Zn-rich Volcanogenic Massive Sulphide (VMS) Deposits

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Abstract

Base metal-dominated volcanogenic massive sulfide (VMS) deposits are important global resources of zinc (Zn) with many deposits having Zn as the main commodity of production. VMS deposits can be classified into Zn-rich, zinciferous, and Zn-anomalous based on global geological resource data. Zinc-rich deposits have Zn >6.1 wt% (geometric mean + one standard deviation) and >1.27 Mt of contained Zn (>90th percentile). Deposits that are high-grade (Zn >6.1 wt%) but have <1.27 Mt are termed zinciferous, whereas deposits that have high tonnages and >1.27 Mt of contained Zn, but low-grades (Zn <6.1 wt%) are referred to as Zn-anomalous deposits. Collectively, these deposits with abundant Zn are termed Zn-enriched deposits.

Most zinc-enriched deposits are VMS sub-types that are associated with felsic volcanic and/or sedimentary rocks (i.e., bimodal felsic, bimodal mafic, and felsic siliciclastic sub-types). Most Zn-enriched deposits are hosted in Phanerozoic sequences, but there are a numerous of Zn-rich, zinciferous, and Zn-anomalous deposits in Archean and Paleoproterozoic rocks. Furthermore, throughout Earth's history Zn-enriched VMS deposits show a distinct secular evolution, with peaks in total contained Zn in the late Archean (~2.7 Ga), Paleoproterozoic (~1.9-1.8 Ga), Cambrian-Ordovician (~510-460 Ma), and Devonian-Mississippian (~390-355 Ma), with subsidiary peaks in the Mesoarchean (~3.0 Ga), Neoproterozoic (~0.75 Ga), Mesozoic (~220-200 Ma), and Cenozoic (~110-90 Ma).

The secular distribution of Zn-enriched, and VMS deposits in general, is directly related to accretionary orogenesis and crustal growth processes. In the Precambrian, the abundance of Zn-rich VMS deposits is attributable to crust-forming events, juvenile crustal growth, and supercontinent formation, particularly in the late Archean and the Paleoproterozoic. Phanerozoic Zn-enriched VMS deposits, although associated with accretionary activity, are not directly associated with the terminal phases of supercontinent formation, and commonly formed a significant period of time (i.e., commonly >100 m.y.) prior to final supercontinent amalgamation, suggesting that other processes were more important in controlling their temporal distribution. Despite associations with accretionary orogenesis, both Precambrian and Phanerozoic Zn-enriched VMS deposits are associated with extensional geodynamic regimes (e.g., mid-ocean ridges, arc rifts, and back-arc basins).

Other factors that were favorable for the formation and siting of Zn-enriched VMS deposits include: 1) sedimentary rocks in the host stratigraphic succession and anoxic basinal conditions, and 2) semi-permeable cap rocks. Sedimentary rocks deposited during reduced marine conditions (i.e., anoxic sediments at the time of VMS formation) can have limited the amount of reduced sulphur in the hydrothermal fluids, and pore waters in the sediment can have added chloride, both of which increased the solubility of metals transported in the hydrothermal fluid. More importantly, sedimentary host rock enhanced the preservation of VMS deposits, and the formation of large Zn-enriched deposits because they favoured subseafloor replacement-style VMS mineralizing processes. Marine basinal anoxic conditions were important for the formation of some Phanerozoic VMS deposits (particularly felsic siliciclastic-types). Anoxic ambient conditions (either local or large-scale) resulted in a stratified water column with H_2S-rich bottom waters that prevented the oxidative weathering of VMS deposits, and also provided additional reduced sulphur to fix metals discharged from hydrothermal vents. The additional H_2S present in the water column may have allowed for the more efficient trapping of metals and the formation of larger tonnage Zn-rich VMS deposits (e.g., Brunswick Number 12, New Brunswick, Canada). The additional reducing conditions also likely prevented the oxidation of deposits, thereby increasing their preservation potential in the geological record. Cap rocks (e.g., barite, chert, carbonate, semi-permeable tuff, shales) that immediately overlie mineralization were critical for having increased the efficiency of zone-refining processes and resulted in abundant Zn-Pb dissolution, re-precipitation and upgrading of Zn grades in deposits leading to high-grade Zn-rich and zinciferous VMS deposits.

Various lines of evidence (e.g., fluid inclusions, metal assemblages, mass balance constraints) suggest that magmatic fluid and metal contributions may have been be important in large (e.g., Kidd Creek, Ontario, Canada; Brunswick Number 12, New Brunswick, Canada; Neves Corvo, Portugal) and/or high-grade Zn-rich deposits (e.g., Buchans, Newfoundland, Hellyer, Tasmania, Australia). None of the evidence uniquely suggests that magmatism contributes Zn to these deposits; however, given their size and/or grade it is conceivable that significant Zn may be derived from magmatic fluids. This question should be at the forefront of research on Zn budgets in VMS deposits in the near future.

Introduction

Volcanogenic massive sulphide (VMS) deposits are comprised of massive (>80 volume percent) sulphide lenses that are commonly polymetallic (e.g., Zn-Pb-Cu-Au-Ag) and formed at or near the seafloor from metal-bearing hydrothermal fluids that circulated in the subsurface (Franklin et al., 1981a; Lydon, 1984, 1988; Large, 1992; Franklin et al., 2005; Galley et al., 2007b). These deposits are commonly hosted by volcanic, volcano-sedimentary, and sedimentary rocks, and are also termed volcanic-hosted massive sulphide (VHMS), volcanic-associated massive sulphide (VAMS), and volcanic-sedimentary-hosted massive sulphide deposits (VSMS)(e.g., Large, 1992; Barrie and Hannington, 1999; Galley et al., 2007b). Volcanogenic massive sulphide deposits are important sources of base (Cu, Zn, Pb) and precious metals (Au, Ag), as well as other by-product metals (e.g., Co, Sn, Se, Mn, Cd, In, Bi, Te, Ga, Ge, As, Sb, and Hg); historically they have contributed about 22% to global Zn production (Singer, 1995; Galley et al., 2007b).

Volcanogenic massive sulphide deposits occur in rocks from Archean to present, and have been discovered on every continent except Antarctica (e.g., Franklin et al., 1981b; Lydon, 1984, 1988; Large, 1992; Allen et al., 1996a; Allen et al., 1996b; Ohmoto, 1996; Saez et al., 1996; Large et al., 2001; Franklin et al., 2005; Tornos, 2006; Galley et al., 2007b). Additionally, VMS deposits are one of the only ore deposit types for which there are good modern analogues, as seafloor massive sulphide deposits (SMS) occur in many settings on the modern seafloor

(e.g., Von Damm, 1990; Humphris et al., 1995; Herzig and Hannington, 1996; Scott, 1997; Hannington et al., 2005), and information from their study has resulted in VMS deposits becoming one of the best understood ore deposit types.

Herein we provide an overview of the current state of knowledge of VMS deposits and their classification, with particular emphasis on Zn-enriched deposits. We examine the relationship between grade and tonnage of Zn in VMS deposits and define what constitutes a Zn-enriched deposit, evaluate this as a function of VMS deposit type and age, and elucidate the controls on their genesis and siting. The content is tempered by our familiarity with certain deposits and districts, but we draw on the large body of work in the literature, as well as material from other manuscripts in this volume (e.g., Boyce et al., this volume; Huston et al., this volume).

Volcanogenic Massive Sulphide Deposits

There have been several exhaustive reviews of the genesis of VMS deposits (Hutchinson, 1973; Sato, 1973; Spooner and Fyfe, 1973; Large, 1977; Spooner, 1977; Solomon and Walshe, 1979; Franklin et al., 1981a; Ohmoto and Skinner, 1983; Huston and Large, 1987; Lydon, 1988; Galley, 1993; Ohmoto, 1996; Huston et al., 2001; Franklin et al., 2005; Hannington et al., 2005). Volcanogenic massive sulphide deposits form from submarine, seawater convection systems driven by magmatic heat (e.g., subvolcanic intrusions; Fig. 1), with or without a magmatic fluid contribution (e.g., Spooner and Fyfe, 1973; Spoon-
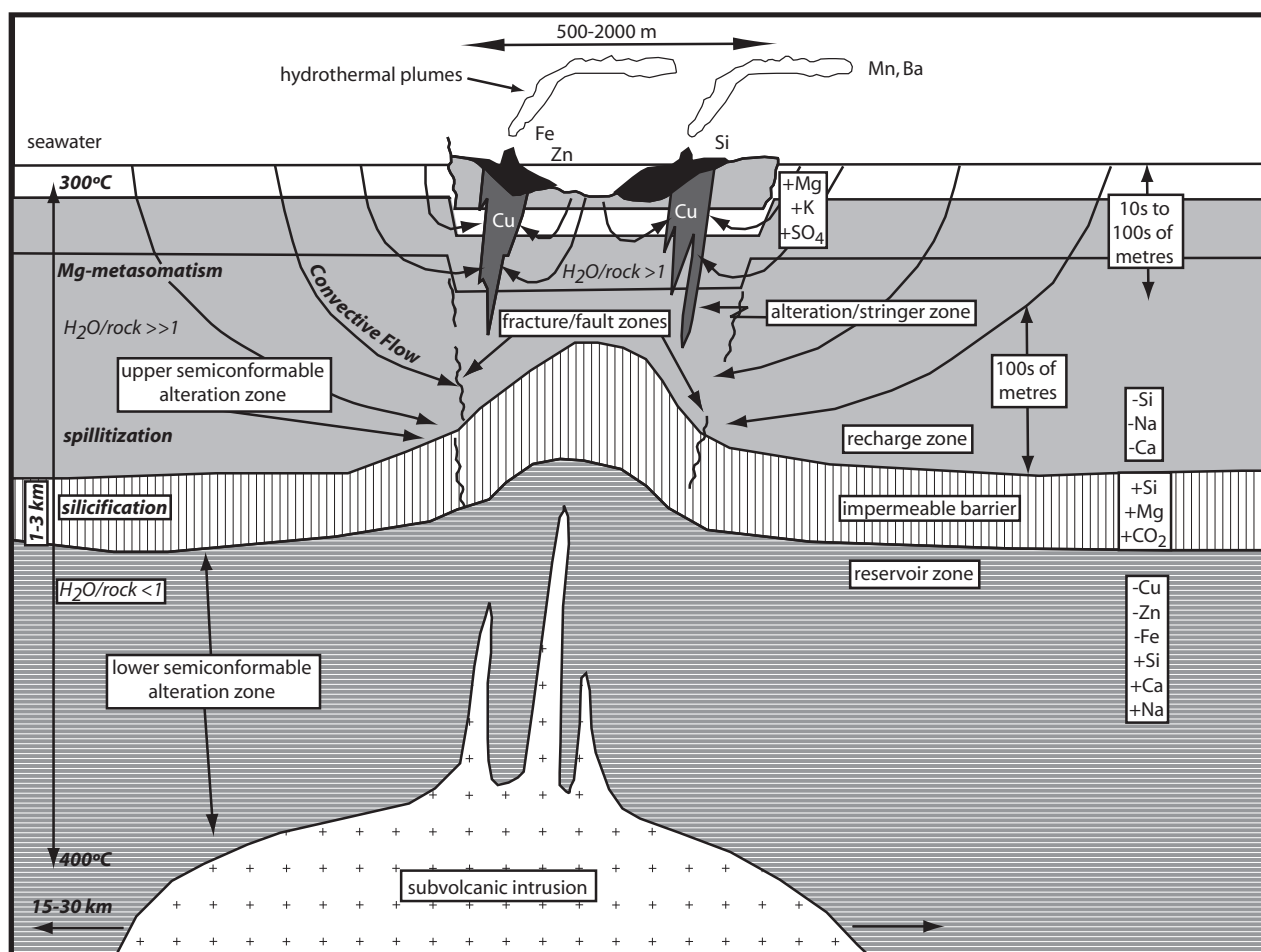

Figure 1. Schematic cross-sectional model of the architecture and genesis of volcanogenic massive sulphide deposits. + and – for given elements represent elements gained or lost during fluid-rock interaction. From Galley (1993) and Franklin et al. (2005).

Table 1. Classification of base metal-rich VMS deposits. Modified from Barrie and Hannington (1999), Franklin et al. (2005), and Galley et al. (2007). Tectonic environments also from Piercey (2011).

