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The role of granites in volcanic-hosted massive sulphide ore-forming systems: an assessment of magmatic–hydrothermal contributions

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Abstract Assessment of geological, geochemical and isotopic data indicates that a significant subgroup of volcanic-hosted massive sulphide (VHMS) deposits has a major or dominant magmatic–hydrothermal source of ore fluids and metals. This group, which is typically characterised by high Cu and Au grades, includes deposits such as those in the Neoarchean Doyon-Bousquet-LaRonde and Cambrian Mount Lyell districts. These deposits are distinguished by aluminous advanced argillic alteration assemblages or metamorphosed equivalents intimately associated with ore zones. In many of these deposits, $\delta^{34}S_{sulphide}$ is low, with a major population below −3‰; $\delta^{34}S_{sulphate}$ differs from coexisting seawater and

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$\Delta^{34}S_{sulphate–sulphide} \sim$ 20–30‰. These characteristics are interpreted as the consequence of disproportionation of magmatic SO_2 as magmatic–hydrothermal fluids ascended and cooled and as a definitive evidence for a significant magmatic–hydrothermal contribution. Other characteristics that we consider diagnostic of significant magmatic–hydrothermal input into VHMS ore fluids include *uniformly* high (>3 times modern seawater values) salinities or very ^{18}O-enriched ($\delta^{18}O$>5‰) ore fluids. We do not consider other criteria [e.g. variable salinity, moderately high $\delta^{18}O_{fluid}$ (2–5‰), $\delta^{34}S_{sulphide}$ near 0‰, metal assemblages or a spatial association with porphyry Cu or other clearly magmatic-hydrothermal deposits] that have been used previously to advocate significant magmatic–hydrothermal contributions to be diagnostic as they can be produced by non-magmatic processes known to occur in VHMS mineral systems. However, in general, a small magmatic–hydrothermal contribution cannot be excluded in most VHMS systems considered. Conclusive data that imply minimal magmatic–hydrothermal contributions are only available in the Paleoarchean Panorama district where coeval seawater-dominated and magmatic–hydrothermal systems appear to have been physically separated. This district, which is characterised by chloritic and sericitic alteration assemblages and lacks aluminous advanced argillic alteration assemblages, is typical of many VHMS deposits around the world, suggesting that for "garden variety" VHMS deposits, a significant magmatic–hydrothermal contribution is not required. Other than deposits associated with advanced argillic alteration assemblages, the only deposit for which we ascribe a major magmatic–hydrothermal contribution is the Devonian Neves Corvo deposit. This deposit differs from other deposits in the Iberian Pyrite Belt and around the world in being extremely Sn-rich, with the Sn closely associated with Cu and in having formed from high ^{18}O-rich fluids ($\delta^{18}O_{fluid} \sim$ 8.5‰).

We consider these characteristics, particularly the last, as diagnostic of a significant magmatic hydrothermal contribution. Our analysis indicates that two subgroups of VHMS deposits have a major magmatic–hydrothermal contribution: Cu/Au-rich deposits with aluminous alteration assemblages and reduced, very Sn-rich deposits in which Sn was introduced in a high-temperature ore assemblage. Comparison with "normal" VHMS deposits suggests that these subgroups of VHMS deposits may form in specialised tectonic environments. The Cu/Au-rich deposits appear to form adjacent to magmatic arcs, an environment conducive to the generation of hydrous, oxidised melts by melting metasomatised mantle in the wedge above the subducting slab. This contrasts with the back-arc setting of "normal" VHMS deposits in which relatively dry granites (In this contribution, we use the term granite *sensu latto*) formed by decompression melting drive seawater-dominated hydrothermal circulation. The tectonic setting of highly Sn-rich VHMS deposits such as Neves Corvo is less clear; however, thick continental crust below the ore-hosting basin may be critical, as it is in other Sn deposits.

