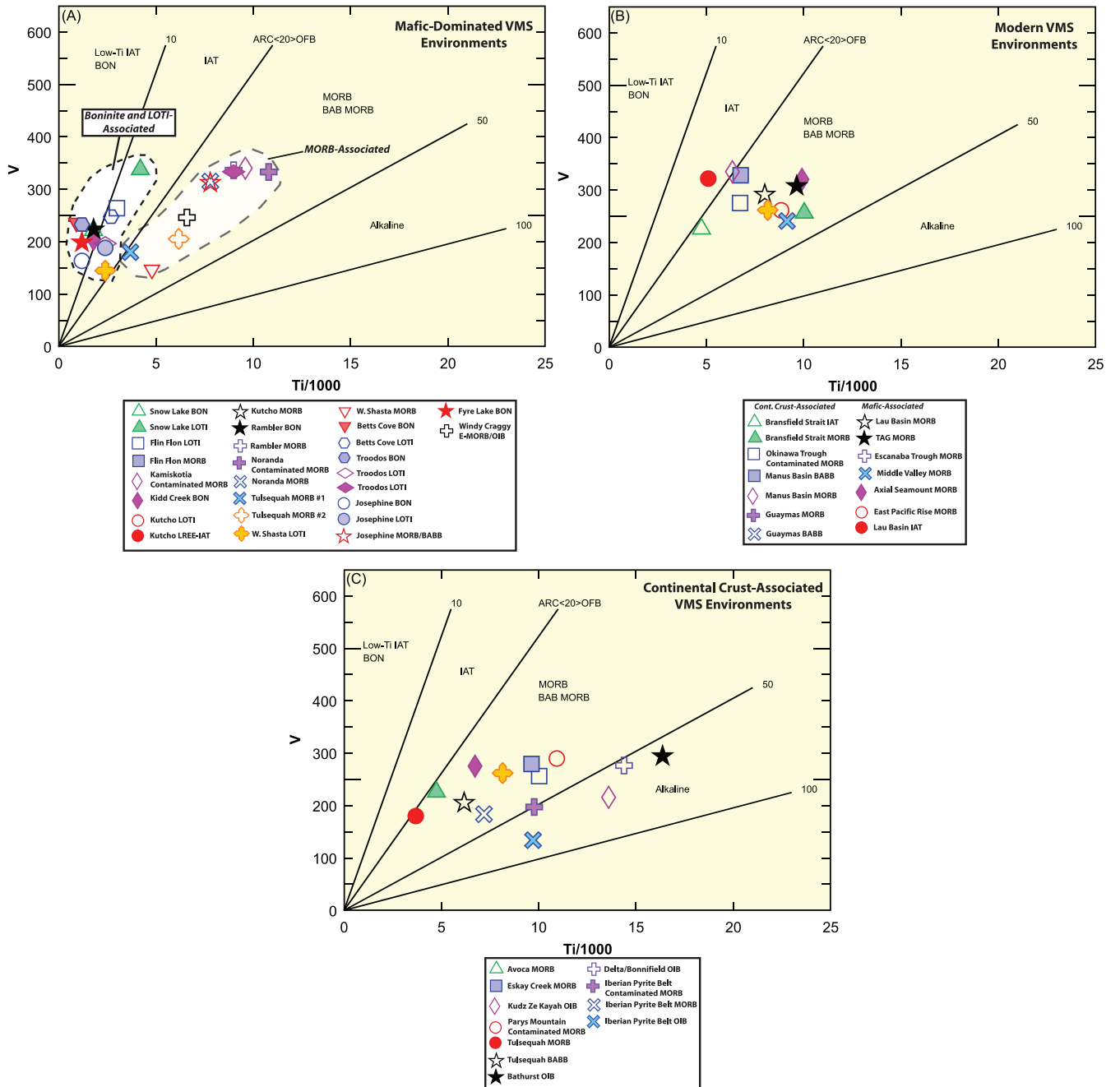
Fig. 5. Ti-V discrimination diagram for (**A**) mafic-dominated VMS environments, (**B**) modern environments, and (**C**) continental-crust associated settings. Data sources are listed in Appendix 1. Diagram from Shervais (1982).

to FIII suites of rhyolites (Lesher *et al.* 1986*b*). 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 basltic crust at shallow levels in the crust (e.g. Lesher

et al. 1986*b*; 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.* 1986*b*; 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
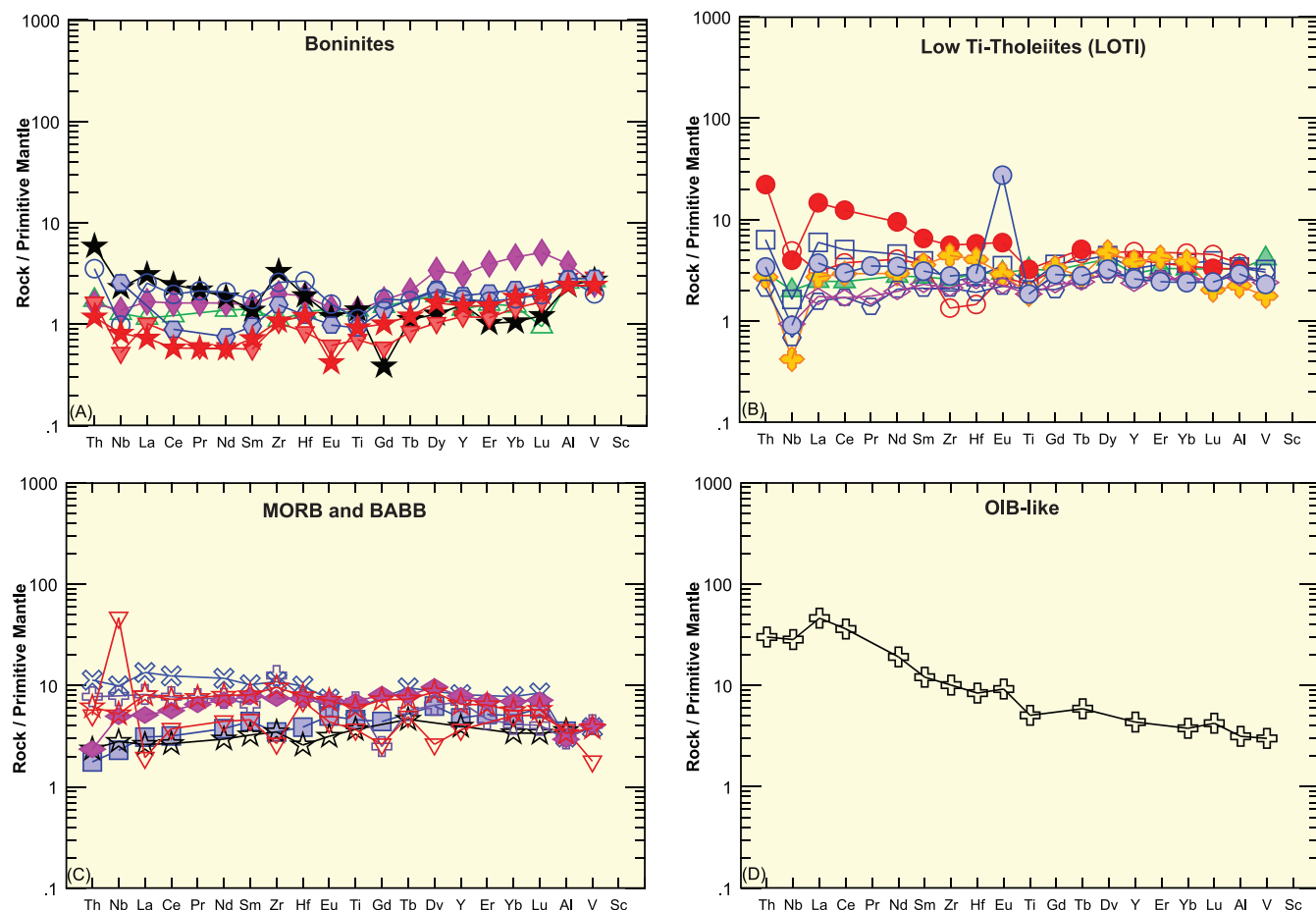
Fig. 6. Primitive mantle-normalized plots for mafic rocks associated with VMS deposits in mafic-dominated VMS environments, including: (**A**) boninite; (**B**) low-Ti island arc tholeiite; (**C**) mid-ocean ridge basalt (MORB) and back-arc basin basalt (BABB); and (**D**) ocean island basalt (OIB)-like. Data sources in Appendix 1.
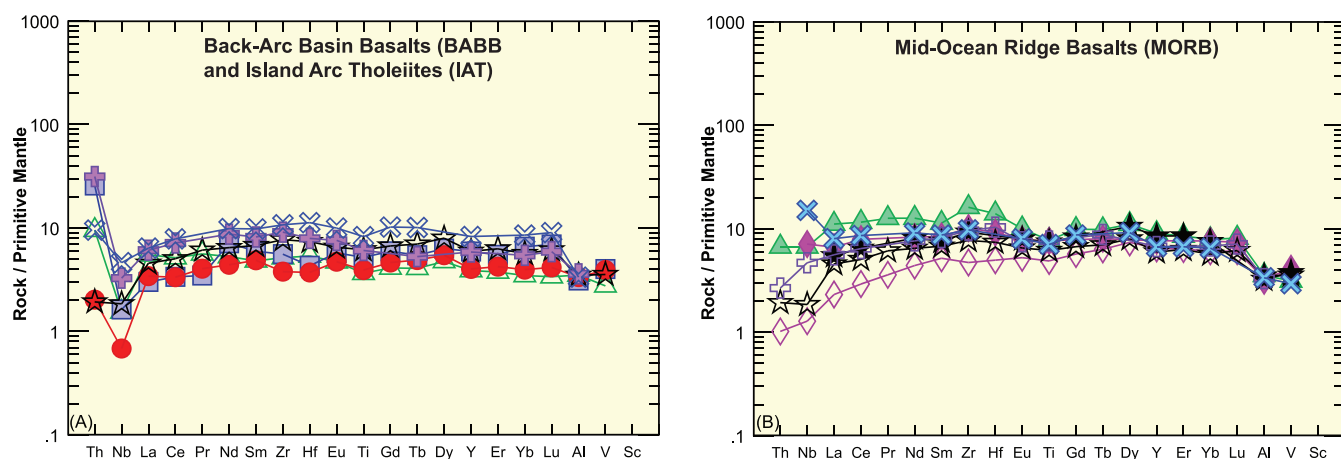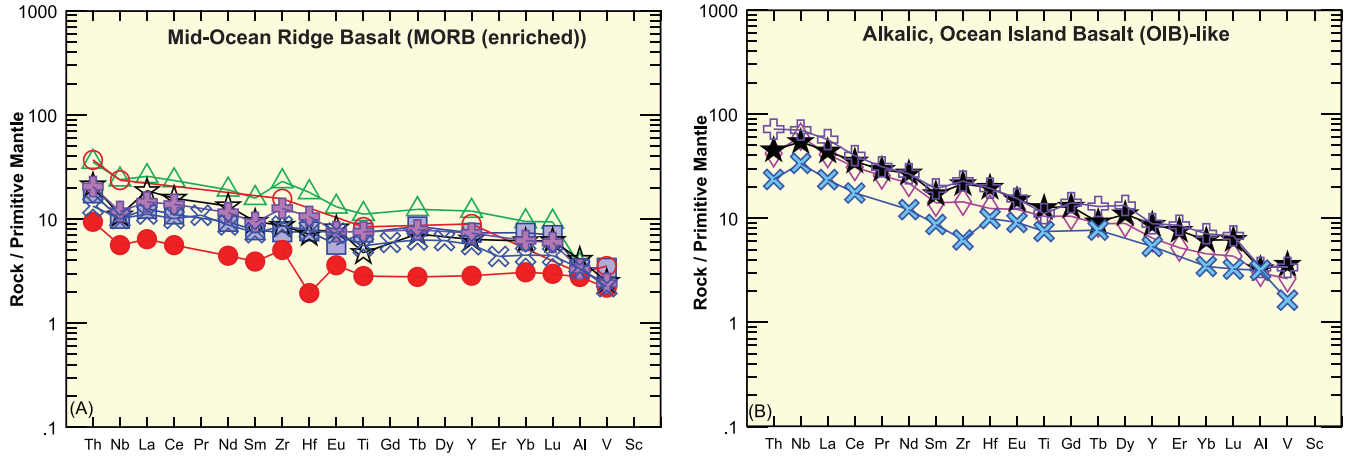