VMS Sub-Type	Rock Types	Ore Hosts	Metals	Tectonic Envrionments of Formation	Equivalent Alternative Classification	Examples
Mafic	Mafic volcanic and intrusive rocks, with or without ultramafic Commonly ophiolite environments.	Mafic extrusive and intrusive rocks. Rare in ultramafic rocks.	Cu-Zn	Back-arc, forearc, and mid-ocean ridge.	Cyprus-type. Cu-rich.	Deposits in Cyprus, Oman, Appalachian Ophiolites (e.g., Little Deer, Tilt Cove, Bay of Islands).
Mafic Siliciclastic	Mafic volcanic with mafic and ultramafic intrusive rocks and abundant siliciclastic sedimentary rocks.	Mafic volcanic and/or mafic/ultramafic intrusive rocks.	Cu-(Co-Zn-Ni)	Sedimented back-arc and forearc environments. Sedimented ridges.	Besshi-type. Cu-(Co)-rich. Outokumpu-type. Pelitic mafic.	Deposits in Besshi district, Japan, Windy Craggy, Outokumpu.
Bimodal Mafic	Bimodal sequences with mafic rocks>>felsic rocks.	Felsic volcanic rocks>>mafic rocks.	Cu-Zn-Pb-(Au-Ag)	Rifted primitive arcs +/- back-arc (MORB-rich) and forearc (boninite-rich).	Noranda-type. Cu-Zn-Pb.	Deposits in the Noranda and Flin Flon-Snow Lake districts; some deposits in mid and south Urals
Bimodal Felsic	Bimodal sequences with felsic>mafic. rocks.	Felsic volcanic rocks.	Zn-Pb-Cu-(Au-Ag)	Rifted continental arcs.	Kuroko-type Zn-Pb-Cu-type.	Deposits in Kuroko district, Mount Read Belt, Skellefte district, Bergslagen district.
Felsic Siliciclastic	Bimodal sequences with felsic volcanic+volcaniclastic+sedimentary rocks>mafic rocks. Abundant graphitic sedimentary rocks and iron formation.	Felsic volcanic and volcaniclastic rocks and sedimentary rocks.	Zn-Pb-Cu-(Ag-Au)	Sedimented continental rifts/continental arc rifts/back-arcs.	Bathurst-type. Iberian Pyrite Belt-type. Zn-Pb-Cu-type.	Deposits in the Bathurst district and Iberian Pyrite Belt.

er, 1977; Cathles, 1983; Galley, 1993; Skirrow and Franklin, 1994; Yang and Scott, 1996; Cathles et al., 1997; Barrie et al., 1999; Hannington et al., 1999b; de Ronde et al., 2005; Franklin et al., 2005; de Ronde et al., 2011). The fluids that form VMS are modified seawater (+/-magmatic fluids), whereas metals are leached from basement rocks (e.g., Seyfried and Bischoff, 1977; Spooner, 1977; Bischoff and Seyfried, 1978; Seyfried and Bischoff, 1981; Galley, 1993; Skirrow and Franklin, 1994; Franklin et al., 2005), with or without a contribution from magmas (e.g., Stanton, 1991, 1994; Yang and Scott, 1996; Hannington et al., 1999b; de Ronde et al., 2005; de Ronde et al., 2011). Hydrothermal fluids emanate from vents and mix with seawater, resulting in the deposition of sulphides on the seafloor (exhalative) or in the shallow subseafloor (subseafloor replacement) (e.g., Sato, 1973; Solomon and Walshe, 1979; Franklin et al., 1981a; Lydon, 1988; Ohmoto, 1996; Franklin et al., 2005). The hydrothermal evolution of VMS systems is commonly diachronous and in some deposits results in zone refining and a well-developed metal zoning where the deposits have an outer Zn-Pb-(Ba-Au-Ag)-rich rim underlain by a more Cu-(Au)-rich core and both of these are underlain by a stringer zone (Large, 1977; Solomon and Walshe, 1979; Franklin et al., 1981b; Eldridge et al., 1983; Ohmoto et al., 1983; Lydon, 1984, 1988; Large, 1992; Ohmoto, 1996; Franklin et al., 2005; Schardt and

Large, 2009). Not all deposits, however, exhibit this well-developed zoning and some are predominantly Zn-Pb- or Cu-bearing, with or without precious metals (Franklin et al., 2005, and references therein).

The metal associations described above have been previously used to classify VMS deposits; however, although non-genetic, this type of classification does not consider the subtleties between deposit sub-type host rocks and tectonic environments of formation, and both of these can significantly impact the Zn-budgets of VMS deposits. The most widely accepted classification of VMS deposits considers lithostratigraphy, tectonic environment of formation, and metals contained within the deposits (Fig. 1; Table 1) (Barrie and Hannington, 1999; Franklin et al., 2005; Galley et al., 2007b).

Grade-Tonnage Data: Defining Zinc-Rich Deposits

There are over 800 significant (>200,000 tonnes) VMS deposits in the world (Franklin et al., 2005; Galley et al., 2007b; Huston et al., 2010), of which 650 have Zn reported as part of their resource. The database used herein is modified from Huston et
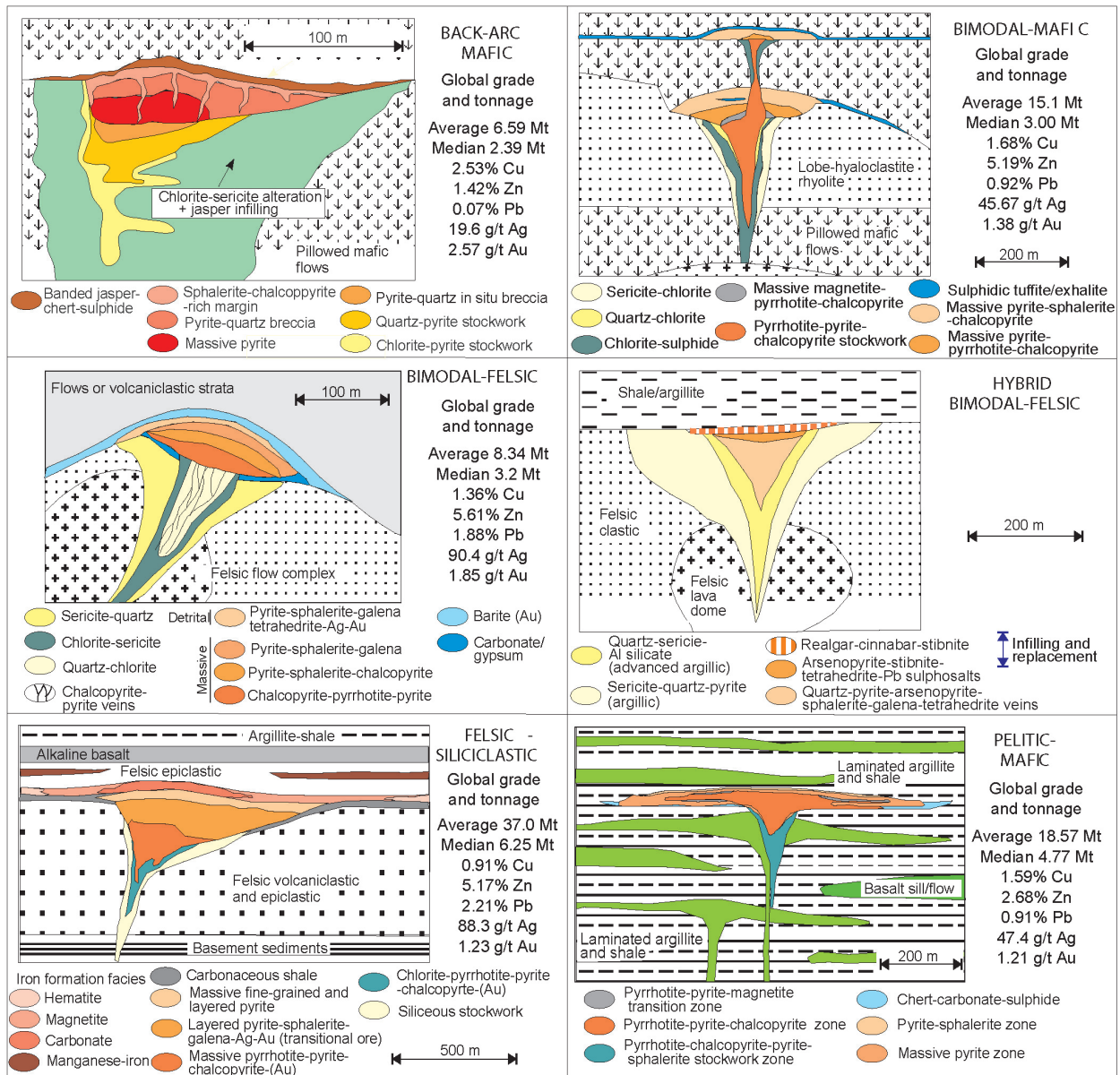
Figure 2. Schematic cross-sections of the various volcanogenic massive sulphide (VMS) deposit types depicting host rocks, hydrothermal alteration, and mineralization; from Galley et al. (2007b), after the classifications of Barrie and Hannington (1999) and Franklin et al. (2005). Also presented are the average and median tonnages, and average grades of different sub-types of VMS updated using the database of Franklin et al. (2005), as modified and updated by Galley et al. (2007b) and Huston et al. (2010).

al. (2010), which is an update of the Franklin et al. (2005) and Galley et al. (2007b) databases. The resource data are given as geological resources and include production, resources, and reserves, and in most cases these data are not National Instrument 43-101 or Joint Ore Reserves Committee (JORC) compliant, and do not necessarily reflect the economic contents of Zn in these deposits. There are limitations to using compiled data. For example, production data focus on specific commodities and if Zn is not the main commodity mined it may introduce bias in the dataset (e.g., lower Zn contents than are actually present geologically; Singer, 1995; Franklin et al., 2005; Galley et al., 2007b; Mercier-Langevin et al., 2011). Other factors such as metal recovery, head grades, and mining method can also affect the resource data, but in many cases are not accounted for in global databases (e.g., Singer, 1995; Franklin et al., 2005; Galley et al., 2007b; Mercier-Langevin et al., 2011).

The origin of Zn and its concentration in VMS deposits is well understood, and is generally thought to have occurred at low (<250°C) temperatures, commonly early in a deposit's history (Lydon, 1988; Large, 1992; Ohmoto, 1996; Franklin et al., 2005). Zinc is commonly associated with Pb in VMS deposits (Fig. 3a), but has a very poor correlation with Cu (Fig. 3b), as Cu only mobilized at higher (>300°C) temperatures (Barton and Bethke, 1987; Eldridge et al., 1988), typically in the later stages of deposit formation, through partial to complete dissolution of previously formed Zn-Pb mineralization and replacement by Cu-bearing minerals (Eldridge et al., 1983; Lydon, 1988; Large, 1992; Ohmoto, 1996). Many Zn-(Pb)-bearing VMS deposits have moderate to high Ag grades; however, this relationship is not universal and there are many deposits with abundant Zn but little to no Ag (Fig. 3c). There is poor to no correlation between Zn and Au grades (Fig. 3d).

The distribution of Zn grades in VMS deposits, shown in Figure 4a, displays strong negative skewing towards low values (i.e., negatively skewed) with ~45 % of the deposits with <4.5 wt% Zn, the average Zn grade for VMS in the database. The skewed nature of the data is typical of mineral resource data (Sangster, 1977; Sangster, 1980; Singer, 1995; Franklin et al., 2005; Mercier-Langevin et al., 2011), and is evidenced by the difference between the mean and median values (Fig. 4a). This indicates that the arithmetic mean and standard deviation are not the most appropriate [even inappropriate?] statistical measures to evaluate the data. In contrast, log transformed data show a distribution that is much closer to normal, with mean (geometric) of 2.67 wt% Zn and a standard (geometric) deviation of 3.41 wt% Zn. The log-normalized distribution (Fig. 4b) and the geometric mean are less sensitive to outliers and is more statistically representative of the entire database and is not skewed by a small number of high-grade deposits (Fig. 4a,b). The log-transformed data are also in broad agreement with cumulative probability plots; however, it is clear that there are multiple Zn grade populations within the dataset (Fig. 4c).

Contained Zn tonnages are also strongly (negatively) skewed by a few deposits with very high contained Zn. The average contained Zn is 0.47 Mt, but the median is 0.11 Mt, with a very high standard deviation (Fig. 5a). The log-transformed data have a near-normal distribution with a geometric mean of 0.11 Mt, similar to the median of the entire dataset, but with a very high geometric standard deviation of 6.61 Mt (Fig. 5b). The near-

normal distribution is evident in the cumulative probability plot, which shows only one inflection point (Fig. 5c).