Introduction

Over the last several decades, there has been an increasing tendency to infer a significant magmatic–hydrothermal component to a large number of ore deposit types. Although there is a broad consensus that many deposits spatially associated with intrusions, such as porphyry and skarn deposits (Seedorf et al. 2005; Meinert et al. 2005) which were formed mostly by magmatic–hydrothermal fluids, the relative importance of the magmatic–hydrothermal component of other deposits is controversial. For instance, the importance of magmatic–hydrothermal fluids in adularia–sericite (low sulphidation) epithermal veins became controversial in the 1970s and 1980s, with some authors advocating an evolved meteoric-dominated ore fluid (e.g. Kamilli and Ohmoto 1977; Heald et al. 1987) and others advocating a significant magmatic–hydrothermal component (e.g. Simmons 1995), sometimes based on the same data. More recently, a number of authors (e.g. de Ronde 1995, among others) have advocated a significant magmatic–hydrothermal contribution for volcanic-hosted massive sulphide deposits. This contrasts with the situation in the 1980s when most workers on these deposits considered the ore fluids to have been mostly evolved seawater (e.g. Franklin et al. 1981; Ohmoto and Skinner 1983)

However, even in the 1980s and early 1990s, some workers (e.g. Urabe 1987; Stanton 1990, 1994; Sawkins and Kowalik 1981) argued for a significant magmatic–hydrothermal component to volcanic-hosted massive sulphide ore fluids, and beginning in the mid-1990s, an

increasing group of workers, including the authors of this contribution, advocated a significant magmatic–hydrothermal component for at least some volcanic-hosted massive sulphide systems based on geological and geochemical data from both modern and ancient deposits (e.g. Large et al. 1996; Huston et al. 1995; Yang and Scott 1996; Relvas et al. 2001; Gemmell et al. 2004). Like the controversy over adularia–sericite epithermal deposits, some of the same data have been used to advance points of views advocating both significant and insignificant magmatic–hydrothermal contributions to volcanic-hosted massive sulphide systems.

The purpose of this contribution was to critically review the geological and geochemical criteria used to advocate for, and against, magmatic–hydrothermal contributions in volcanic-hosted massive sulphide systems and then use selected well-documented modern and ancient systems (Fig. 1) to gauge the importance of magmatic–hydrothermal fluids and metal inputs in volcanic-hosted massive sulphide systems. In choosing case studies, we have selected systems that are typical of volcanic-hosted massive sulphide deposits as well as other systems that have characteristics (e.g. alteration assemblages and metal assemblages) that are atypical of these systems. In some cases, we contrast typical and atypical deposits from the same district or geological province. Based on the general review and the case studies, we then assess the importance of magmatic–hydrothermal fluids in volcanic-hosted massive sulphide and related systems and propose the most robust criteria for recognising, or excluding, their input. Finally, we discuss possible controls on the evolution and incorporation of magmatic–hydrothermal fluids into volcanic-hosted massive sulphide (VHMS) hydrothermal systems.