Fig. 7. Primitive mantle-normalized plots for mafic rocks associated with VMS deposits in modern oceans, including: (**A**) back-arc basin basalt and island arc tholeiite; and (**B**) mid-ocean ridge basalt (MORB). Data sources in Appendix 1. Symbols as in Figure 5.

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.* 2001*b*; 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.

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.
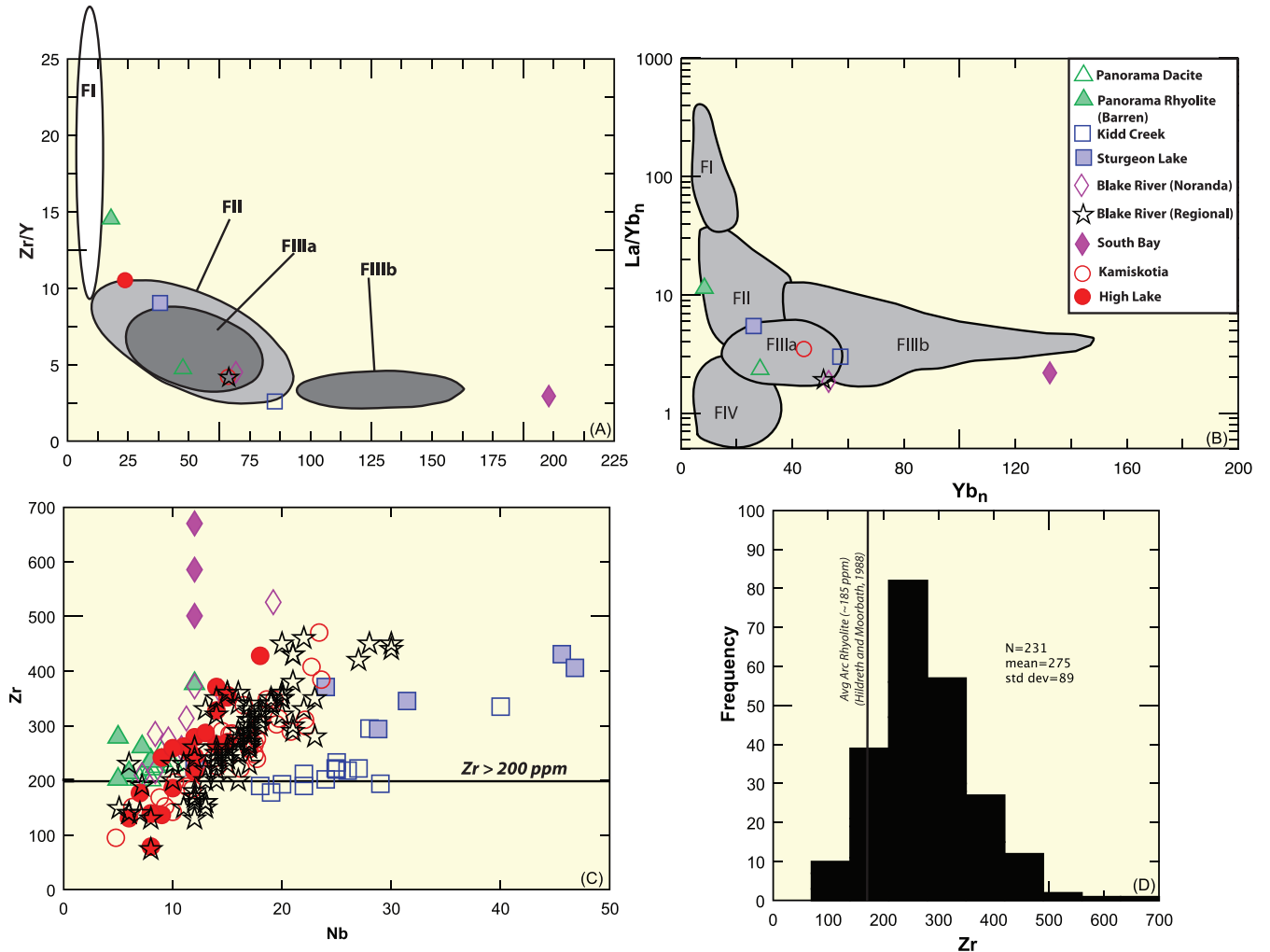

Fig. 9. Key diagrams for felsic rocks associated with Archean VMS deposits. (**A**) Zr/Y–Y diagram with FI to FIII affinities (from Lesher *et al*. 1986*b*); (**B**) La/Yb$_n$–Yb$_n$ with FI-FIII affinities (from Lesher *et al*. 1986*b*; Hart *et al*. 2004); (**C**) Zr–Nb plot (from Leat *et al*. 1986); 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.

continental rift, intracontinental rifts, and continental back-arc rifts).

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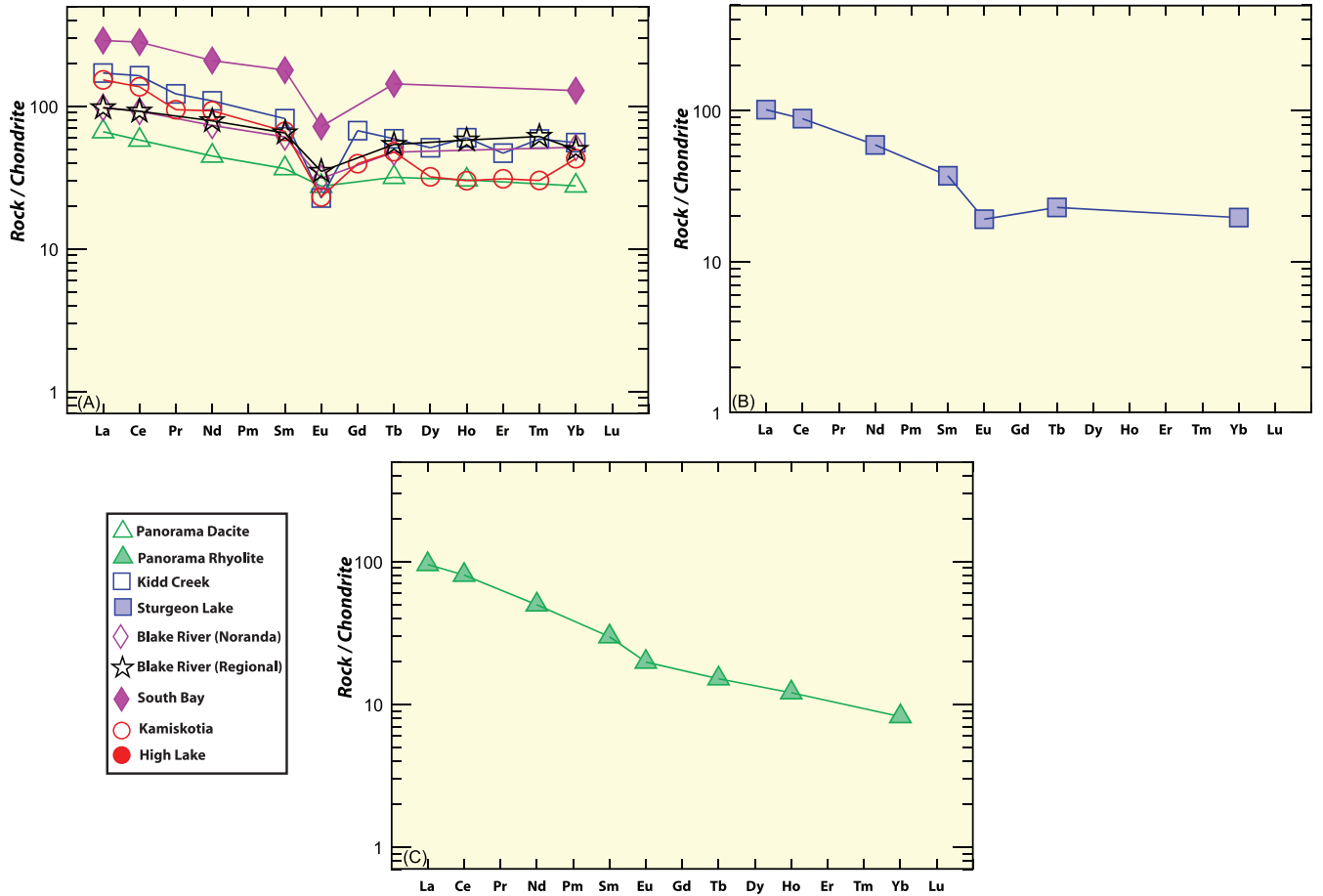
Fig. 10. Chondrite-normalized REE plots for averages of: (**A**) Archean FIII rhyolites; (**B**) Archean FII rhyolites; and (**C**) Archean FI rhyolite. Data sources in Appendix 1.
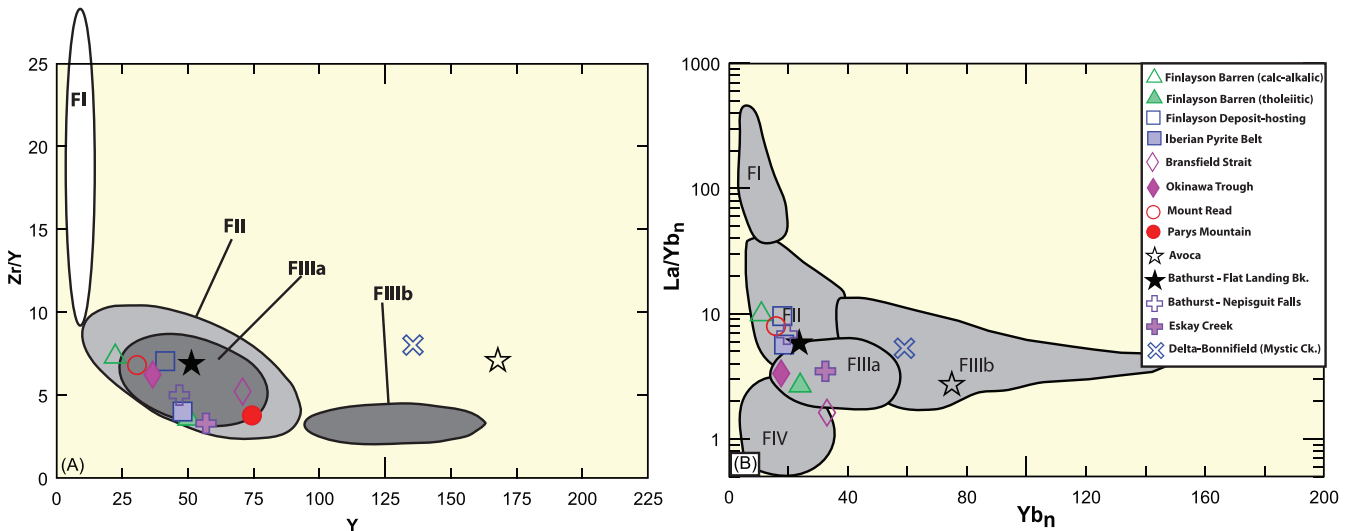