To define Zn-rich VMS deposits we have employed an approach similar to that used by Mercier-Langevin et al. (2011) for Au-rich VMS deposits that considers both grade and the tonnage of contained Zn (Fig. 6). *Zinciferous* deposits have grades greater than the geometric mean plus one geometric standard deviation (Zn >6.1 wt%; Fig. 6). *Zn-anomalous* deposits have grades lower than this but have contained Zn greater than the 90th percentile (i.e., >1.27 Mt contained Zn). *Zn-rich* deposits have >6.1 wt% Zn and >1.27 Mt contained Zn (Fig. 6). For contained Zn we have chosen the 90th percentile because the geometric mean and geometric standard deviation are too restrictive, and only four deposits would be considered Zn-rich using this definition (Fig. 6). We use the term *Zn-enriched* for deposits that collectively are either Zn-rich, zinciferous, or Zn-anomalous.

Zn-rich, zinciferous and Zn-anomalous deposits are almost exclusively hosted by stratigraphy that contains a large proportion of felsic rocks (Figures 6-7). Zinc-rich VMS deposits are dominantly classified as bimodal felsic, felsic siliciclastic, and bimodal mafic, whereas zinciferous deposits are predominantly bimodal felsic, bimodal mafic, and bimodal siliciclastic. Zinc-anomalous deposits are mostly felsic siliciclastic, bimodal mafic, and bimodal felsic; mafic siliciclastic are relatively minor contributors to the three categories, and there are no significant
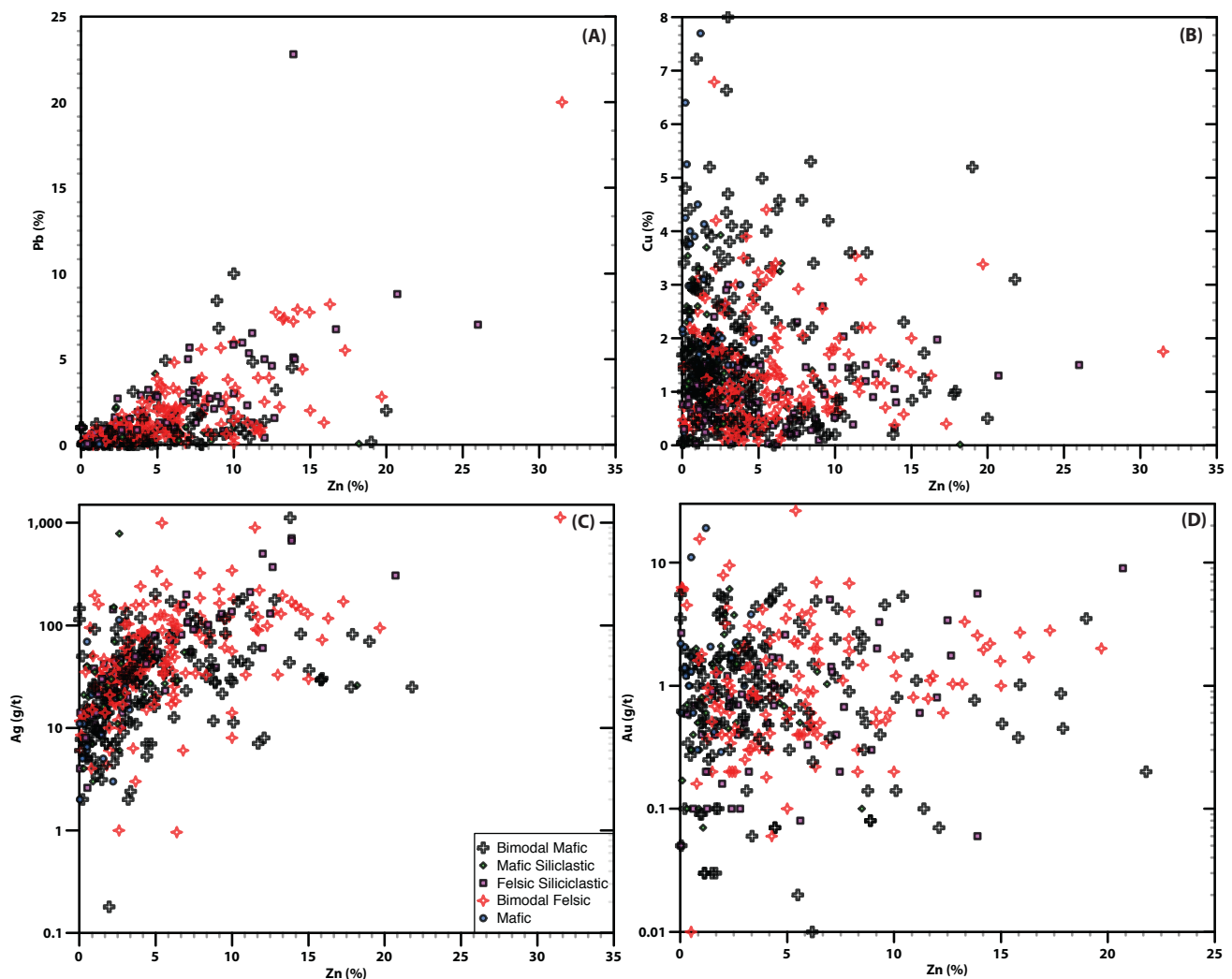

Figure 3. Bivariate plots of Zn grade versus other metals in VMS deposits: A. Pb; B. Cu; C. Ag; and D. Au.

mafic deposits in any of these categories (Figures 6-7). Figure 8 plots the secular distribution of the various categories of Zn-bearing deposits, and shows that the most Zn-rich, zinciferous and Zn-anomalous deposits were formed in the Phanerozoic era, followed by the Archean and Proterozoic.
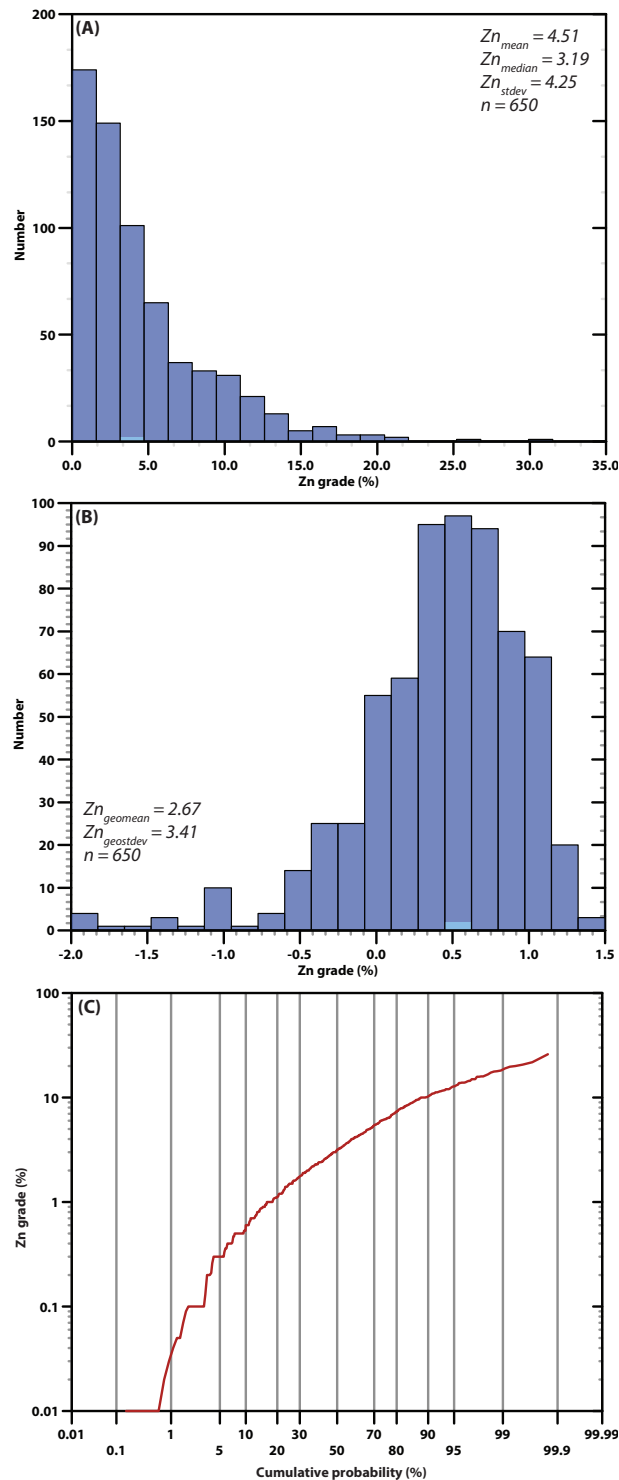
The secular distribution (and controls?) of contained Zn is further illustrated in Figures 8 and 9. Zinc-rich, zinciferous and Zn-anomalous deposits all predominate in the Phanerozoic (Fig. 8). The next most prevalent epoch for zinciferous deposits after the Phanerozoic is the Archean, and Zn-anomalous deposits are

Figure 4. A. Frequency histogram of Zn grades illustrating the non-normal distribution of raw data. Mean and standard deviations are shown on the plot. B. Log transformation of the grade data illustrating the much closer to normal distribution of data. Geometric mean and geometric standard deviations are shown on the plot. C. Cumulative probability plot for log transformed Zn grades in VMS deposits.
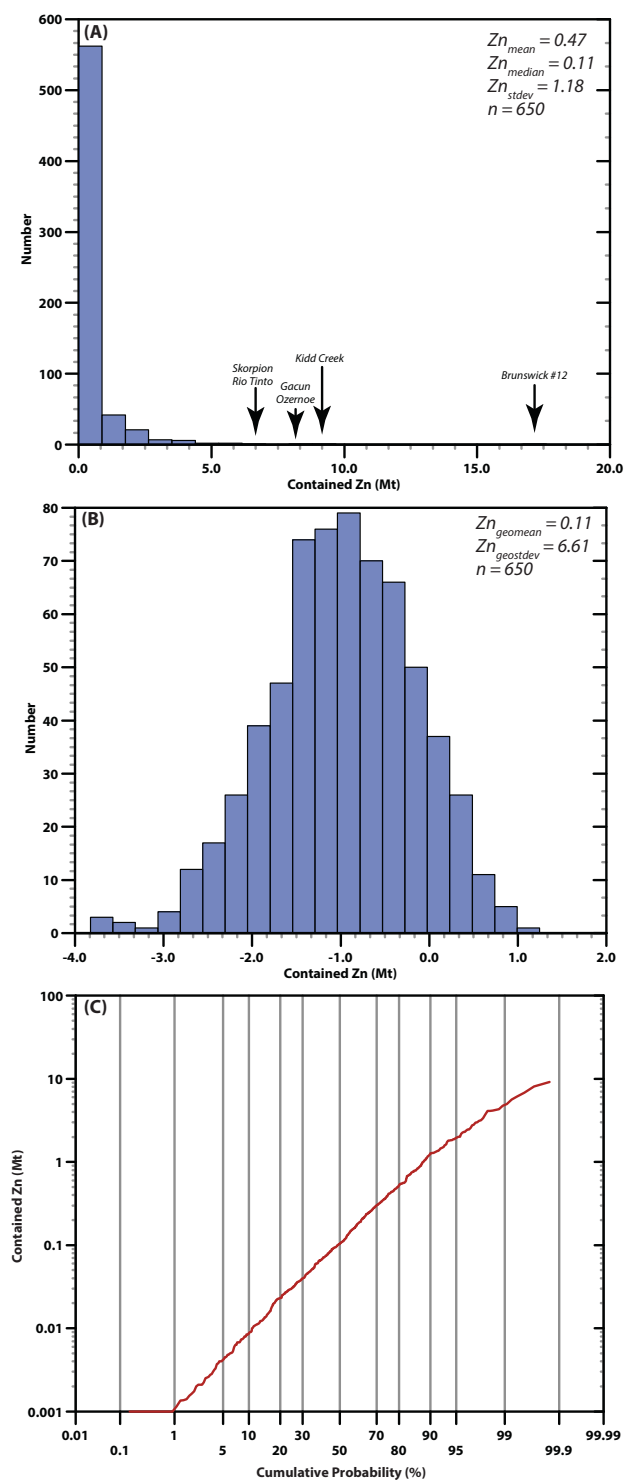
Figure 5. A. Frequency distribution of contained Zn in VMS deposits for raw data. B. Frequency distribution of log-transformed data of contained Zn in VMS deposits with geometric mean and standard deviation. C. Cumulative probability plot for log-transformed contained Zn in VMS deposits.

mostly formed in the Proterozoic and not in the Archean (Fig. 8). Distributions of zinc-rich, zinciferous and Zn-anomalous deposits also show distinct temporal control. Figure 9 shows the distributions of deposits relative to estimated volume of juvenile crust formed, a proxy for net planetary crustal growth. There is a clear episodicity of deposit formation in the Precambrian, with distinctive peaks in the Archean at (~2.7-2.8 Ga), Paleoproterozoic (~1.9-1.8 Ga), and lesser, but still significant peaks in the Mesoarchean (~3.0 Ga) and Neoproterozoic (~0.75 Ga)(Fig. 9). There is much greater variability for the Phanerozoic with distinctive peaks in the Cambrian-Ordovician (~510-460 Ma) and Devonian-Mississippian (~390-355 Ma), with subsidiary peaks in the Mesozoic and Cenozoic (Fig. 9)(see also Franklin et al., 2005; Galley et al., 2007b; Huston et al., 2010). The cumulative contained Zn is variable but is greatest of all in the Phanerozoic, particularly in the Palaeozoic (Fig. 9).