Criteria used to assess involvement of granites in VHMS systems

The criteria used to infer the origin of metals in VHMS deposits are based on a wide array of approaches, including theoretical considerations, experimental work, fluid inclusion and stable isotope data, investigations of modern submarine hydrothermal systems, and alteration and metallogenic studies incorporating both mineral assemblages and geochemistry. Broadly, these approaches can be divided into three groups: (1) geological, including geological relationships and the distribution and mineralogy of alteration assemblages; (2) geochemical, including mass balance constraints, the metallogeny of ores, the composition of ore and related minerals, and the composition of hydrothermal fluids; and (3) isotopic, including stable and radiogenic systems. In this section, we assess criteria that have been used to advocate wall-rock leaching and direct magmatic contributions as metal sources in VHMS depos-
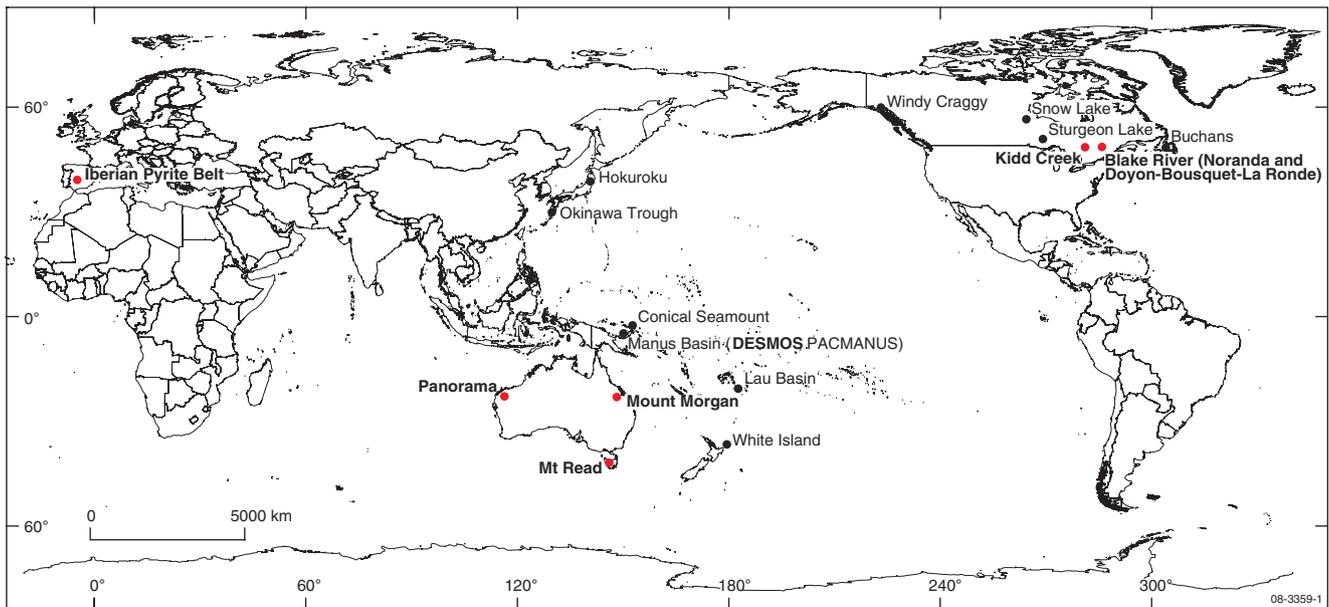
Fig. 1 Map of the world showing the location of deposits/districts discussed in text

its. In this discussion, we attempt to identify criteria that are diagnostic, rather than permissive, of a particular interpretation, although this is not always possible.

Geologic criteria

In some deposit types (e.g. porphyry and skarn), a close spatial association with magmatic rocks is one of the key criteria to infer a largely magmatic–hydrothermal origin for fluids and metals that formed the deposits. This spatial association may be strengthened by zonation of alteration assemblages about the intrusion. In VHMS districts, this close spatial association is largely missing: Coeval magmatic bodies are generally hundreds to thousands of metres removed from deposits, making inferences of magmatic–hydrothermal contributions to the ores more tenuous. Rather, geological arguments inferring magmatic–hydrothermal contributions to VHMS systems are less direct, commonly the correlation of granite-related alteration assemblages with those associated with the VHMS deposits, or correlating magmatic–hydrothermal deposits, such as greisens and some veins, with VHMS deposits in the same district.

Geological relationships

In a number of districts, a magmatic–hydrothermal input into VHMS hydrothermal systems has been inferred from the presence of alteration or mineralised zones within, or associated with, intrusive complexes spatially or temporally associated with the VHMS deposits. For instance, Large et al. (1996) proposed a magmatic–hydrothermal contribution to the Cambrian Mount Lyell Cu–Au ore

system based on similarities in alteration assemblages to alteration assemblages developed around coeval granites. In particular, they noted that magnetite±pyrite±apatite assemblages at the Prince Lyell deposit were similar to magnetite-pyrite±chalcopyrite±apatite assemblages developed in chloritically altered volcanic rocks proximal to inferred granite bodies 10 km south of the deposit.