Fig. 11. Rhyolite discrimination diagrams for average values for post- Archean continental crust-associated rhyolites. (**A**) Zr/Y–Y diagram with FI to FIII affinities (from Lesher *et al*. 1986*b*); and (**B**) La/Yb$_n$–Yb$_n$ with FI-FIII affinities (from Lesher *et al*. 1986*b*; Hart *et al*. 2004). 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).
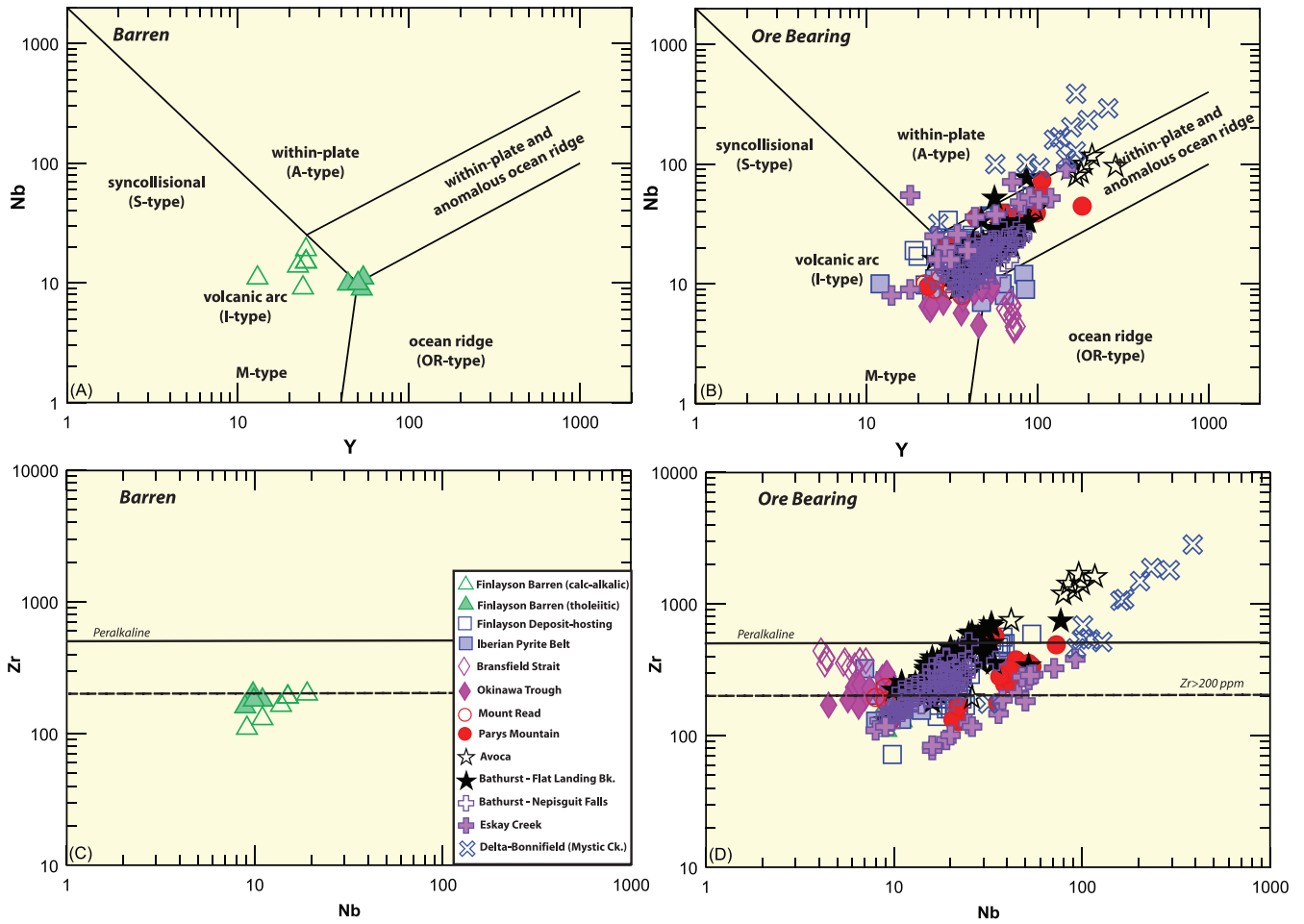
Fig. 12. Tectonic discrimination diagrams for post-Archean continental crust-associated rhyolites. Nb-Y discrimination diagram for (**A**) VMS barren rhyolites and (**B**) VMS-hosting rhyolites. Note the tendency towards within-plate (A-type) (non-arc) affinities (diagram from Pearce *et al.* 1984). Zr–Nb plot of Leat *et al.* (1986) with (**C**) VMS barren rhyolites and (**D**) VMS-hosting rhyolites. Although overlapping the VMS-hosting rhyolites tend towards higher HFSE contents (e.g. Zr>200 ppm), with some tending towards peralkalic compositions. Data sources in Appendix 1.
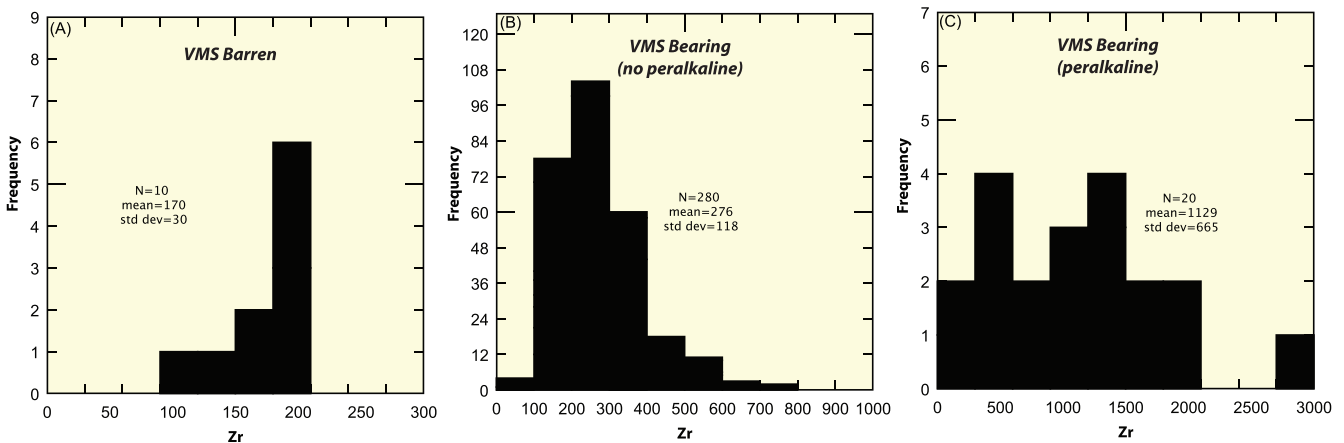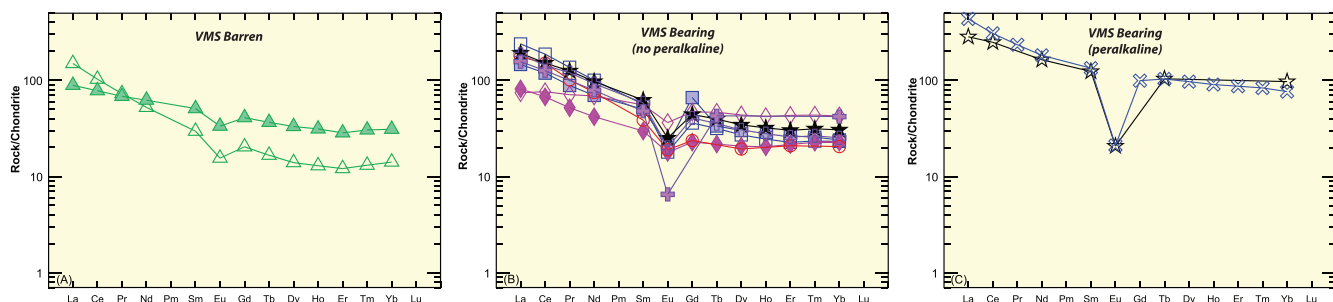

Fig. 13. Frequency histograms for Zr in post-Archean rhyolites associated with continental crust for: (**A**) VMS- barren rhyolites; (**B**) VMS-associated rhyolites without peralkalic affinities; and (**C**) VMS-associated rhyolites with peralkalic affinities. Note that all VMS- associated rhyolites have elevated Zr contents. Data sources in Appendix 1.