Major Processes Controlling Zn-Rich VMS Deposits

Although Zn-enriched VMS deposits are a significant contributor to global Zn resources, the controls on their genesis and siting have not previously been evaluated fully. We suggest that there are several controls that favor the formation and distribution of

VMS deposits in general, including: 1) accretionary orogenesis; 2) presence of abundant sedimentary rocks in the host succession and concomitant ocean anoxia at the depositional site; 3) presence of cap rocks; and 4) magmatic-derived metal contributions. Some Zn-enriched VMS deposit formational processes are universal to all VMS deposits in general (e.g., accretionary orogenesis), whereas others are specific to Zn-enriched VMS deposit environments (e.g., abundance of sedimentary rocks). It is therefore important to discuss these processes collectively to provide a holistic understanding of the controls on Zn-enriched VMS deposits.

Accretionary Orogenesis

Throughout geological time VMS deposits formed in extensional geodynamic regimes and during accretionary orogenesis (e.g., Piercey, 2011, and references therein). Accretionary orogenesis is not unique to Zn-enriched deposits, as most VMS deposits formed during this process (e.g., Galley et al., 2007b; Huston et al., 2010; Piercey, 2011; Hannington, 2014). Nevertheless, as it is a first order control on all VMS, accretionary orogenesis warrants discussion in the context of Zn-enriched deposits. In the modern oceans, seafloor massive sulphide (SMS) deposits are more prevalent at mid-ocean ridges than in arcs and back-
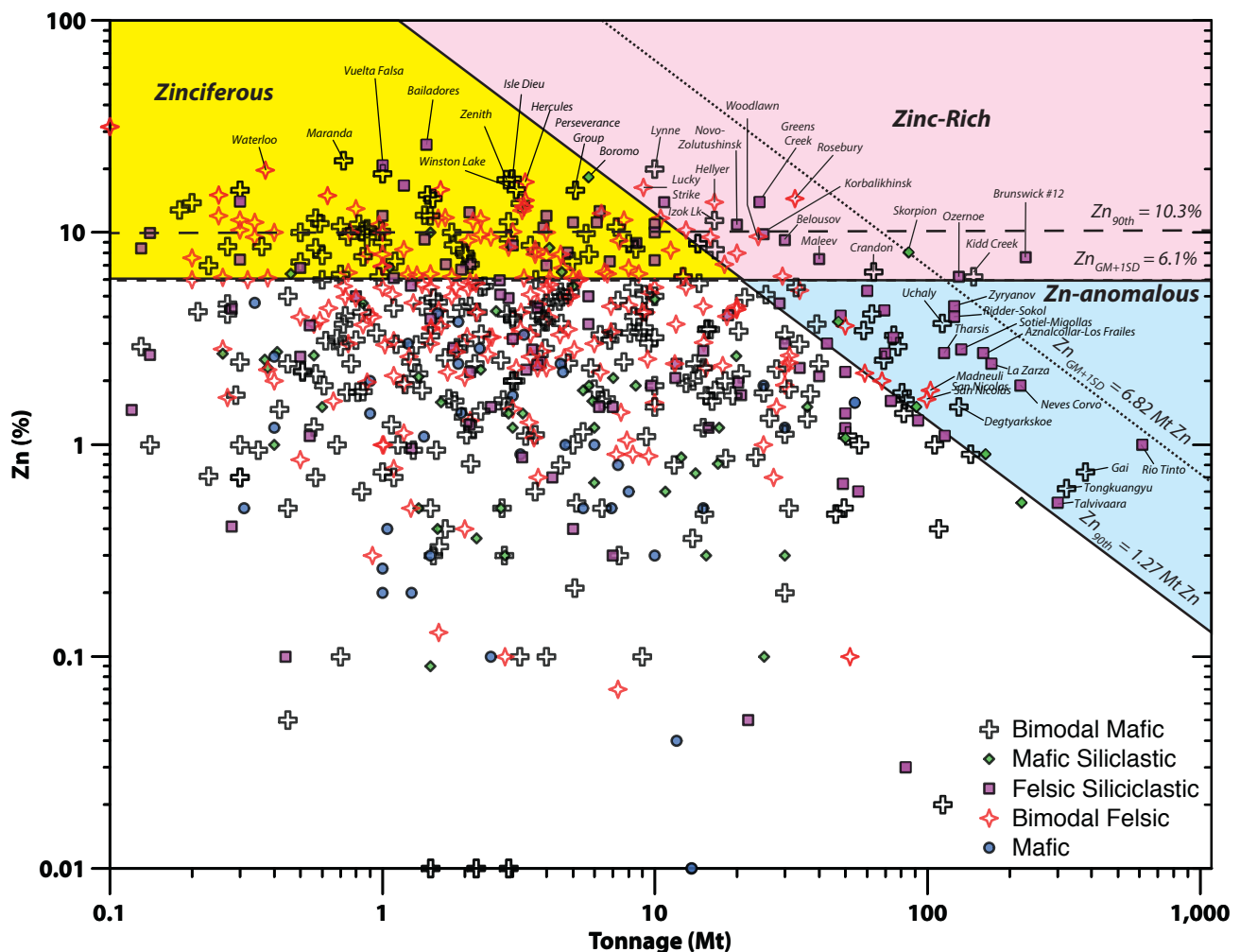