A number of VHMS-associated intrusive complexes around the world contain small stockwork- or vein-style Cu–Mo, Cu–Sn–Zn and Au–Cu deposits. In the Sturgeon Lake, Ontario and Noranda, Quebec districts, Cu–Mo stockwork zones within spatially associated intrusive complexes (Beidelman Bay and Flavrian-Powell complexes, respectively) have been used to infer a magmatic–hydrothermal contribution into these hydrothermal systems (Poulsen and Franklin 1981; Kennedy 1985). However, based on field and geochronological evidence, Galley et al. (2000) and Galley (2003) demonstrated that the Cu–Mo stockwork zones postdated VHMS formation by up to 14 million years.

Better, though not definitive, evidence for a temporal and possible genetic link between magmatic-related and VHMS ores is present in the Doyon-Bousquet-LaRonde district, Québec (see below for a more detailed discussion), where crosscutting relationships suggest that stockwork Au/Cu-bearing quartz–sulphide veins at the Doyon deposit formed coeval with the latter phase of the Mooshla intrusive complex (Gossselin 1998; Galley and Lafrance 2007). Coeval gold-rich VHMS deposits at Bousquet and LaRonge have a similar metallogeny, suggesting linkage of the VHMS and stockwork Au–Cu deposits with the Mooshla intrusive complex.

As demonstrated above, the presence of magmatic–hydrothermal prospects or alteration zones within, or associated with, intrusive complexes spatially related to VHMS districts does not necessarily imply a significant magmatic–hydrothermal contribution to the VHMS hydrothermal system. In three of the five cases discussed above, geochronological and isotopic data demonstrate that the magmatic–hydrothermal prospects were not temporally linked to the VHMS deposits. Additional evidence, in conjunction with geological relationships, as discussed below, is required to infer the presence of a significant magmatic–hydrothermal contribution to VHMS hydrothermal systems.

Alteration assemblages

The vast majority of VHMS deposits are characterised by proximal alteration assemblages dominated by quartz, chlorite, white mica (sericite) and pyrite, and their metamorphosed equivalents (Franklin et al. 1981). At depth, proximal, commonly pipe-like, alteration zones extend into semi-conformable zones that contain, in addition to these minerals, epidote and albite as common minerals (Galley 1993; Huston et al. 2006). Although some of these minerals are present in alteration zones associated directly with magmatic–hydrothermal ore deposits (e.g. porphyry Cu and skarn deposits: Seedorf et al. 2005; Meinert et al. 2005), we do not consider them diagnostic of a magmatic–hydrothermal contribution as modelling by Seyfried et al. (1999) indicates that they can form by the interaction of seawater with rock as it is heated in a convective hydrothermal system. More recently, however, a growing class of VHMS deposits has been recognised that are characterised by aluminous advanced argillic alteration assemblages with an abundance of pyrophyllite, kaolinite and alunite, and less common minerals such as topaz, zunyite and woodhouseite (Sillitoe et al. 1996; Huston and Kamprad 2001; Dubé et al. 2007). These minerals also typify high-sulphidation (acid sulphate) epithermal systems (Heald et al. 1987).

Over the last two decades, there has been a growing consensus that advanced argillic alteration assemblages in high-sulphidation epithermal systems are the product of magmatic–hydrothermal fluid interactions based on their association with porphyry systems and the geochemistry of the fluids and altered rocks (Hedenquist et al. 1994; Cooke and Simmons 2000). In epithermal systems, advanced argillic alteration assemblages form through two different processes. In low-sulphidation systems, H_2S-bearing vapour produced by boiling at depths condenses into meteoric water in the vadose zone where oxidation of the H_2S results in very low pH fluids that interact with rocks near the surface to produce alunite–kaolinite–opal alteration

assemblages. These assemblages have limited depth extent: Movement of these fluids downwards to the water table neutralises them, restricting the distribution of advanced argillic assemblages in low-sulphidation systems to within a few tens of metres of the land surface (Cooke and Simmons 2000). Generally, advanced argillic assemblages in low-sulphidation epithermal systems are barren of ore.