PETROCHEMICAL ASSEMBLAGES

Very few past studies have considered coincidently the geo-chemical attributes of both felsic and mafic rocks; most studies focus on felsic (e.g. Lesher *et al.* 1986*b*; 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 lithogeo-chemical 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

Fig. 14. Chondrite-normalized rare earth element plots for post-Archean rhyolites associated with continental crust for: (**A**) VMS-barren rhyolites; (**B**) VMS-associated rhyolites without peralkalic affinities; and (**C**) VMS- associated rhyolites with peralkalic affinities. Symbols as in Figure 12. Data sources in Appendix 1.
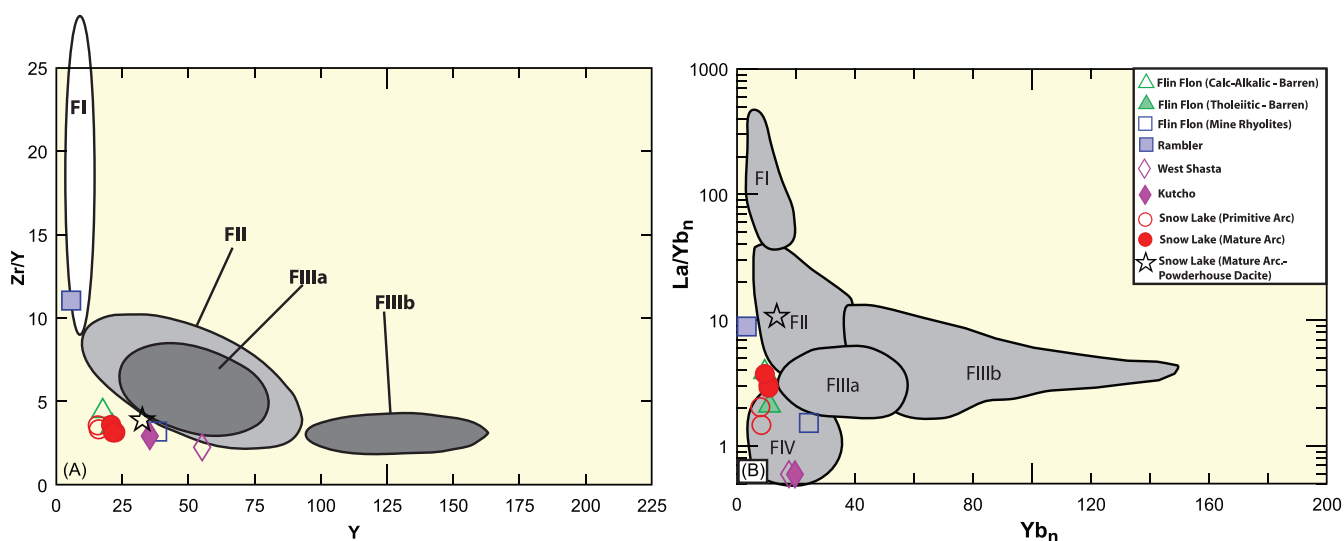
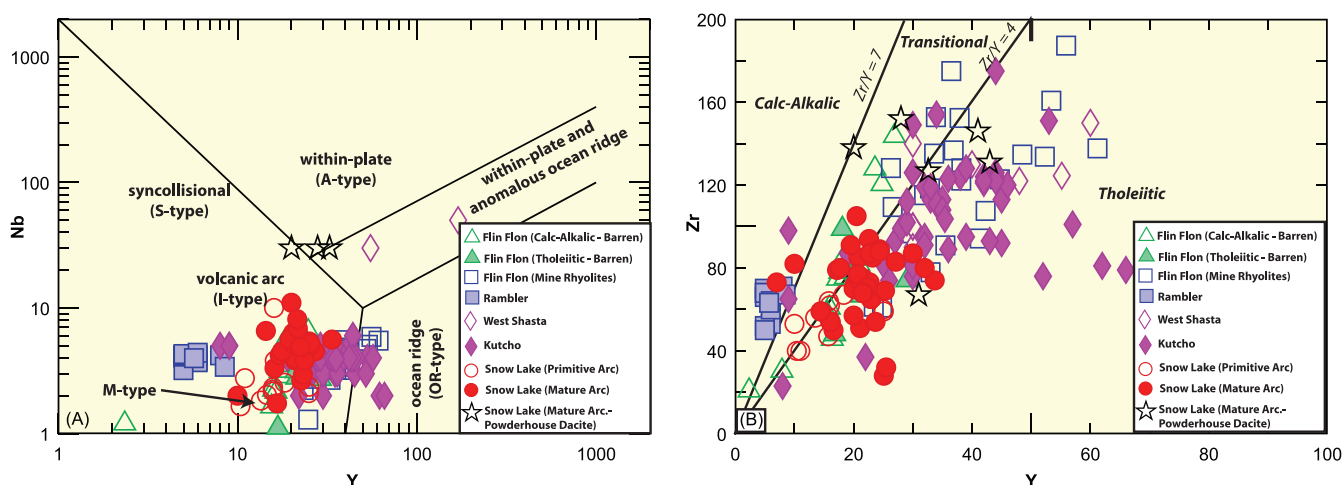**Fig. 15.** Rhyolite discrimination diagrams for average values for post-Archean mafic-associated rhyolites. (**A**) Zr/Y–Y diagram with FI–FIII affinities (from Lesher *et al.* 1986*b*); and (**B**) La/Yb_n–Yb_n with FI–FIII affinities (from Lesher *et al.* 1986*b*; Hart *et al.* 2004). Data sources in Appendix 1.


Fig. 16. Discrimination diagrams for post-Archean mafic-associated rhyolites. (**A**) Nb–Y diagram illustrating that most VMS-associated rhyolites in mafic-dominated settings have M-type affinities (diagram from Pearce *et al.* 1984). (**B**) Zr–Y plot illustrating the tholeiitic character of most VMS- associated rhyolites in mafic-dominated settings (diagram modified from Barrett & MacLean 1999). Data sources in Appendix 1.

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
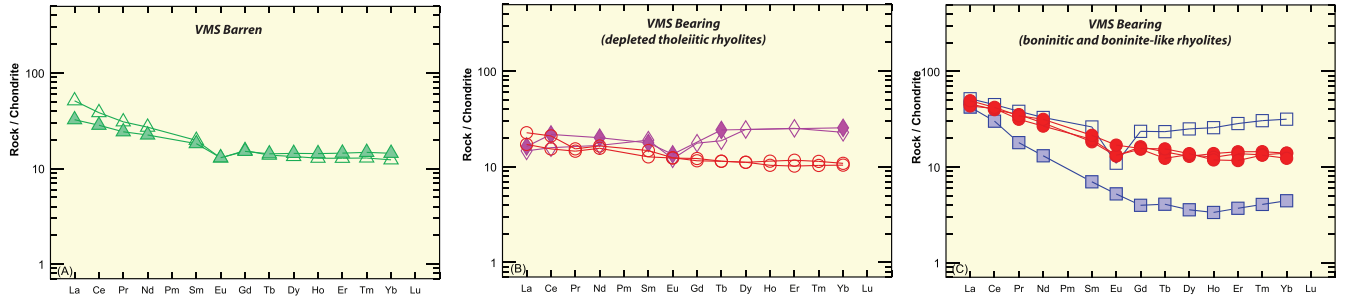
Fig. 17. Chondrite-normalized rare earth element plots for average post- Archean rhyolites associated with mafic dominated settings. (**A**) VMS-barren rhyolites; (**B**) VMS-associated rhyolites with tholeiitic affinities; and (**C**) VMS-associated rhyolites with boninitic affinities. Symbols as in Figure 16. Data sources in Appendix 1.
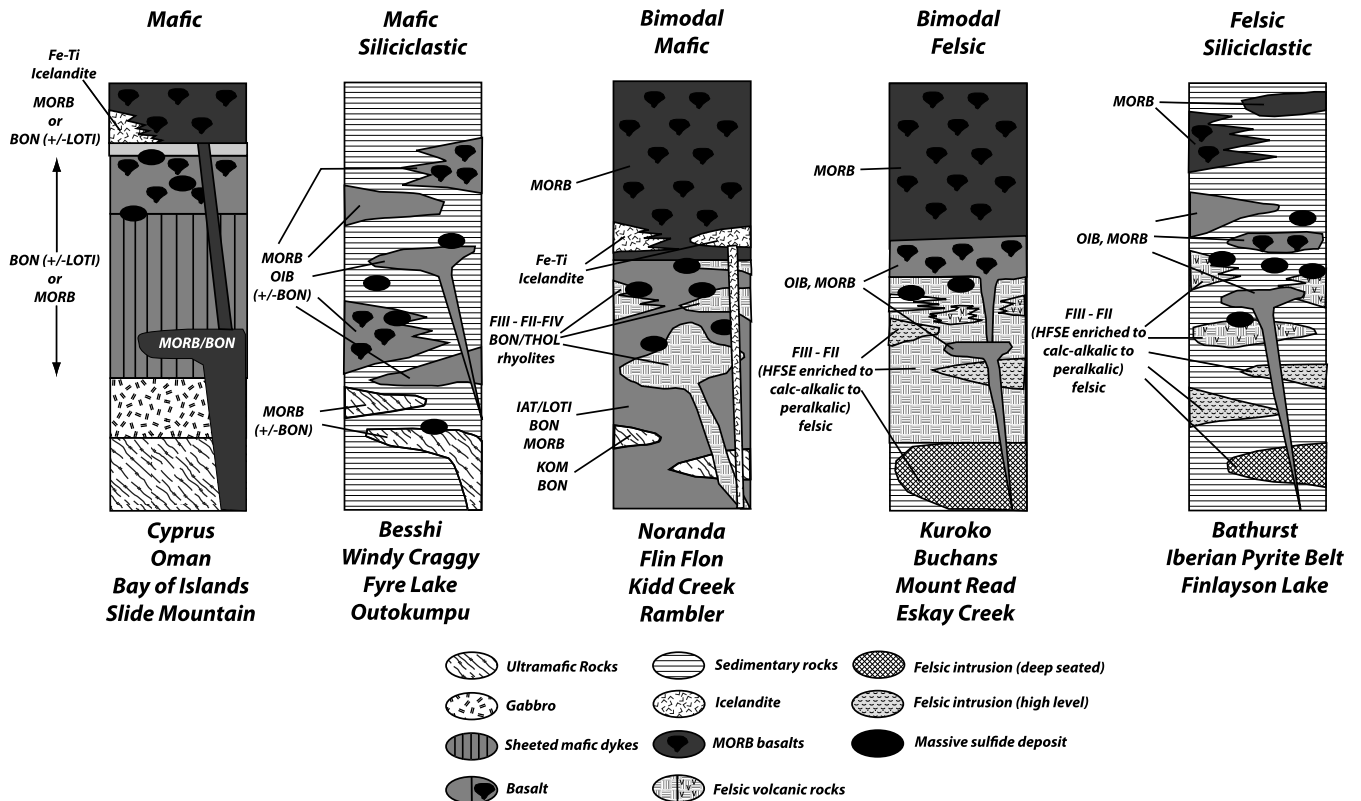
Fig. 18. Petrochemical assemblages for various VMS deposit environments and deposit types. Based on concepts presented herein and Piercey (2007).