Figure 6. Grade-tonnage plot for volcanogenic massive sulphide deposits illustrating the various classifications of Zn-enriched VMS deposits, including Zn-rich (>6.1wt%, >1.27 Mt contained Zn), zinciferous (>6.1 wt%, <1.27 Mt contained Zn), and Zn-anomalous (<6.1 wt%, >1.27 Mt contained Zn). Also shown for comparison are the 90th percentile for contained Zn in VMS deposits (1.27 Mt contained Zn) and the geometric mean plus one geometric standard deviation (6.82 Mt contained Zn). Similarly, the geometric mean plus one geometric standard deviation (6.1 wt% Zn) and 90th percentile for Zn grade (10.3 wt%) are also shown.
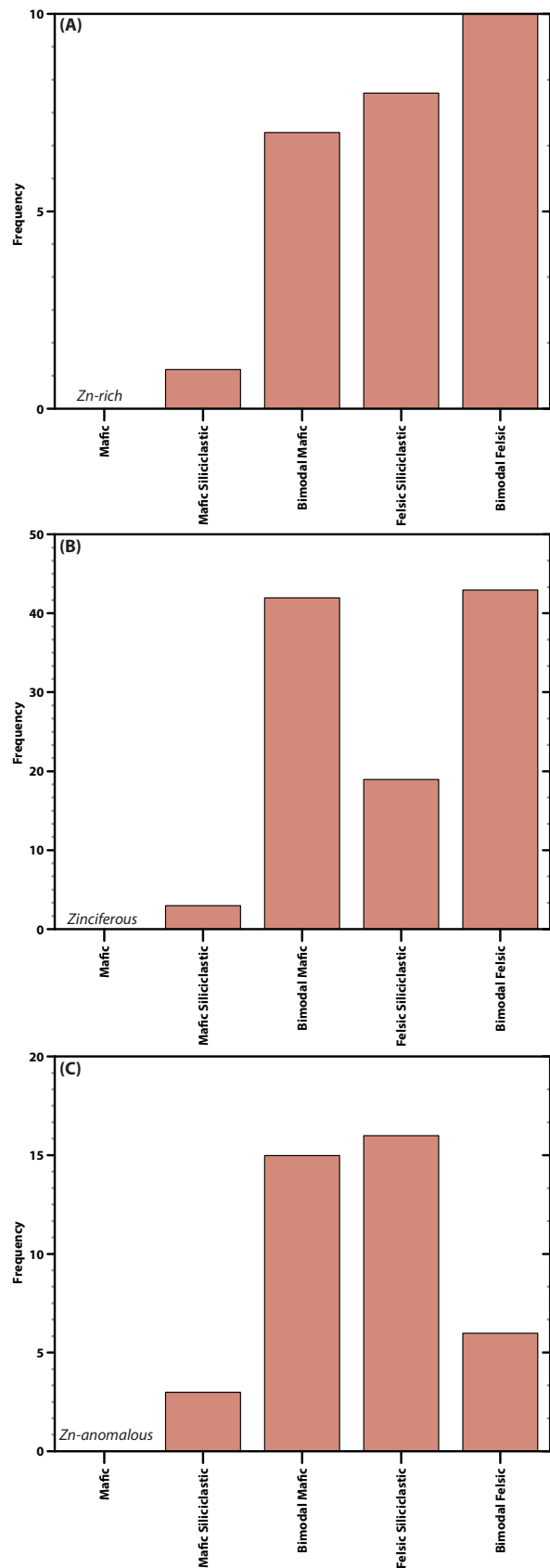
Figure 7. Frequency histograms of Zn-enriched deposits as a function of VMS deposit sub-type: A. Zn-rich; B. zinciferous; and C. Zn-anomalous. Those deposit sub-types associated with felsic and sedimentary rocks (i.e., bimodal mafic, bimodal felsic and felsic siliciclastic) are those that are Zn enriched.
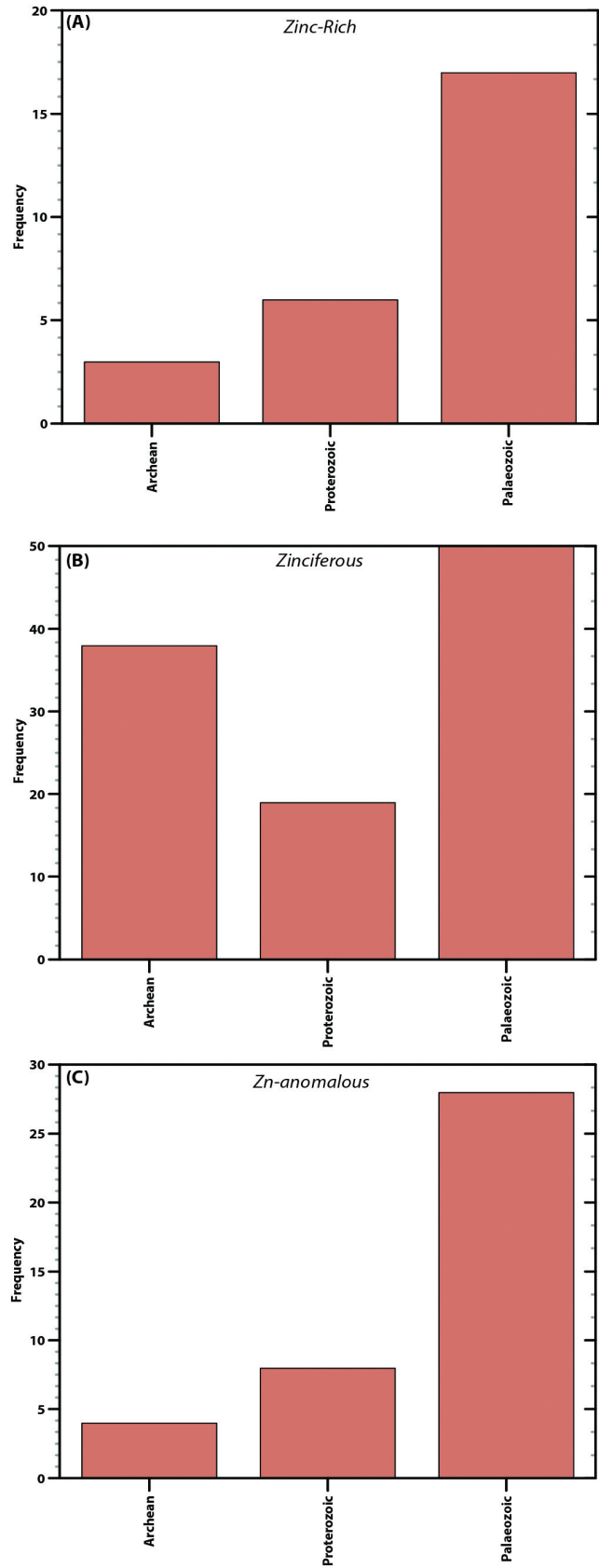
Figure 8. Distribution of Zn-enriched deposits as a function of geological era: A. Zn-rich. B. Zinciferous. C. Zn-anomalous.
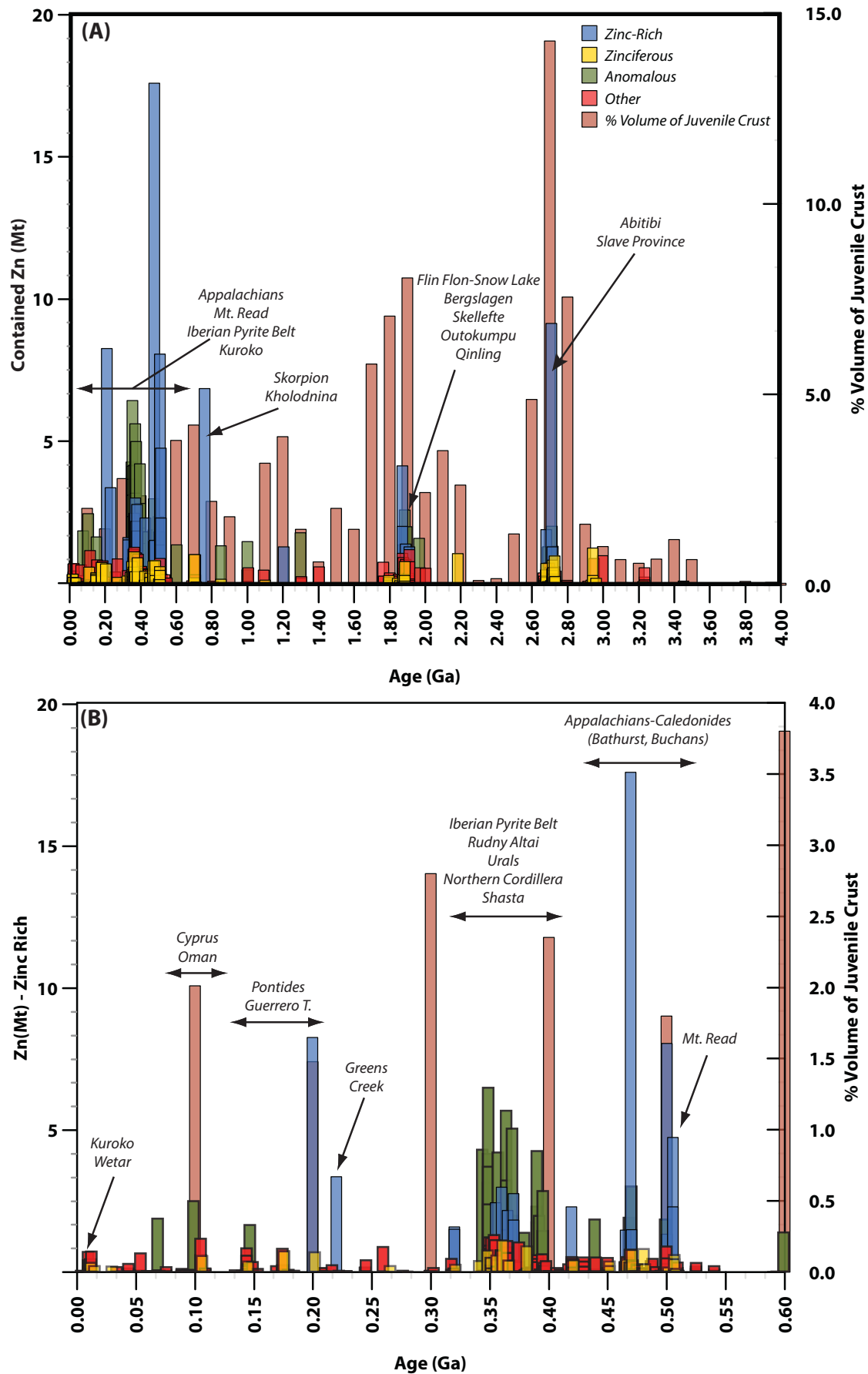
Figure 9. Histogram of contained Zn in VMS deposits as a function of time for Zn-enriched and other VMS deposits types. Also shown are estimated juvenile crust produced, a proxy for net planetary crustal growth. Juvenile crustal growth data from Condie and Aster (2010) and calculated based on modified approach of Condie (1990; 1995).
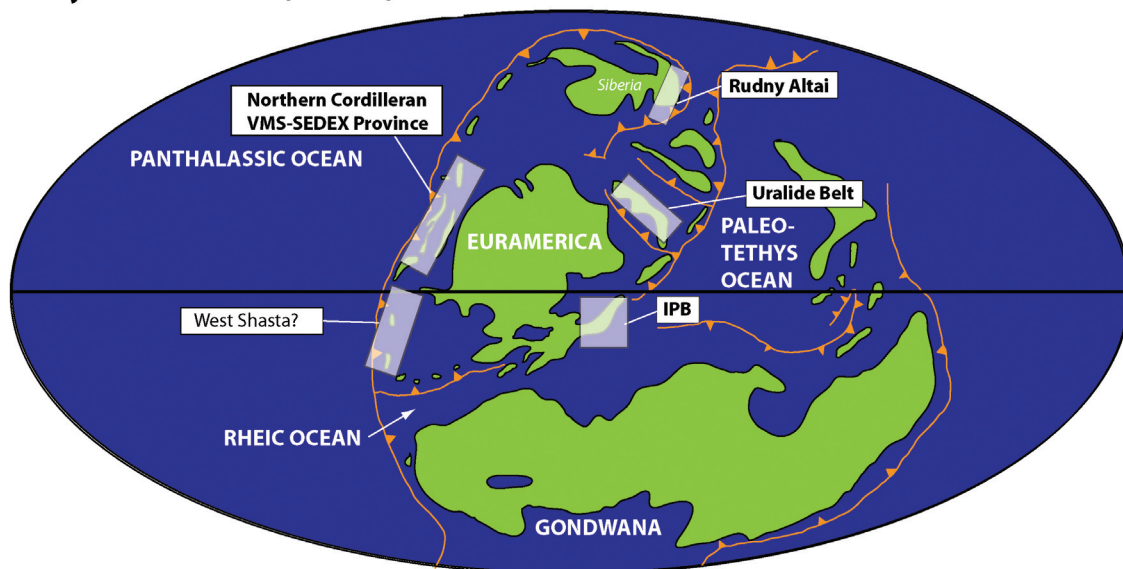
Early Carboniferous (356 Ma)

Figure 10. Paleogeographic reconstruction of the Early Carboniferous Earth by Scotese (2002) illustrating the occurrence of VMS camps in accretionary geodynamic settings. Despite their association with accretionary tectonism, the deposits are associated with extensional regimes within a broader accretionary framework.

arc basins (e.g., de Ronde et al., 2005; Hannington et al., 2005; Hannington and Monecke, 2009). However, this is an artifact of exploration history, as only recently has there been a focus on modern arc-associated SMS deposit exploration (e.g., de Ronde et al., 2005; Hannington et al., 2005; Hannington and Monecke, 2009). In contrast, the vast majority of VMS deposits in the ancient record occur within arc, arc-rift, forearc, and back-arc basin sequences formed during accretionary orogenesis; very few (if any) ancient VMS deposits were formed at mid-ocean ridges (e.g., Galley et al., 2007b; Huston et al., 2010; Piercey, 2011).

A commonly used measure of crust-mantle evolution is the secular trend of accretionary orogenesis and temporal distribution of juvenile crust formation (McCulloch and Bennett, 1994; Condie, 2000; Condie and Aster, 2010) (Fig. 8). The occurrence of juvenile crust is interpreted to reflect widespread magmatic activity, some of which may be linked to mantle plume activity (particularly in the Precambrian), extraction of new crust from the mantle, and subsequent preservation by accretion to cratonic nuclei during supercontinent formation (e.g.,Condie, 2000, 2001; Condie, 2005; Condie and Aster, 2010). Although the bin widths for the histograms for juvenile crustal growth and the age distribution for contained Zn in VMS deposits shown in Figure 9 are slightly different, there is a correlation between juvenile crustal growth episodes and contained Zn distribution in the Precambrian. In particular, the major pulses of Precambrian mineralization correspond to the amalgamation of the late Archean (~2.7 Ga) supercontinent Kenorland and the Paleoproterozoic supercontinent (~1.9-1.8 Ga) Nuna (Groves et al., 2005a; Groves et al., 2005b; Kerrich et al., 2005; Huston et al., 2010). The relationship between juvenile crustal growth and contained Zn in VMS deposits is weaker for the Phanerozoic (Fig. 9), and this reflects a shift to modern-style plate tectonics (Stern, 2005; Stern, 2008) and decreased plume-related tectonism (e.g., Condie, 2000, 2001; Condie, 2005; Condie and Aster, 2010).

Accretionary tectonism remained important in Phanerozoic VMS deposit formation, howerver (e.g., Nelson and Colpron, 2007; van Staal, 2007). For example, the major pulse of VMS formation in the Cambrian-Ordovician (Fig. 9) is related to ac-

cretionary processes along Gondwanan (e.g., Mount Read Belt, Tasmania, Australia; Bathurst Mining Camp, New Brunswick, Canada; Tally Pond district, Newfoundland, Canada) and Laurentian (e.g., Buchans camp, Newfoundland, Canada, Scandinavian Caledonide deposits) margins within the Iapetus Ocean (Large, 1992; Goodfellow et al., 2003a; Vokes et al., 2003; Piercey, 2007; van Staal, 2007). The second major pulse of Zn-enriched VMS formation in the Devonian to earliest Mississippian, and indeed in Earth's history (Figures 8-9), is associated with accretionary orogenesis in the Uralian, Altaid, Cordillera, and Variscan orogens (Fig. 10) (e.g., Herrington et al., 2002; Herrington et al., 2005; Tornos, 2006). Although these two major accretionary tectonic events in the early to middle Palaeozoic ultimately lead to the formation of the supercontinent Pangea in the late Palaeozoic, VMS formation and accretionary orogenesis cannot be directly attributed to supercontinent formation, unlike the Precambrian where the relationship of VMS to supercontinent formation is much more intimate (Huston et al., 2010). In the Phanerozoic many Zn-rich VMS camps or districts formed over 100 m.y. prior to the final amalgamation of the Pangean supercontinent (Fig. 6). For example, deposits in the Mount Read district and the Appalachians-Caledonides range from ~510-465 Ma, yet final amalgamation of the Appalachians into the Pangean supercontinent commenced in the Devonian (~340 Ma) and ceased in the Permian (~260 Ma)(e.g., van Staal and Barr, 2012).