In contrast, highly acidic fluids in high-sulphidation epithermal systems are produced by the disproportionation of magmatically derived SO_2 according to the reaction:

$$4SO_{2(g)} + 4H_2O_{(l)} \Leftrightarrow 3HSO_4^- + H_2S_{(aq)} + 3H^+. \qquad (1)$$
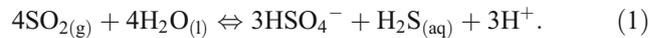
This reaction, which begins to occur at 400°C (Ohmoto and Rye 1979), produces highly acidic fluids that react with rock to form vertically extensive alteration zones that commonly contain higher temperature minerals such as pyrophyllite, in addition to kaolinite and alunite. In many high-sulphidation epithermal systems, these advanced argillic assemblages are intimately associated with ores (e.g. Sillitoe 1993).

Where present, advanced argillic alteration zones in VHMS systems tend to be vertically extensive and are commonly associated with ores. These characteristics, in combination with the presence of higher temperature minerals such as pyrophyllite (e.g. Mount Lyell) in some deposits, suggest that these assemblages formed from acidic fluids produced by disproportionation of magmatic SO_2. The other mechanism for producing advanced argillic assemblages in epithermal systems, the condensation of vapour in the vadose zone, is less likely in VHMS systems as vadose zones do not develop subaqueously. Hence, we consider the presence of advanced argillic alteration assemblages as good evidence for the involvement of magmatic–hydrothermal sulphur when associated with VHMS deposits. Conversely, the presence of quartz–chlorite–sericite assemblages is not considered to be diagnostic of the presence or absence of a magmatic–hydrothermal contribution to VHMS systems.

Geochemical criteria

In the late 1970s and early 1980s, an international research project documented the geology and geochemistry of VHMS deposits in the Miocene Hokuroku district in Japan (Ohmoto and Skinner 1983 and references therein), providing many concepts of ore genesis that have since been confirmed by studies of modern VHMS (i.e. black smoker) systems. Although many of the researchers in this project concluded that most metals were sourced by leaching of underlying rocks (e.g. Ohmoto et al. 1983), other researchers advocated a direct magmatic–hydrothermal source for metals for this district and others around the globe (e.g. Sawkins and

Kowalik 1981; Urabe 1987; Urabe and Marumo 1991). Both groups used similar data sets (e.g. isotopic, fluid inclusion, etc.) to advocate, in many cases, contradictory conclusions, suggesting that many of these data sets were not diagnostic. In the section below, we assess these data sets, including the composition of the ores, the trace element composition of ore minerals and the composition of ore fluids, along with mass balance considerations, to determine which, if any, diagnose the relative importance of evolved seawater (and wall-rock leaching) and magmatic–hydrothermal fluids to the fluid and metal budget of VHMS deposits.

Ore metallogeny

Hedenquist and Lowenstern (1994) showed that in the White Island geothermal system, more than 1 Mt of Cu metal was delivered by magmatic–hydrothermal emanations. Moreover, the Cu in porphyry Cu deposits is universally interpreted to have been derived directly from degassing magmas (Seedorf et al. 2005), suggesting a direct magmatic–hydrothermal contribution of a large proportion of global Cu resources. Similarly, a majority of the world's Mo, Sn and W resources also appear to have a magmatic–hydrothermal source (Seedorf et al. 2005; Meinert et al. 2005). However, direct magmatic contributions for Zn and

Pb are more difficult to demonstrate, and a direct magmatic contribution can be excluded from major Zn–Pb deposit types, including Mississippi Valley-type and Mt Isa-type deposits, as significant coeval magmatism does not characterise these systems (Leach et al. 2001; Huston et al. 2006). Hence, one potential criterion for sourcing of metals directly from a magmatic–hydrothermal source is the metallogeny of the ores, particularly metals such as W.