Table 2. *Petrochemical assemblages of mafic and felsic rocks commonly associated with different VMS deposit classes.*

VMS Deposit Class	Mafic	Felsic
Mafic	Boninite, low-Ti tholeiite, MORB	–
Mafic Siliciclastic	MORB, alkalic, boninite (rare)	–
Bimodal Mafic	MORB, boninite, low-Ti tholeiite (calc-alkalic and island arc tholeiites present but rarer)	Archean–FIII rhyolites. Proterozoic–Phanerozoic-tholeiitic rhyolites, boninitic rhyolites.
Bimodal Felsic	MORB, alkalic	HFSE-enriched rhyolites (A-type), peralkaline and calc-alkalic rhyolites (rarer)
Felsic Siliciclastic	MORB, alkalic	HFSE-enriched rhyolites, peralkaline, and calc-alkalic rhyolites (rarer)

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.* 2001*a*). 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. Lafleche *et al.* 1992*a*; Lafleche *et al.* 1992*b*; 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.* 2001*b*; 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.* 2002*a*; Piercey *et al.* 2002*b*; Rogers & van Staal 2003). For example, in the Bathurst camp the deposits are hosted by HFSE-enriched felsic rocks (Flat Landing Brook and Nepisiguit Falls formations) and cross-cut and overlain by alkalic basalt (Brunswick 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 porphyries which are overlain by the MORB-type basalt (Wolverine basalt) (Piercey *et al.* 2002*b*); 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 dominated 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-barren 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 rock 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 petrochemical 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 arc 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 tholeiitic 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. Fyre 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.

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); Blake River Group (Noranda): Lafleche *et al.* (1992*a*, *b*); West Shasta: Brouxel *et al.* (1988), Bence & Taylor (1985), and Lapierre *et al.* (1985); Betts Cove: Bedard (1999); Troodos: Cameron (1985) and Rogers *et al.* (1989); Ice Deposit: Piercey (unpublished data); Josephine (Turner Albright): Harper (2003); Fyre Lake: Piercey *et al.* (2001*a*, 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); Kudz Ze Kayah (Finlayson Lake): Piercey *et al.* (2002*a*); Parys Mountain: Barrett *et al.* (2001); Tulsequah: Sebert & Barrett (1996); Bathurst: Rogers & van Staal (2003); Delta-Bonnifield: 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.* (1986*b*); Noranda: Lesher *et al.* (1986*b*) and Péloquin (1999) (regional); South Bay: Lesher *et al.* (1986*b*); Kamiskotia: Hart (1984), Barrie & Pattison (1999); and High Lake: Petch (2004).

Post-Archean felsic rocks from mafic-dominated settings

Flin Flon: Syme (1998); Rambler (Ming): Bailey (2002) and Piercey *et al.* (1997); West Shasta: Bence & Taylor (1985) and Lapierre *et al.* (1985); Kutcho: Barrett *et al.* (1996); and Snow Lake: Bailes & Galley (1999, 2001).

Post-Archean felsic rocks from continental crust-dominated settings

Eskay Creek: Barrett & Sherlock (1996); Delta-Bonnifield: Dusel-Bacon *et al.* (2004); Finlayson Lake: Piercey *et al.* (2001*b*); Iberian Pyrite Belt: Almodóvar *et al.* (1997); Bransfield Strait: Petersen *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).

REFERENCES

ALLAN, J.F., BATIZA, R. & LONSDALE, P.F. 1987. Petrology and chemistry of lavas from seamounts flanking the East Pacific Rise axis, 21 degrees N; implications concerning the mantle source composition for both seamount and adjacent EPR lavas. *In:* KEATING, B.H., FRYER, P., BATIZA, R. & BOEHLERT, G.W. (eds) *Seamounts, islands, and atolls.* American Geophysical Union, San Francisco, CA, USA, American Geophysical Monograph **43**, 255–282.

ALLEN, R.L. 1992. Reconstruction of the tectonic, volcanic, and sedimentary setting of strongly deformed Zn–Cu massive sulfide deposits at Benambra, Victoria. *Economic Geology*, **87**, 825–854.

ALLEN, R.L., LUNDSTROM, I, RIPA, M. & CHRISTOFFERSON, H. 1996. Facies analysis of a 1 9 Ga, continental margin, back-arc, felsic caldera province with diverse Zn-Pb-Ag-(Cu-Au) sulfide and Fe oxide deposits, Bergslagen region, Sweden. *Economic Geology*, **91**, 979–1008.

ALMODÓVAR, G.R., SÁEZ, R., PONS, J.M., MAESTRE, A., TOSCANO, M. & PASCUAL, E. 1997. Geology and genesis of the Aznalcóllar massive sulphide deposits, Iberian Pyrite Belt, Spain. *Mineralium Deposita*, **V33**, 111–136.

BAILES, A.H. & GALLEY, A.G. 1999. Evolution of the Paleoproterozoic Snow Lake arc assemblage and geodynamic setting for associated volcanic-hosted massive sulphide deposits, Flin Flon Belt, Manitoba, Canada. *Canadian Journal of Earth Sciences*, **36**, 1789–1805.

BAILES, A.H. & GALLEY, A.G. 2001. *Geochemistry and tectonic setting of volcanic and intrusive rocks in the VMS-hosting Snow Lake arc assemblage, Flin Flon Belt, Manitoba: a preliminary releas of the geochemical data set.* Manitoba Department of Industry, Trade and Mines, Open File Report OF2001-6.

BAILEY, J. 2002. *Chemostratigraphy Surrounding the Ming Mine VMS Mineralization in the Northern Pacquet Harbour Group (PHG) and correlations with the southern PHG, Baie Verte Peninsula, Newfoundland.* B.Sc.(Hons.), Memorial University of Newfoundland and Labrador.

BARRETT, T.J. & MACLEAN, W.H. 1999. Volcanic sequences, lithogeochemistry, and hydrothermal alteration in some bimodal volcanic-associated massive sulfide systems. *In:* BARRIE, C.T. & HANNINGTON, M.D. (eds) *Volcanic-Associated Massive Sulfide Deposits: Processes and Examples in Modern and Ancient Environments.* Society of Economic Geologists, Reviews in Economic Geology **8**, 101–131, Socorro, NM, USA.

BARRETT, T.J. & SHERLOCK, R.L. 1996. Geology, lithogeochemistry, and volcanic setting of the Eskay Creek Au-Ag-Cu-Zn deposit, northwestern British Columbia. *Exploration and Mining Geology*, **5**, 339–368.

BARRETT, T.J., MACLEAN, W.H. & TENNANT, S.C. 2001. Volcanic sequence and alteration at the Parys Mountain volcanic-hosted massive sulfide deposit, Wales, United Kingdom: Applications of immobile element lithogeochemistry. *Economic Geology*, **96**, 1279–1306.

BARRETT, T.J., THOMPSON, J.F.H. & SHERLOCK, R.L. 1996. Stratigraphic, lithogeochemical and tectonic setting of the Kutcho Creek massive sulfide deposit, northern British Columbia. *Exploration and Mining Geology*, **5**, 309–338.

BARRIE, C.T. 1995. Zircon thermometry of high-temperature rhyolites near volcanic-associated massive sulfide deposits. Abitibi subprovince, Canada. *Geology*, **23**, 169–172.

BARRIE, C.T. & HANNINGTON, M.D. 1999. Classification of volcanic-associated massive sulfide deposits based on host-rock composition. *In:* BARRIE, C.T. & HANNINGTON, M.D. (eds) *Volcanic-Associated Massive Sulfide Deposits: Processes and Examples in Modern and Ancient Environments.* Society of Economic Geologists, Reviews in Economic Geology **8**, 1–11, Socorro, NM, USA.

BARRIE, C.T. & PATTISON, J. 1999. Fe-Ti basalts, high silica rhyolites, and the role of magmatic heat in the genesis of the Kam-Kotia volcanic-associated massive sulfide deposit, western Abitibi Subprovince, Canada. *Economic Geology Monographs*, **10**, 577–592.

BARRIE, C.T., CATHLES, L.M., ERENDI, A., SCHWAIGER, H. & MURRAY, C. 1999. Heat and fluid flow in volcanic-associated massive sulfide-forming hydrothermal systems. *In:* BARRIE, C.T. & HANNINGTON, M.D. (eds) *Volcanic-Associated Massive Sulfide Deposits: Processes and Examples in Modern and Ancient Environments.* Society of Economic Geologists, Reviews in Economic Geology **8**, 201–219.

BARRIE, C.T., LUDDEN, J.N. & GREEN, T.H. 1993. Geochemistry of volcanic rocks associated with Cu-Zn and Ni-Cu deposits in the Abitibi Subprovince. *Economic Geology*, **88**, 1341–1358.

BAU, M. 1991. Rare-earth element mobility during hydrothermal and metamorphic fluid-rock interaction and the significance of the oxidation state of europium. *Chemical Geology*, **93**, 219–230.

BEDARD, J.H. 1999. Petrogenesis of boninites from the Betts Cove Ophiolite, Newfoundland, Canada; identification of subducted source components. *Journal of Petrology*, **40**, 1853–1889.

BEDARD, J.H., LAUZIERE, K., TREMBLAY, A. & SANGSTER, A. 1999. Evidence for forearc seafloor-spreading from the Betts Cove Ophiolite, Newfoundland; oceanic crust of boninitic affinity. *Tectonophysics*, **284**, 223–245.

BENCE, A.E. & TAYLOR, B.E. 1985. Rare earth elements systematics of West Shasta metavolcanic rocks; petrogenesis and hydrothermal alteration. *Economic Geology*, **80**, 2164–2176.

BROUXEL, M., LAPIERRE, H., MICHARD, A. & ALBAREDE, F. 1988. Geochemical study of an early Paleozoic island-arc-back-arc basin system; Part 2, Eastern Klamath, early to middle Paleozoic island-arc volcanic rocks (Northern California); with Suppl. Data 88-15. *Geological Society of America Bulletin*, **100**, 1120–1130.