Despite an association with accretionary orogenic activity throughout Earth's history, most (if not all) VMS deposits were formed during extensional geodynamic activity within these accretionary orogens, within arc rifts and back-arc basins (Lentz, 1998; Piercey, 2011, and references therein). A similar case can be made for modern SMS deposits that form(ed) in extensional settings at mid-ocean ridges, back-arc basins, and rifted arcs (e.g., de Ronde et al., 2005; Hannington et al., 2005). In addition, VMS deposits are spatially and temporally associated with specific magmatic suites and magmatic assemblages that formed at high temperatures (i.e., >900°C) within extensional geodynamic settings (Lesher et al., 1986; Swinden, 1991; Barrie, 1995; Lentz, 1998; Syme et al., 1999; Piercey, 2011). The combination of high-temperature magmatism within an exten-
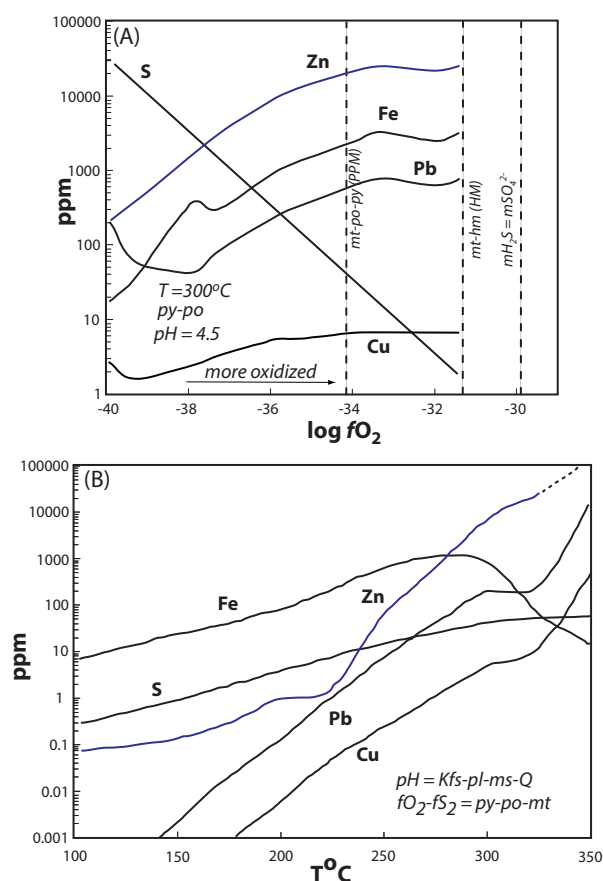
Figure 11. A. Plot of metal and reduced sulphur solubilities versus fugacity of oxygen at 300°C with fixed pH and fS_2 controlled by the pyrite-pyrrhotite buffer. With increasing fO_2 there is an increase in base metal solubilities. B. Plot of metal and reduced sulphur solubilities versus temperature with fO_2-fS_2 controlled by the pyrite-pyrrhotite-magnetite buffer and the pH controlled by a typical sedimentary assemblage (K-feldspar-plagioclase-muscovite-quartz). With increasing temperature there is increase in base metal solubilities; note that large amounts of Zn can be carried at temperatures <300°C. Further details on (A) and (B) are discussed in the text. From Tornos and Heinrich (2008).

sional tectonic setting provide the requisite heat to drive hydrothermal circulation and the crustal permeability to focus fluid flow that led to VMS formation (Lesher et al., 1986; Swinden, 1991; Barrie, 1995; Lentz, 1998; Syme et al., 1999; Piercey, 2011)

Sedimentary Rocks, Sedimentary Sequences, and Global Anoxia: Metals, Fluids, Sulphur and Preservation

Clastic sedimentary and volcanic sedimentary rocks are important in the genesis of many Zn-rich, zinciferous, and Zn-anomalous VMS deposits, particularly those of the high tonnage felsic siliciclastic-type (Figures 6-7). Experimental and thermodynamic data suggest that under identical conditions more Zn can be extracted from sediments and sedimentary rocks than from igneous basement rocks (Thornton and Seyfried, 1987; James et al., 2003; Franklin et al., 2005; Tornos and Heinrich, 2008). Thorton and Seyfried (1987) showed experimentally that reactions with sedimentary rocks at 300°C and 500 bars could create

a metalliferous fluid similar to modern SMS fluids. They further showed that the SMS fluids would be buffered to low pH (~3-4) at 300°C, and at these pH values as much Zn and Pb could be leached from the sediment into the hydrothermal fluid as could be generated from basalt at higher temperatures (Franklin et al., 2005). Tornos and Heinrich (2008) have shown via thermodynamic calculations that carbonaceous shales can buffer the H_2S/SO_4 ratio of a VMS forming fluid and thus limit the amount of reduced sulphur in the fluid (Fig. 11a). Furthermore, with increasing temperature such fluids could have carried more Zn (and other base metals; Fig. 11b), and the low reduced sulphur content of the fluid resulted in the precipitation of less than 1% of the base metals en-route to the site of deposition (Tornos and Heinrich, 2008). The Tornos and Heinrich (2008) model indicates that there is the requirement for an external source of sulphur at the site of deposition, and this may explain a common association of many Phanerozoic sediment-rich VMS systems with global anoxic periods (Goodfellow and Peter, 1996; Goodfellow et al., 2003b; see below).

Pore fluids from sediments may also enhance the capacity for Zn and base metal transport in VMS-forming hydrothermal fluids (Tornos and Heinrich, 2008). It is well established that salinity plays a significant role in the transport of Zn in hydrothermal fluids (Huston and Large, 1987; Barrett and Anderson, 1988; Huston et al., 2010; see also Williams-Jones et al., this volume), and this is particularly important for sediment-hosted (SEDEX) base metal deposits (Lydon, 1983; Hanor, 1997, 1999; Cooke et al., 2000; Hitzman et al., 2010). The pore fluids in sediments of footwall host stratigraphic sequences likely contributed additional chloride to the VMS-forming hydrothermal fluids, above and beyond that already contributed by entrained and modified seawater (Lydon, 1988; Ohmoto, 1996), thereby enhancing the metal carrying capacity and metal content of the VMS-forming hydrothermal fluids.

Sediment- and shale-rich environments are also commonly associated with global anoxic events and deposits formed therein have features that are hybrid between VMS and sediment-hosted Zn-Pb deposits (i.e., SEDEX). Global and local anoxic periods led to the formation of H_2S-rich bottom waters (i.e., euxinic), and this H_2S is widely accepted as the source for sulphur in SEDEX deposits (e.g., Goodfellow, 1987, 2004; Large et al., 2005; Goodfellow, 2007a; Leach et al., 2010). The role of oceanic anoxia in the formation of VMS deposits remains controversial, however. Some workers argue that regional to globally anoxic conditions were critically necessary for the formation of some large Zn-enriched VMS deposits (e.g., Eastoe and Gustin, 1996; Goodfellow and Peter, 1996; Goodfellow et al., 2003b). Other workers argue that venting of VMS hydrothermal fluids within basinal depressions formed anoxic brine pools of local extent (Solomon, 2008b, a). The brine pool model requires that the mineralizing fluids ultimately became denser than seawater on cooling and ponded at the seafloor to form a brine pool. Fluid inclusions in gangue minerals within mineralization should, therefore, have salinities greater than about twice that of seawater (the minimum salinity at which fluids would have reversed buoyancy and ponded at the seafloor upon mixing with seawater). Furthermore, sulphur in the deposits is expected to have been derived via thermochemical sulphate reduction (TSR), as well as minor bacterial sulphate reduction (BSR), of seawater sulphate. However, available data contradict the brine pool model. Firstly, most fluid inclusions studies in deposits such as the Brunswick Number 12 deposit have salinities <½ that of seawater, indicating that the fluids would have always been buoyant and never formed a brine pool (Goodfellow and Peter, 1999). Secondly, the sulphur isotope systematics of many deposits formed during periods of global anoxia (e.g., Brunswick Number 12; Wolverine, Yukon, Canada) indicate that sulphur was not derived solely from TSR of seawater sulphate, but originates from multiple sources (see following paragraph; Good-
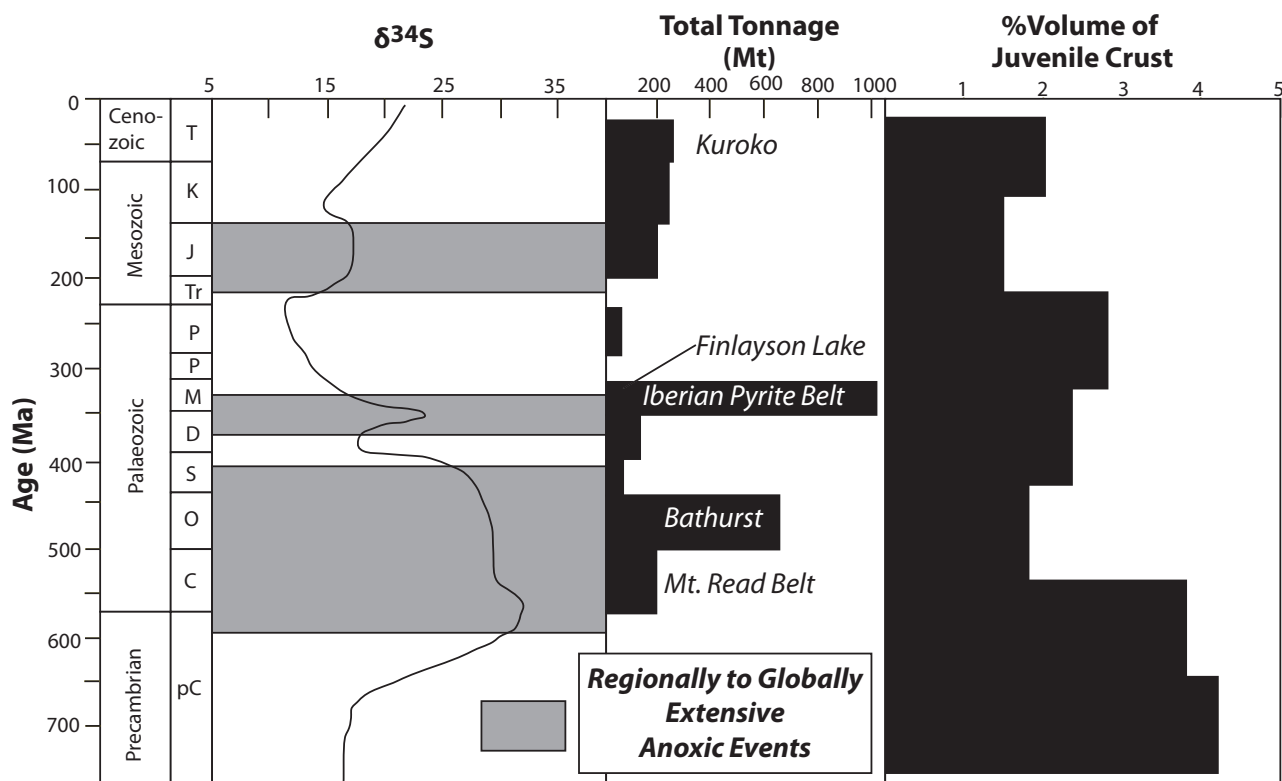
Figure 12. Secular variation of the sulphur isotope composition of seawater sulphate, with global anoxic periods shown in grey; these periods of anoxia are associated with positive shifts in δ³⁴S. Also shown are cumulative tonnages of VMS for the Phanerozoic and juvenile crustal growth. There are a number of deposits and camps in the Phanerozoic associated with global anoxic periods (e.g., Bathurst Mining Camp, New Brunswick, and Iberian Pyrite belt, Spain and Portugal). Notably, VMS deposits and anoxia do not strongly correspond to periods of Phanerozoic juvenile crustal growth, unlike the Archean and Paleoproterozoic, where VMS deposit formation is strongly linked to juvenile crust generation (see Figure 8). Figure modified from Goodfellow et al. (2003b). Juvenile crustal growth estimates from Condie and Aster (2010). Global sulphur isotope curve from Claypool et al. (1980).

fellow and Peter, 1996; Goodfellow and Peter, 1999; Goodfellow et al., 2003b; Bradshaw et al., 2008). These characteristics do not support a local, auto-generated anoxic brine pool model and indicate that basin-wide, regional anoxia was important in the formation of some deposits.