BROWN, A.V. & JENNER, G.A. 1989. Geological setting, petrology and chemistry of Cambrian boninite and low-Ti tholeiite lavas in western Tasmania. *In:* CRAWFORD, A.J. (ed.) *Boninites*. Unwin Hyman, London, United Kingdom, 232–263.

CAMERON, W.E. 1985. Petrology and origin of primitive lavas from the Troodos ophiolite, Cyprus. *Contributions to Mineralogy and Petrology*, **89**, 239–255.

CAMPBELL, I.H., FRANKLIN, J.M., GORTON, M.P., HART, T.R. & SCOTT, S.D. 1981. The role of subvolcanic sills in the generation of massive sulfide deposits. *Economic Geology*, **76**, 2248–2253.

CAMPBELL, I.H., LESHER, C.M., COAD, P., FRANKLIN, J.M., GORTON, M.P. & THURSTON, P.C. 1984. Rare-earth element mobility in alteration pipes below massive Cu-Zn sulfide deposits. *Chemical Geology*, **45**, 181–202.

COLPRON, M., LOGAN, J.M. & MORTENSEN, J.K. 2002. U-Pb zircon age constraint for late Neoproterozoic rifting and initiation of the lower Paleozoic passive margin of western Laurentia. *Canadian Journal of Earth Sciences*, **39**, 133–143.

CRAWFORD, A.J., BECCALUVA, L. & SERRI, G. 1981. Tectono-magmatic evolution of the West Philippine-Mariana region and the origin of boninites. *Earth and Planetary Science Letters*, **54**, 346–356.

CRAWFORD, A.J., CORBETT, K.D. & EVERARD, J.L. 1992. Geochemistry of the Cambrian volcanic-hosted massive sulfide-rich Mount Read Volcanics, Tasmania, and some tectonic implications. *Economic Geology*, **87**, 597–619.

CRAWFORD, A.J., FALLOON, T.J. & GREEN, D.H. 1989. Classification, petrogenesis, and tectonic setting of boninites. *In:* CRAWFORD, A.J. (ed.) *Boninites and related rocks*. Unwin-Hyman, London, 1–49.

DATE, J., WATANABE, Y. & SAEKI, Y. 1983. Zonal alteration around the Fukazawa Kuroko deposits, Akita Prefecture, northern Japan. *In:* OHMOTO, H. & SKINNER, B.J. (eds) *Kuroko and Related Volcanogenic Massive Sulfide Deposits*. Economic Geology, Monograph **5**, 365–386, Lancaster, PA, USA.

DAVIS, A.S. & CLAGUE, D.A. 1987. Geochemistry, mineralogy, and petrogenesis of basalt from the Gorda Ridge. *Journal of Geophysical Research*, **92**, 10,467–410,483.

DAVIS, A.S., CLAGUE, D.A. & FRIESEN, W.B. 1994. *Petrology and mineral chemistry of basalt from Escanaba Trough*. U. S. Geological Survey Bulletin, Report: B 2022, 153–170.

DUSEL-BACON, C., WOODEN, J.L. & HOPKINS, M.J. 2004. U-Pb zircon and geochemical evidence for bimodal mid-Paleozoic magmatism and syngenetic base-metal mineralization in the Yukon-Tanana Terrane, Alaska. *Geological Society of America Bulletin*, **116**, 989–1015.

EWART, A., BRYAN, W.B., CHAPPELL, B.W. & RUDNICK, R.L. 1994. Regional geochemistry of the Lau-Tonga arc and backarc systems. *Proceedings of the Ocean Drilling Program, Scientific Results*, **135**, 385–425.

FALLOON, T.J. & DANYUSHEVSKY, L.V. 2000. Melting of refractory mantle at 1·5, 2 and 2·5 GPa under anhydrous and H2O-undersaturated conditions: Implications for the petrogenesis of high-Ca boninites and the influence of subduction components on mantle melting. *Journal of Petrology*, **41**, 257–283.

FRANKLIN, J.M., GIBSON, H.L., GALLEY, A.G. & JONASSON, I.R. 2005. Volcanogenic Massive Sulfide Deposits. *In:* HEDENQUIST, J.W., THOMPSON, J.F.H., GOLDFARB, R.J. & RICHARDS, J.P. (eds) *Economic Geology 100th Anniversary Volume*. Society of Economic Geologists, Littleton, CO, 523–560.

GALLEY, A.G. 1993. Characteristics of semi-conformable alteration zones associated with volcanogenic massive sulphide districts. *Journal of Geochemical Exploration*, **48**, 175–200.

GALLEY, A.G. 1996. Geochemical characteristics of subvolcanic intrusions associated with Precambrian massive sulphide deposits. *In:* WYMAN, D.A. (ed.) *Trace Element Geochemistry of Volcanic Rocks: Applications for Massive Sulphide Exploration*. Geological Association of Canada Short Course Notes, **12**, 239–278, St. John's, NL, Canada.

GALLEY, A.G. 2003. Composite synvolcanic intrusions associated with Precambrian VMS-related hydrothermal systems. *Mineralium Deposita*, **38**, 443–473.

GIBSON, H.L. 1989. *The geology and reconstruction of the Mine sequence and the Noranda cauldron of the Noranda complex, northwestern Québec*. PhD Thesis, Carleton University, Ottawa, ON, Canada.

GIBSON, H.L. 2005. Volcanic-hosted ore deposits. *In:* MARTI, J. & ERNST, G.G.J. (eds) *Volcanoes in the Environment*. Cambridge University Press, New York, NY, USA, 332–386.

GIBSON, H.L. & WATKINSON, D.H. 1990. Volcanogenic massive sulphide deposits of the Noranda cauldron and shield volcano, Québec. *In:* RIVE, M., VERPAELST, P., GAGNON, Y., LULIN, J.-M., RIVERIN, G. & SIMARD, A. (eds) *The Northwestern Québec Polymetallic Belt: A summary of 60 years of mining exploration*. Canadian Institute of Mining and Metallurgy Special Publication, **43**, 119–132, Montreal, QC, Canada.

GIBSON, H.L., MORTON, R.L. & HUDAK, G.J. 1999. Submarine volcanic processes, deposits, and environments favorable for the location of volcanic-associated massive sulfide deposits. *In:* BARRIE, C.T. & HANNINGTON, M.D. (eds) *Volcanic-Associated Massive Sulfide Deposits: Processes and Examples in Modern and Ancient Environments*. Reviews in Economic Geology, **8**, 13–51, Socorro, NM, USA.

GIBSON, H.L., WATKINSON, D.H. & COMBA, C.D.A. 1983. Silicification: Hydrothermal alteration in an Archean geothermal system within the Amulet Rhyolite Formation, Noranda, Quebec. *Economic Geology*, **78**, 954–971.

GOODFELLOW, W.D., CECILE, M.P. & LEYBOURNE, M.I. 1995. Geochemistry, petrogenesis, and tectonic setting of lower Paleozoic alkalic and potassic volcanic rocks, Northern Canadian Cordillera Miogeocline. *Canadian Journal of Earth Sciences*, **32**, 1236–1254.

HANNINGTON, M.D., JONASSON, I.R., HERZIG, P.M. & PETERSEN, S. 1995. Physical and chemical processes of seafloor mineralization at mid-ocean ridges. *In:* HUMPHRIS, S.E., ZIERENBERG, R.A., MULLINEAUX, L.S. & THOMSON, R.S. (eds) *Seafloor Hydrothermal Systems: Physical, Chemical, Biological and Geological Interactions*. American Geophysical Union, Monograph, **91**, 115–157, Washington, DC, USA.

HARPER, G.D. 2003. Tectonic implications of boninite, arc tholeiite, and MORB magma types in the Josephine Ophiolite, California, Oregon. *In:* DILEK, Y. & ROBINSON, R T. (eds) *Ophiolites in Earth History*. Geological Society, London, Special Publications, **218**, 207–230.

HART, T.R. 1984. *The geochemistry and petrogenesis of a metavolcanic and intrusive sequence in the Kamiskotia area, Timmins, Ontario*. M.Sc. Thesis, University of Toronto, Canada.

HART, T.R., GIBSON, H.L. & LESHER, C.M. 2004. Trace element geochemistry and petrogenesis of felsic volcanic rocks associated with volcanogenic massive Cu-Zn-Pb sulfide deposits. *Economic Geology*, **99**, 1003–1013.

HAWKINS, J.W. 1995. Evolution of the Lau Basin–Insights from ODP Leg 135. *In:* TAYLOR, B. & NATLAND, J. (eds) *Active Margins and Marginal Basins of the Western Pacific*. American Geophysical Union Monograph, **88**, 125–173, Washington, DC, USA.

HICKEY, R.L. & FREY, F.A. 1982. Geochemical characteristics of boninite series volcanics: implications for their source. *Geochimica et Cosmochimica Acta*, **46**, 2099–2115.

HOCKER, S.M., THURSTON, P.C. & GIBSON, H.L. 2005. *Volcanic stratigraphy and controls on mineralization in the Genex Mine area, Kamiskotia area; Discover Abitibi Initiative*. Ontario Geological Survey Sudbury, ON, Canada, Open File Report 6156, 143 (+1 map).

ISHIKAWA, Y., SAWAGUCHI, T., YWAYA, S. & HORIUCHI, M. 1976. Delineation of prospecting targets for Kuroko deposits based on modes of volcanism of underlying dacite and alteration haloes. *Mining Geology*, **26**, 105–117.

JENNER, G.A. 1981. Geochemistry of high-Mg andesites from Cape Vogel, Papua New Guinea. *Chemical Geology*, **33**, 307–322.

JENNER, G.A. 1996. Trace element geochemistry of igneous rocks: Geochemical nomenclature and analytical geochemistry. *In:* WYMAN, D.A. (ed.) *Trace Element Geochemistry of Volcanic Rocks: Applications for Massive Sulfide Exploration*. Geological Association of Canada, Short Course Notes, **12**, 51–77, St. John's, NL, Canada.

KELLER, R.A., FISK, M.R., SMELLIE, J.L., STRELIN, J.A. & LAWVER, L.A. 2002. Geochemistry of back arc basin volcanism in Bransfield Strait, Antarctica; subducted contributions and along-axis variations. *Journal of Geophysical Research*, **107**, 17.

KEMP, A.I.S. 2003. Plutonic boninite-like rocks in an anatectic setting; tectonic implications for the Delamerian Orogen in southeastern Australia. *Geology*, **31**, 371–374.

KEPEZHINSKAS, P., MCDERMOTT, F. *et al.* 1997. Trace element and Sr–Nb–Pb isotopic constraints on a three-component model of Kamchatka Arc petrogenesis. *Geochemica et Cosmochimica Acta*, **61**, 577–600.

KERRICH, R. & WYMAN, D.A. 1997. Review of developments in trace-element fingerprinting of geodynamic settings and their implications for mineral exploration. *Australian Journal of Earth Sciences*, **44**, 465–487.

KERRICH, R., WYMAN, D.A., FAN, J. & BLEEKER, W. 1998. Boninite series; low Ti-tholeiite associations from the 2.7 Ga Abitibi greenstone belt. *Earth and Planetary Science Letters*, **164**, 303–316.

KRANIDIOTIS, P. & MacLEAN, W.H. 1987. Systematics of chlorite alteration at the Phelps Dodge massive sulfide deposit, Matagami, Quebec. *Economic Geology*, **82**, 1898–1911.

LAFLECHE, M.R., DUPUY, C. & BOUGAULT, H. 1992*a*. Geochemistry and petrogenesis of Archean mafic volcanic rocks of the southern Abitibi Belt, Quebec. *Precambrian Research*, **57**, 3–4.

LAFLECHE, M.R., DUPUY, C. & DOSTAL, J. 1992*b*. Tholeiitic volcanic rocks of the Late Archean Blake River Group, southern Abitibi greenstone belt: origin and geodynamic implications. *Canadian Journal of Earth Sciences*, **29**, 1448–1458.

LANGMUIR, C.H., KLEIN, E.M. & PLANK, T. 1992. Petrological systematics of mid-ocean ridge basalts: Constraints on melt generation beneath ocean ridges. *In:* MORGAN, J.P., BLACKMAN, D.K. & SINTON, J.M. (eds) *Mantle Flow and Melt Generation at Mid-Ocean Ridges*. American Geophysical Union, **71**, 183–280, Washington, DC, USA.

LAPIERRE, H., ALBAREDE, F., ALBERS, J., CABANIS, B. & COULON, C. 1985. Early Devonian volcanism in the eastern Klamath Mountains, California; evidence for an immature island arc. *Canadian Journal of Earth Sciences*, **22**, 214–227.

LARGE, R.R., DOYLE, M., RAYMOND, O., COOKE, D., JONES, A. & HEASMAN, L. 1996. Evaluation of the role of Cambrian granites in the genesis of world class VHMS deposits in Tasmania. *Ore Geology Reviews*, **10**, 215–230.

LEAT, P.T., JACKSON, S.E., THORPE, R.S. & STILLMAN, C.J. 1986. Geochemistry of bimodal basalt-subalkaline/peralkaline rhyolite provinces within the southern British Caledonides. *Journal of the Geological Society*, **143**, 259–273.

LENTZ, D.R. 1998. Petrogenetic evolution of felsic volcanic sequences associated with Phanerozoic volcanic-hosted massive sulfide systems: the role of extensional geodynamics. *Ore Geology Reviews*, **12**, 289–327.

LENTZ, D.R. 1999. Petrology, geochemistry and oxygen isotopic interpretation of felsic volcanic and related rocks hosting the Brunswick 6 and 12 massive sulfide deposits (Brunswick Belt), Bathurst Mining Camp, New Brunswick, Canada. *Economic Geology*, **94**, 57–86.

LESHER, C.M., GIBSON, H.L. & CAMPBELL, I.H. 1986*a*. Composition-volume changes during hydrothermal alteration of andesite at Buttercup Hill, Noranda District, Quebec. *Geochimica et Cosmochimica Acta*, **50**, 2693–2705.

LESHER, C.M., GOODWIN, A.M., CAMPBELL, I.H. & GORTON, M.P. 1986*b*. Trace element geochemistry of ore-associated and barren felsic metavolcanic rocks in the Superior province, Canada. *Canadian Journal of Earth Sciences*, **23**, 222–237.

MACLEAN, W.H. 1988. Rare earth element mobility at constant inter-REE ratios in the alteration zone at the Phelps Dodge massive sulphide deposit, Matagami, Quebec. *Mineralium Deposita*, **23**, 231–238.

MACLEAN, W.H. & KRANIDIOTIS, P. 1987. Immobile elements as monitors of mass transfer in hydrothermal alteration; Phelps Dodge massive sulfide deposit, Matagami, Quebec. *Economic Geology*, **82**, 951–962.

MCCONNELL, B.J., STILLMAN, C.J. & HERTOGEN, J. 1991. An Ordovician basalt to peralkaline rhyolite fractionation series from Avoca, Ireland. *Journal of the Geological Society*, **148**, 711–718.

MCKENZIE, D. & BICKLE, M.J. 1988. The volume and composition of melt generated by extension of the lithosphere. *Journal of Petrology*, **29**, 625–679.

MCKENZIE, D. & O'NIONS, R.K. 1991. Partial melt distributions from inversion of rare earth element concentrations. *Journal of Petrology*, **32**, 1021–1091.

MCPHIE, J. & ALLEN, R.L. 1992. Facies architecture of mineralised submarine volcanic sequences: Cambrian Mount Read Volcanics, western Tasmania. *Economic Geology*, **87**, 587–596.

MEFFRE, S., AITCHISON, J.C. & CRAWFORD, A.J. 1996. Geochemical evolution and tectonic significance of boninites and tholeiites from the Koh ophiolite, New Caledonia. *Tectonics*, **15**, 67–83.

MITJAVILA, J.M., MARTI, J. & SORIANO, C. 1997. Magmatic evolution and tectonic setting of the Iberian pyrite belt volcanism. *Journal of Petrology*, **38**, 727–755.

MORTENSEN, J.K. & GODWIN, C.I. 1982. Volcanogenic massive sulfide deposits associated with highly alkaline rift volcanics in the southeastern Yukon Territory. *Economic Geology*, **77**, 1225–1230.

PARADIS, S., LUDDEN, J.N. & GELINAS, L. 1988. Evidence for contrasting compositional spectra in comagmatic intrusive and extrusive rocks of the late Archean Blake River Group, Abitibi, Quebec. *Canadian Journal of Earth Sciences*, **25**, 134–144.

PEARCE, J.A., HARRIS, N.B.W. & TINDLE, A.G. 1984. Trace element discrimination diagrams for the tectonic interpretation of granitic rocks. *Journal of Petrology*, **25**, 956–983.

PEARCE, J.A., VAN DER LAAN, S.R. *et al.* 1992. Boninite and harzburgite from Leg 125 (Bonin-Mariana forearc); a case study of magma genesis during the initial stages of subduction, *Proceedings of the Ocean Drilling Program, Scientific Results*, **125**, 623–659.

PÉLOQUIN, A.S. 1999. *Reappraisal of the Blake River Group stratigraphy and its place in the Archean volcanic record*. PhD Thesis, Université de Montréal, Canada.

PETCH, C.A. 2004. The Geology and Mineralization of the High Lake Volcanic-hosted Massive Sulfide Deposit, Nunavut. *Exploration and Mining Geology*, **13**, 37–47, Socorro, NM, USA.

PETER, J.M. & SCOTT, S.D. 1999. Windy Craggy, northwestern British Columbia; the world's largest besshi-type deposit. *In:* BARRIE, C.T. & HANNINGTON, M.D. (eds) *Volcanic-associated massive sulfide deposits; processes and examples in modern and ancient settings.* Society of Economic Geologists, Reviews in Economic Geology, **8**, 261–295.

PETERSEN, S., HERZIG, P.M., SCHWARZ-SCHAMPERA, U., HANNINGTON, M.D. & JONASSON, I.R. 2004. Hydrothermal precipitates associated with bimodal volcanism in the central Bransfield Strait, Antarctica. *Mineralium Deposita*, **39**, 358–379.

PIERCEY, S.J. 2007. An overview of the use of petrochemistry in the regional exploration for volcanogenic massive sulfide (VMS) deposits. *In:* MILKEREIT, B. (ed.) *Proceedings of Exploration 07: Fifth Decennial International Conference on Mineral Exploration*. Toronto, ON, 223–246, X–CD Technologies.

PIERCEY, S.J., JENNER, G.A. & WILTON, D.H.C. 1997. The stratigraphy and geochemistry of the southern Pacquet Harbour Group, Baie Verte Peninsula, Newfoundland; implications for mineral exploration. *In:* PEREIRA, C.P.G. & WALSH, D.G. (eds) *Current Research*. Newfoundland and Labrador Department of Mines and Energy, 119–139.

PIERCEY, S.J., MURPHY, D.C., MORTENSEN, J.K. & PARADIS, S. 2001*a*. Boninitic magmatism in a continental margin setting, Yukon-Tanana Terrane, southeastern Yukon, Canada. *Geology*, **29**, 731–734.

PIERCEY, S.J., PARADIS, S., MURPHY, D.C. & MORTENSEN, J.K. 2001*b*. Geochemistry and paleotectonic setting of felsic volcanic rocks in the Finlayson Lake volcanic-hosted massive sulfide (VHMS) district, Yukon, Canada. *Economic Geology*, **96**, 1877–1905.

PIERCEY, S.J., MURPHY, D.C., MORTENSEN, J.K., PARADIS, S. & CREASER, R.A. 2002*a*. Geochemistry and tectonic significance of alkalic mafic magmatism in the Yukon-Tanana Terrane, Finlayson Lake Region, Yukon. *Canadian Journal of Earth Sciences*, **39**, 1729–1744.

PIERCEY, S.J., PARADIS, S., PETER, J.M. & TUCKER, T.L. (eds) 2002*b*. Geochemistry of basalt from the Wolverine volcanic-hosted massive-sulphide deposit, Finlayson Lake district, Yukon Territory. *Current Research 2002-A3*. Geological Survey of Canada, 1–11.

PIERCEY, S.J., MURPHY, D.C., MORTENSEN, J.K. & CREASER, R.A. 2004. Mid-Paleozoic initiation of the northern Cordilleran marginal back-arc basin: Geological, geochemical and neodymium isotopic evidence from the oldest mafic magmatic rocks in Yukon-Tanana terrane, Finlayson Lake district, southeast Yukon, Canada. *Geological Society of America Bulletin*, **116**, 1087–1106.

PIERCEY, S.J., PETER, J.M., MORTENSEN, J.K., PARADIS, S., MURPHY, D.C. & TUCKER, T.L. 2008. Petrology and U-Pb geochronology of footwall porphyritic rhyolites from the Wolverine volcanogenic massive sulfide deposit, Yukon, Canada: Implications for the genesis of massive sulfide deposits in continental margin environments. *Economic Geology*, **103**, 5–33.

PRIOR, G.J., GIBSON, H.L., WATKINSON, D.H., COOK, R.E. & HANNINGTON, M.D. 1999. Rare earth and high field strength element geochemistry of the Kidd Creek rhyolites, Abitibi greenstone belt, Canada: Evidence for Archean felsic volcanism and volcanogenic massive sulfide ore formation in an Iceland-style rift environment. *In:* HANNINGTON, M.D. & BARRIE, C.T. (eds) *The Giant Kidd Creek Volcanogenic Massive Sulfide Deposit, Western Abitibi Subprovince, Canada.* Society of Economic Geologists, Littleton, CO, Economic Geology Monograph 10, 457–483.