Although anoxic (euxinic) conditions were not requisite in the formation of VMS deposits, most Phanerozoic felsic siliciclastic-type deposits have very strong sedimentological, geochemical and isotopic indicators that anoxia was critical to their genesis: 1) low Mn contents of the host shales; 2) heavy δ³⁴S in sedimentary sulphides within host shales; 3) anomalously high redox sensitive trace element (Mo, V, U, and Re) abundances and high V/(V+Ni) and S/C ratios; 4) lack of cerium anomalies (i.e., Ce/Ce* ~1) in the host shales ; 5) presence of reduced mineral species (e.g., siderite, pyrrhotite); 6) predominance of Ba-rich micas and paucity or absence of barite; and 7) absence of bioturbation (Eastoe and Gustin, 1996; Goodfellow and Peter, 1996; Goodfellow et al., 2003b). In addition, VMS deposit-forming fluids vented into an anoxic water column, such as the bedded ores in the Brunswick Number 12 deposit, have sulphur isotopic values that are much heavier than those that would be expected from TSR of seawater sulphate and/or igneous rock sulphur alone; this indicates there was an additional source of heavy sulphur scavenged from the ambient water column (Eastoe and Gustin, 1996; Goodfellow and Peter, 1996; Goodfellow, 2003; Goodfellow et al., 2003b; Goodfellow, 2007b). Some workers suggest that this is a local phenomenon (Solomon,

2008b; Menor-Salvan et al., 2010; Herrington et al., 2011); however, in other cases there is a strong correlation between positive δ³⁴S excursions in the global seawater curve (indicative of global anoxic conditions), and the size and grade of VMS deposits, indicating that this is a global, rather than a local phenomenon (Fig. 12) (Claypool et al., 1980; Goodfellow, 1987; Eastoe and Gustin, 1996; Goodfellow and Peter, 1996; Goodfellow and Peter, 1999; Goodfellow et al., 2003b).

The association of many giant and super-giant Zn-enriched VMS deposits formed in anoxic (and euxinic) settings is the consequence of: 1) inhibited rate of oxidation of sulphide mounds induced by anoxic conditions, thereby enhancing the preservation potential of the deposits (Eastoe and Gustin, 1996); and 2) more efficient trapping of metals being vented into euxinic (H_2S-rich) bottom waters, in a manner analogous to sedimentary exhalative Zn-Pb systems (Fig. 13)(Goodfellow and Peter, 1996; Bradshaw et al., 2008). In VMS deposits that did not form within anoxic/euxinic basins, the bulk of the sulphur in the mineralization was derived by leaching from igneous host rocks and by TSR of seawater sulphate (e.g., Ohmoto, 1996; Huston et al., 2001; Hannington, 2014). As most VMS forming fluids had metal contents in excess of reduced sulphur contents (Tornos and Heinrich, 2008), this partially limited the amount of sulphide that was precipitated in an oxic (i.e., H_2S-free and oxygenated) setting. In contrast, in anoxic/euxinic environments, there was both sulphur derived from igneous rocks and TSR (i.e., metals and sulphur in the fluid), and reduced sulphur in the

ambient water column (i.e., H_2S at the site of deposition) available, and this greatly increased the amount of metals that were precipitated, and ultimately lead to the formation of much larger deposits (Fig. 14) (Goodfellow and Peter, 1996; Goodfellow et al., 2003b; Goodfellow, 2007b).

H_2S-rich anoxic/euxinic bottom waters were likely not important for Archean and Proterozoic VMS deposits, given the Fe-rich nature of the oceans prior to the Paleoproterozoic, and that the oceanic sulphur cycle was in its infancy (Slack et al., 2007; Slack and Cannon, 2009; Bekker et al., 2010); this likely explains the relatively scarcity of VMS deposits in the period from the Paleoproterozoic up to the latest Neoproterozoic (Fig. 9). In contrast, the role of H_2S-rich euxinic/anoxic oceans was important at some times and places in the Phanerozoic and may be a uniquely Phanerozoic phenomenon (Fig. 9)(Eastoe and Gustin, 1996). Furthermore, although anoxia was important in some Phanerozoic deposits, there are many large Zn-bearing VMS deposits (e.g., Tambo Grande, Peru, and some VMS deposits in the Urals, Russia) that are not associated with anoxia, and other factors are responsible for their large size and amount of contained metals (Herrington et al., 2002; Winter et al., 2004).

Sediment-rich environments and global anoxia were also important for the preservation of deposits and facilitation and promotion of subseafloor replacement processes. Volcanogenic massive sulphide deposits exposed on the seafloor were generally unstable structures and suceptible to oxidative weathering and collapse, and the retrograde solubility of anhydrite and gypsum (e.g., Blounot and Dickson, 1969) commonly led to collapse and erosion of chimney and mound structures. In contrast, the reducing environment associated with anoxia may have inhibited oxidative weathering of sulphide mounds. Furthermore, the presence of sediment cover on the massive sulphide mounds would have shielded deposits from oxidative weathering and erosion, thereby increasing their preservation potential. In addition, sediment-rich and volcaniclastic-rich environments have a disproportionate number of deposits that form from subseafloor replacement rather than mound construction processes. Although exclusive to them, many Zn-rich deposits, including many large and high-grade deposits (e.g., Rosebery, Tasmania, Australia; Kidd Creek, Ontario, Canada) formed via replacement processes (Doyle and Allen, 2003), and these processes were likely critical in forming high tonnage and/or high-grade Zn-enriched VMS deposits in the ancient record.

Cap Rocks: Size and Grade

The presence of a cap rock to seal the VMS hydrothermal system has been considered important by some workers (Hodgson and Lydon, 1977; Campbell et al., 1984; Barriga and Fyfe, 1988). Cap rock herein refers to a rock that covers (caps) the outer part of the VMS deposit, and not the hydrological cap
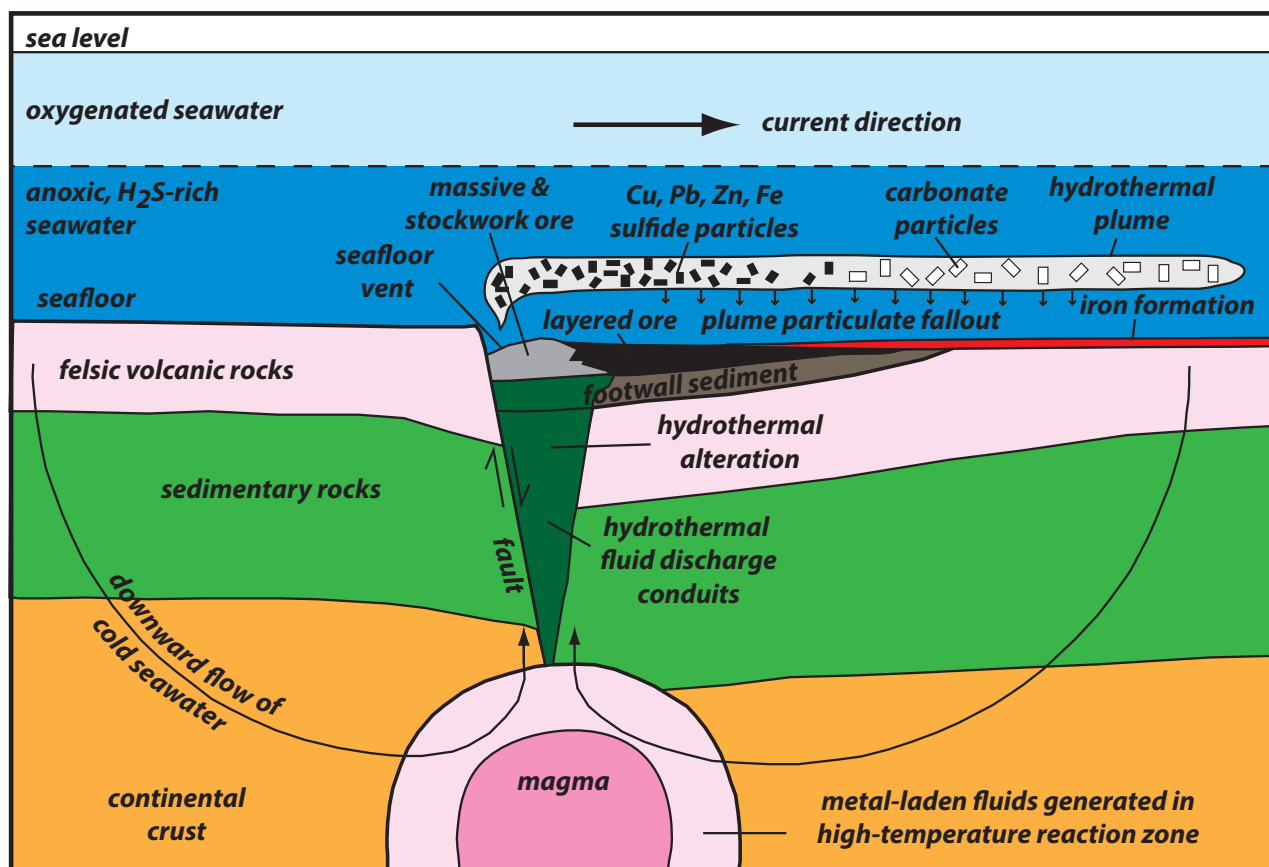

Figure 13. Model for the formation of the Brunswick Number 12 Zn-rich VMS deposit within a euxinic (anoxic, H_2S-rich) basin. The model is very similar to that for VMS deposits formed in oxic seafloor environments, with magma-driven hydrothermal circulation; however, the fluids vented into H_2S-rich, anoxic bottom waters. The discharge of fluids into H_2S-rich bottom waters resulted in greater amounts of metal precipitated upon interaction with the abundant reduced sulphur and played a critical role in the formation of a large deposit; other deposits elsewhere may have formed similarly. Modified from Goodfellow and Peter (1996) and Goodfellow (2007b).

(A) Evolution of high-grade Ba-Zn-Pb-Cu ores

(B) Evolution of lower-grade Zn-Pb-Cu ores

i) Nascent

Barite cap

ii) Intermediate

Metals retained under cap

Loss of Zn

iii) Mature

Legend:
- Barite
- Massive high-grade Zn-Pb sulfide
- Massive low-grade Zn-Pb sulfide
- Stringer zone with anhydrite
- Massive pyrite
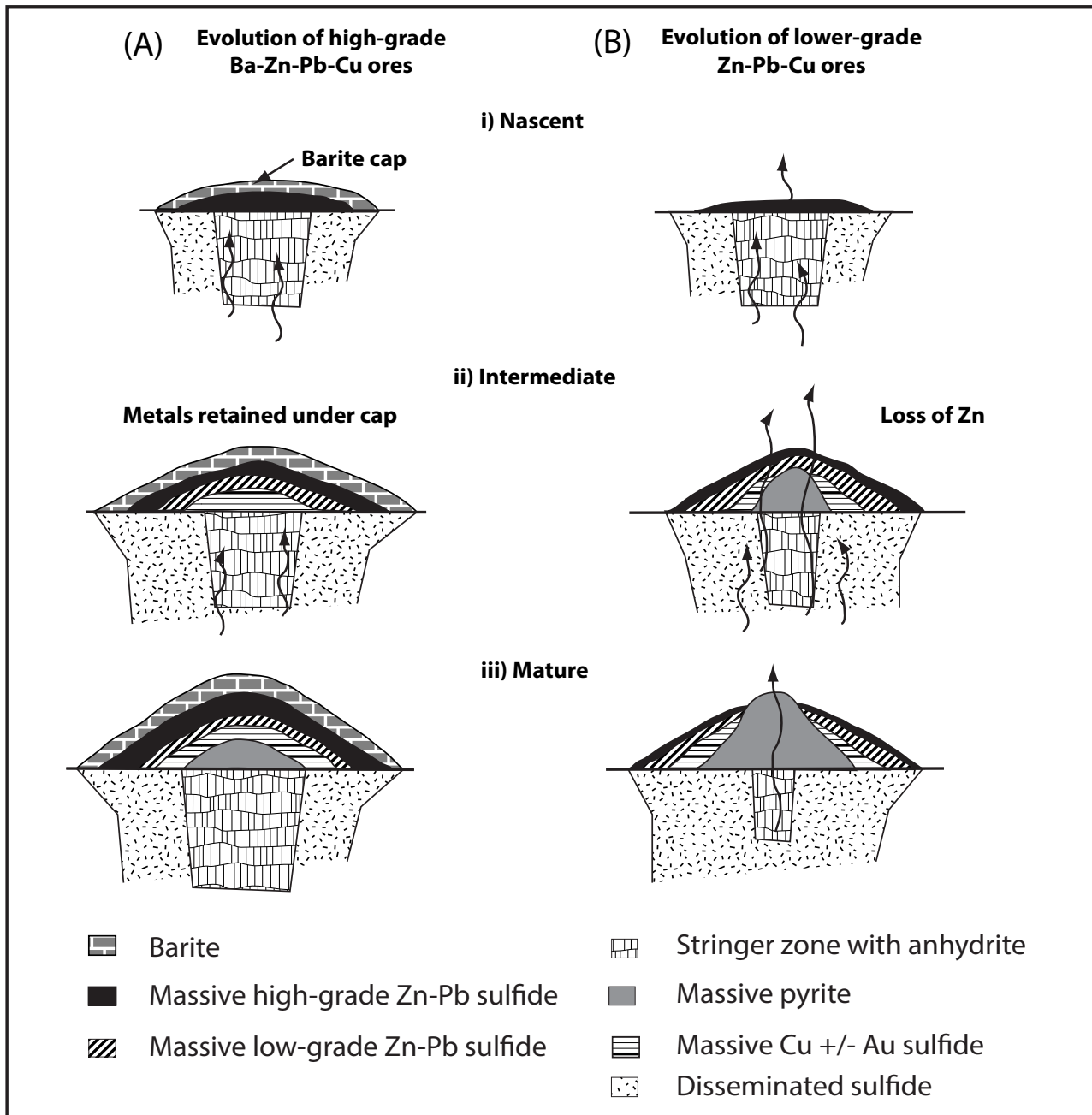- Massive Cu +/- Au sulfide
- Disseminated sulfide