RHODES, J.M., MORGAN, C. & LIIAS, R.A. 1990. Geochemistry of Axial Seamount lavas; magmatic relationship between the Cobb hotspot and the Juan de Fuca Ridge. *Journal of Geophysical Research*, **95**, 12,713–712,733.

ROGERS, N. & VAN STAAL, C.R. 2003. Volcanology and tectonic setting of the northern Bathurst mining camp; Part II, Mafic volcanic constraints on back-arc opening. *In:* GOODFELLOW, W.D., MCCUTCHEON, S.R. & PETER, J.M. (eds) *Massive Sulfide Deposits of the Bathurst Mining Camp, New Brunswick, and Northern Main.* Society of Economic Geologists, Economic Geology Monograph, **11**, 181–201, Lancaster, PA, USA.

ROGERS, N., VAN STAAL, C.R. & THERIAULT, R. 2003. Volcanology and tectonic setting of the northern Bathurst mining camp; Part 1, Extension and rifting of the Popelogan Arc, *In:* GOODFELLOW, W.D., MCCUTCHEON, S.R. & PETER, J.M. (eds) *Massive Sulfide Deposits of the Bathurst Mining Camp, New Brunswick, and Northern Main.* Society of Economic Geologists, Economic Geology Monograph, **11**, 157–179, Lancaster, PA, USA.

ROGERS, N.W., MACLEOD, C.J. & MURTON, B.J. 1989. Petrogenesis of boninitic lavas from the Limassol Forest Complex, Cyprus, *In:* CRAWFORD, A.J. (ed.) *Boninites*. Unwin Hyman, London, United Kingdom, 288–311.

SAEKI, Y. & DATE, J. 1980. Computer application to the alteration data of the footwall dacite lava at the Ezuri Kuroko deposits, Akito Prefecture. *Mining Geology*, **30**, 241–250.

SAUNDERS, A.D., FORNARI, D.J., JORON, J.-L., TARNEY, J. & TREUIL, M. 1982. Geochemistry of basic igneous rocks, Gulf of California, Deep Sea Drilling Project Leg 64. *Initial Reports of the Deep Sea Drilling Project*, **64**, 595–642.

SCOTT, S.D. 1997. Submarine hydrothermal systems and deposits. *In:* BARNES, H.L. (ed.) *Geochemistry of Hydrothermal Ore Deposits*, 3rd Edition. John Wiley and Sons Ltd, New York, 797–875.

SEBERT, C. & BARRETT, T.J. 1996. Stratigraphy, alteration, and mineralization at the Tulsequah chief massive sulfide deposit, northwestern British Columbia. *Exploration and Mining Geology*, **5**, 281–308.

SETTERFIELD, T.N., HODDER, R.W., GIBSON, H.L. & WATKINS, J.J. 1995. The McDougall-Despina fault set, Noranda, Quebec; evidence for fault-controlled volcanism and hydrothermal fluid flow. *Exploration and Mining Geology*, **4**, 381–393.

SHERVAIS, J.W. 1982. Ti-V plots and the petrogenesis of modern and ophiolitic lavas. *Earth and Planetary Science Letters*, **59**, 101–118.

SHINJO, R. & KATO, Y. 2000. Geochemical constraints on the origin of bimodal magmatism at the Okinawa Trough, an incipient back-arc basin. *Lithos*, **54**, 117–137.

SHINJO, R., CHUNG, S.-L., KATO, Y. & KIMURA, M. 1999. Geochemical and Sr-Nd isotopic characteristics of volcanic rocks from the Okinawa Trough and Ryukyu Arc; implications for the evolution of a young, intracontinental back arc basin. *Journal of Geophysical Research*, **104**, 591–610.

SHUKUNO, H., TAMURA, Y., TANI, K., CHANG, Q., SUZUKI, T. & FISKE, R.S. 2006. Origin of silicic magmas and the compositional gap at Sumisu submarine caldera, Izu-Bonin arc, Japan. *Journal of Volcanology and Geothermal Research*, **156**, 187–216.

SINTON, J.M., FORD, L.L., CHAPPELL, B. & MCCULLOCH, M.T. 2003. Magma Genesis and Mantle Heterogeneity in the Manus Back-Arc Basin, Papua New Guinea. *Journal of Petrology*, **44**, 159–195.

SMITH, S.E. & HUMPHRIS, S.E. 1998. Geochemistry of basaltic rocks from the TAG hydrothermal mound (26 degrees 08'), Mid-Atlantic Ridge. *Proceedings of the Ocean Drilling Program, Scientific Results*, **158**, 213–229.

SPITZ, G. & DARLING, R. 1978. Major and minor element lithogeochemical anomalies surrounding the Louvem copper deposit, Val d'Or, Quebec. *Canadian Journal of Earth Sciences*, **15**, 1161–1169.

STAKES, D.S. & FRANKLIN, J.M. 1994. Petrology of igneous rocks at Middle Valley, Juan de Fuca Ridge. *Proceedings of the Ocean Drilling Program, Scientific Results*, **139**, 79–102.

STERN, R.A., SYME, E.C., BAILES, A.H. & LUCAS, S.B. 1995. Paleoproterozoic (1.90-1.86 Ga) arc volcanism in the Flin Flon Belt, Trans-Hudson Orogen, Canada. *Contributions to Mineralogy and Petrology*, **119**, 117–141.

STERN, R.J. & BLOOMER, S.H. 1992. Subduction zone infancy; examples from the Eocene Izu-Bonin-Mariana and Jurassic California arcs. *Geological Society of America Bulletin*, **104**, 1621–1636.

STIX, J., KENNEDY, B. *et al.* 2003. Caldera-forming processes and the origin of submarine volcanogenic massive sulfide deposits. *Geology*, **31**, 375–378.

STOLZ, A.J. 1995. Geochemistry of the Mount Windsor Volcanics; implications for the tectonic setting of Cambro-Ordovician volcanic-hosted massive sulfide mineralization in northeastern Australia. *Economic Geology*, **90**, 1080–1097.

STOLTZ, A.J., VARNE, R., DAVIES, G.R., WHELLER, G.E. & FODEN, J.D. 1990. Magma source components in an arc-continent collision zone: The Flores-Lembata sector, Sunda Arc, Indonesia. *Contributions to Mineralogy and Petrology*, **105**, 585–601.

SUN, S.-S. & MCDONOUGH, W.F. 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *In:* SAUNDERS, A.D. & NORRY, M.J. (eds) *Magmatism in the Ocean Basins*. Geological Society, London, Special Publication, **42**, 313–345.

SWINDEN, H.S. 1991. Paleotectonic settings of volcanogenic massive sulphide deposits in the Dunnage Zone, Newfoundland Appalachians. *Canadian Institute of Mining and Metallurgy Bulletin*, **84**, 59–89.

SWINDEN, H.S. 1996. The application of volcanic geochemistry in the metallogeny of volcanic-hosted sulphide deposits in central Newfoundland. *In:* WYMAN, D.A. (ed.) *Trace Element Geochemistry of Volcanic Rocks: Applications for Massive Sulfide Exploration*. Geological Association of Canada, Short Course Notes, **12**, 329–358, St. John's, NL, Canada.

SWINDEN, H.S., JENNER, G.A., KEAN, B.F. & EVANS, D.T.W. 1989. Volcanic rock geochemistry as a guide for massive sulphide exploration in central Newfoundland. *In:* PEREIRA, C.P.G., WALSH, D.G. & BLACKWOOD, R.F. (eds) *Current Research*. Newfoundland Department of Mines, Report 89-1, 201–219.

SYME, E.C. 1998. *Ore-associated and barren rhyolites in the central Flin Flon Belt: case study of the Flin Flon Mine sequence*. Manitoba Energy and Mines Open File Report OF98-9, 26

SYME, E.C. & BAILES, A.H. 1993. Stratigraphic and tectonic setting of early Proterozoic volcanogenic massive sulfide deposits, Flin Flon, Manitoba. *Economic Geology*, **88**, 566–589.

SYME, E.C., LUCAS, S.B., BAILES, A.H. & STERN, R.A. 1999. Contrasting arc and MORB-like assemblages in the Paleoproterozoic Flin Flon Belt, Manitoba, and the role of intra-arc extension in localizing volcanic-hosted massive sulphide deposits. *Canadian Journal of Earth Sciences*, **36**, 1767–1788.

VALSAMI, E. & CANN, J.R. 1992. Mobility of rare earth elements in zones of intense hydrothermal alteration in the Pindos ophiolite, Greece. *In:* PARSON, L.M., MURTON, B.J. & BROWNING, P. (eds) *Ophiolites and their Modern Oceanic Analogues*. Geological Society, London, Special Publication, **60**, 219–232.

VAN DER LAAN, S.R., ARCULUS, R.J., PEARCE, J.A. & MURTON, B.J. 1992. Petrography, mineral chemistry, and phase relations of the basement boninite series of Site 786, Izu-Bonin forearc. *Proceedings of the Ocean Drilling Program, Scientific Results*, **125**, 171–201.

VAN STAAL, C.R., WINCHESTER, J.A. & BÉDARD, J.H. 1991. Geochemical variations in Middle Ordovician volcanic rocks of the northern Miramichi Highlands and their tectonic significance. *Canadian Journal of Earth Sciences*, **28**, 1031–1049.

VEARNCOMBE, S. & KERRICH, R. 1999. Geochemistry and geodynamic setting of volcanic and plutonic rocks associated with early Archaean volcanogenic massive sulphide mineralization, Pilbara Craton. *Precambrian Research*, **98**, 243–270.

WHITFORD, D.J., KORSCH, M.J., PORRITT, P.M. & CRAVEN, S.J. 1988. Rare-earth element mobility around the volcanogenic polymetallic massive sulfide deposit at Que River, Tasmania, Australia. *Chemical Geology*, **68**, 105–119.

WYMAN, D.A., BLEEKER, W. & KERRICH, R. 1999. A 2 7 Ga komatiite, low Ti tholeiite, arc tholeiite transition, and inferred proto-arc geodynamic setting of the Kidd Creek Deposit; evidence from precise trace element data. *In:* HANNINGTON, M.D. & BARRIE, C.T. (eds) *The Giant Kidd Creek Volcanogenic Massive Sulfide Deposit, Western Abitibi Subprovince, Canada*. Society of Economic Geologists, Littleton, CO, Economic Geology Monograph **10**, 511–528.