Figure 14. The importance of cap rocks in the genesis of Zn-rich VMS deposits as a function of the evolution and maturation (zone refining) of a VMS deposit. A. depicts a deposit formed with a barite cap, and B. depicts a similar deposit formed without a barite cap. Early barite-(anhydrite) caps form during the nascent stage of mound evolution and prevent the 'wash-out' of Zn during the zone refining (i.e., intermediate and evolved stages) of the hydrothermal mound as base metals are retained below the barite cap. This cap is semi-porous and also allows ingress of cold seawater to facilitate mixing, cooling, and metal precipitation, and also contains sites for the nucleation of sulphides. B. Without a cap the base metals deposited during the nascent stages of mound formation are dissolved from the base of the mound by new, hotter, Cu-rich fluids during the intermediate and evolved stages and are zone-refined out of the system. This ultimately results in the metals being dispersed into the water column leading to a lower Zn grade, pyrite-pyrrhotite-chalcopyrite VMS deposit. Diagram from Schardt and Large (2009), building on the concepts from Eldridge et al. (1983), Campbell et al. (1984), and Large (1992a).

(impermeable barrier on Figure 1) rock that seals the hydrothermal reservoir (Hodgson and Lydon, 1977; Franklin et al., 1981a; Franklin et al., 2005). There are various types of cap rocks to VMS deposits, including those that are siliceous (e.g., Barriga and Fyfe, 1988; Liaghat and MacLean, 1992; Jones et al., 2006), argillaceous (e.g., Peter and Scott, 1999; Bradshaw et al., 2008), carbonate (Allen et al., 1996a; Galley et al., 2007a), magnetite-hematite-Mn-oxides (e.g., Leistel et al., 1997; Pe-

ter, 2003), volcaniclastic rocks (Gibson et al., 2000), and barite/anhydrite (e.g., Thurlow and Swanson, 1981; Barrett and Sherlock, 1996; Gemmell and Fulton, 2001). The presence of a semi-permeable cap likely increased precipitation efficiency in a manner akin to global anoxia. Semi-permeable cap rocks may have impeded the dissipation of fluids into the overlying water column and increased the preservation potential of mineralization (Fig. 14)(Goodfellow and Franklin, 1993; Herzig and

Hannington, 1996; Goodfellow and Zierenberg, 1999; Doyle and Allen, 2003; Hannington et al., 2005). Haymon and Kastner (1981), Haymon (1983), Campbell et al. (1984), and Lydon (1988) all argued that semi-permeable cap rocks (e.g., barite, anhydrite, sediment), provided thermal and chemical gradients and allowed cold seawater to ingress into the top of the hydrothermal mounds, thereby allowing any upwelling hydrothermal fluids to have cooled, mixed, and precipitated sulphides within the pore spaces in the cap. Furthermore, they also argued that the cap provided chemical gradients and nucleation sites where sulphides could have precipitated. Therefore, the presence of cap rocks would have resulted in a greater amount of metals precipitated, and formed concomitantly larger deposits than those without cap rocks.

Although not unique to Zn-enriched deposits, cap rocks may also have been critical to the formation of higher grade (e.g., >5 wt% Zn) deposits (e.g., Hodgson and Lydon, 1977; Schardt and Large, 2009), and they are particularly prevalent in bimodal felsic- and bimodal mafic-type VMS deposits. Most high-grade, Zn-rich deposits (e.g., Buchans, Newfoundland, Canada; Hellyer, Tasmania, Australia; Perseverence, Quebec, Canada; Kidd Creek, Ontario, Canada) have cap rocks, and many camps or districts (e.g., Mount Read, Tasmania, Australia; Matagami, Quebec, Canada; Buchans, Newfoundland, Canada and Thalanga-Waterloo, Australia) having numerous high-grade, Zn-rich deposits with cap rocks (Fig. 6). The association of cap rocks with high Zn grade deposits is partly due to their effect on the zone refining processes that occur during VMS deposit formation (Fig. 14). Zone refining is important in many VMS deposits, but its occurrence in areas with cap rocks appears to be important in upgrading Zn-Pb grades. In particular, the metal zonation present in many VMS deposits reflects the early deposition of Zn-Pb-Ba-rich sulphides due to the mixing and cooling of metal-bearing hydrothermal fluids with seawater at low temperatures (<200°C); these early formed Zn-Pb sulphide precipitates were then subsequently dissolved and remobilized by higher temperature (>300°C) Cu-rich fluids as the hydrothermal system matured (Large, 1992; Ohmoto, 1996). During the deposition of the Cu-rich basal part (keel) of many VMS deposit lenses, the dissolution of early Zn-Pb-Ba may have resulted in one of two scenarios depending on the presence or absence of a cap rock (Fig. 12). Where there was no cap rock, early-formed Zn-Pb sulphides were dissolved and "washed out" as the dissolved Zn and Pb were dispersed into the overlying water column leaving a residual chalcopyrite-pyrite-pyrrhotite-rich (or pyrite-pyrrhotite alone) deposit (Fig. 12). In contrast, in deposits with a semi-porous cap, cold seawater would have ingressed, and this would have created thermal and chemical gradients that allowed the re-precipitation of the Zn and Pb in Zn-Pb-bearing fluids, and a coarsening and partial recrystallization of Zn-Pb-Ba-rich sulphides, thereby increasing the Zn-Pb grades of the sulphides (Fig. 14) (Haymon, 1983; Campbell et al., 1984; Large, 1992; Schardt and Large, 2009).

Is magmatism important in the formation of Zn-enriched VMS deposits?

Magmatic fluids were clearly important in the genesis of some modern SMS (Stanton, 1994; Yang and Scott, 1996; de Ronde et al., 2005; de Ronde et al., 2011) and some ancient VMS deposits (Huston et al., 2011; Hannington, 2014), and it has been speculated for some time that magmatic fluids contributed metals to VMS deposits (Sato, 1977; Kowalik et al., 1981; Stanton, 1990; Stanton, 1991; Urabe and Marumo, 1991). The relationship between magmatic fluids and Zn-enriched VMS deposits has not been fully evaluated and requires much further work. Nevertheless, there is evidence to suggest that some large Zn-enriched VMS deposits, and some high-grade Zn-rich to zinciferous deposits likely contain metals contributed from magmatic

fluids. In many high-tonnage, Zn-rich VMS deposits, including Brunswick Number 12 and Kidd Creek, mineralization displays enrichments in so-called magmatic suite elements (e.g., Sn-Bi-In-As-Sb) and contains abundant Sb-As-rich sulphosalts as well as Sn-In-rich assemblages that are interpreted to have been derived from magmatic fluids (Hannington et al., 1999a; Goodfellow and McCutcheon, 2003; Goodfellow, 2007b; McClenaghan et al., 2009; Huston et al., 2011). In the Zn-anomalous, high tonnage Neves Corvo deposit, zinc mineralization is also associated with abundant Sn-In-rich lodes (so-called "rubané), which have stable isotopic characteristics that suggest inputs of magmatic fluid into the hydrothermal system (Relvas et al., 2006a; Relvas et al., 2006b). In some higher grade Zn-rich VMS deposits like the Lucky Strike deposit in the Buchans Camp, zinc mineralization is associated with bladed barite and abundant sulphosalts, most of which are Ag-rich (Strong, 1981) and are a permissive indicator of magmatic input of Ag (and Zn). Furthermore, Kowalik et al. (1981) and Sawkins and Kowalik (1981) used stable isotopic data and mass balance modeling to argue that magmatic fluids were involved in the genesis of the Buchans deposits. Similarly, Zn-rich deposits such as Hellyer, and the Zn-anomalous Neves Corvo deposits have fluid inclusions that more saline than seawater (Costa et al., 1983; Zaw et al., 1996; Moura, 2005) that are permissive of involvement of magmatic fluids and metals in deposit formation (de Ronde, 1995; Franklin et al., 2005; Huston et al., 2011). Finally, in SMS analogues to Zn-enriched bimodal felsic-type deposits in the Manus Basin, Yang and Scott (1996) have documented high metal contents (including >2 wt% Zn) in melt inclusions in volcanic rocks that are an indicator of magmatic contributions of base metals to Zn-enriched VMS hydrothermal systems.

These data provide circumstantial evidence that magmatic fluid has provided chloride, zinc, and perhaps other trace metals to certain large and high-grade Zn deposits. The question remains as to whether Zn originates from magmatic fluids, and if so, how much, or whether this is a casual or causal relationship. The possible contribution of magmatic fluids to VMS deposits remains a salient outstanding research theme in VMS deposit research.

Implications for Exploration

There are various controls on the genesis and siting of Zn-rich VMS deposits; however, it is important to note that not all of the controls discussed above are universally present in Zn-rich deposits or districts. Nevertheless, most economic and globally significant Zn-rich VMS deposits and camps have characteristics that indicate many of these controls influenced their formation. The global search for high-value, Zn-rich VMS deposits requires selection of areas for exploration that possess as many of the outlined characteristics as possible. Furthermore, it requires integrated exploration strategies that are scalable (i.e., regional to nano-scale) that integrate field geologic information (e.g., from outcrop mapping, prospecting, drill core logging), surficial and rock geochemical data, and ground and airborne potential field geophysical surveys (e.g., electromagnetic, magnetic, gravity, induced polarization) data to vector within areas of high potential. Highly talented, thoughtful explorers are also critical to exploration success; however, this is not unique to VMS exploration.

Although much is known about Zn-rich VMS deposits, and the effective methods for their exploration, they commonly remain difficult targets to explore for. Despite the large amounts of contained metal and large tonnages of some deposits, they are relatively small targets (i.e., commonly hundreds of meters in diameter), and many occur at depths beyond the limits of currently available geological, geochemical, and geophysical detection methods. Despite these challenges, they remain at-

tractive targets for Zn in the foreseeable future, and the numerous outstanding discoveries made in the last decade (e.g., Lalor, Snow Lake belt, Manitoba, Canada; Perserverence, Mattagami, Quebec, Canada) illustrate they are still a target of interest to many explorers.

Conclusions

Volcanogenic massive sulphide deposits are important global sources of Zn and can be classified into Zn-rich (Zn >6.1 wt%, >1.27 Mt contained Zn), zinciferous (Zn >6.1 wt%, <1.27 Mt contained Zn), and Zn-anomalous (Zn <6.1 wt%, >1.27 Mt contained Zn) deposits, collectively termed Zn-enriched deposits. Zinc-enriched deposits are preferentially associated with felsic volcanic rocks and/or sedimentary host rocks (i.e., bimodal felsic, bimodal mafic, and felsic siliciclastic deposit sub-types). All Zn-enriched deposits are preferentially hosted in Phanerozoic sequences, but there are significant deposits in Archean and Paleoproterozoic rocks, and they show a distinctive secular evolution associated with supercontinent amalgamation.

Zinc-enriched deposits are controlled by a number of key processes including: 1) accretionary orogenesis; 2) abundant sedimentary host rocks deposited during periods of global anoxia; and 3) presence of cap rocks. In some deposits magmatic fluids may contribute metals, chloride, and other trace elements and may play a ritical role in the generation of large and/or high-grade Zn-enriched deposits. The interrelationship of tectonics, ambient redox conditions, subseafloor replacement processes, preservation potential, and zone refining all influence the formation of Zn-enriched VMS deposits, and most deposits show the coincidence of many of these processes. Successful exploration strategies require the integration of geological, geochemical, and geophysical methods to identify the locations on Earth where these salient processes operated spatially and temporally in unison.

Acknowledgements

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