Barrie and Hannington (1999) proposed a fivefold classification for VHMS deposits based on their host rock compositions and suggested that metal abundances in the ores depended largely on the chemical composition of the host sequences. Figure 2 shows variations in 100Cu/(Cu+Zn) for major deposits (i.e. deposits containing over 0.5 Mt of either Zn or Cu) according to this classification. Inspection of this figure suggests that: (1) Deposits from the same district tend to possess similar Cu ratios; (2) for the same host rocks, larger deposits tend to have lower Cu ratios relative to smaller deposits, a characteristic previously noticed by Kerr and Gibson (1993); and (3) a few deposits (underlined in Fig. 2) have anomalously high Cu ratios relative to other deposits with similar host rock compositions. As Zn is more soluble than Cu over the entire spectra of hydrothermal conditions relevant for VHMS generation, Zn will be preferentially leached relative to Cu as fluids
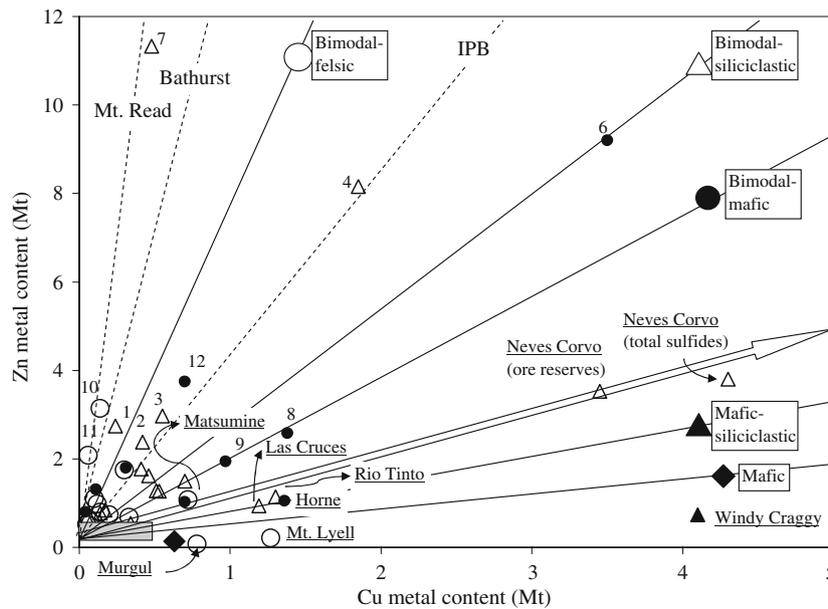
Fig. 2 Variations in the Cu ratio [100Cu/(Cu+Zn)] for deposits containing over 0.5 Mt of Zn and/or Cu as a function of the Barrie and Hannington (1999) classification of deposits. *Solid lines* represent the trends for each category of VHMS, i.e. mafic (*solid diamonds*, mean Cu ratio=74.0); mafic–siliciclastic (*solid triangles*, mean Cu ratio= 62.5); bimodal-mafic (*solid circles*, mean Cu ratio=35.4); bimodal-siliciclastic (*open triangles*, mean Cu ratio=28.1); and bimodal-felsic (*open circles*, mean Cu ratio=11.6). *Broken lines* represent the trends for three well-known VHMS districts: Mount Read, Tasmania; Bathrust, Canada; and Iberian Pyrite Belt. *Arrow* represents the trend defined by the Neves Corvo, Rio Tinto and Las Cruces deposits. Deposits quoted with numbers are as follows: (1) Los FraIles; (2) Sotiel; (3) Tharsis; (4) Aljustrel; (5) Migollas; (6) Kidd Creek; (7) Brunswick #12; (8) Flin Flon; (9) Geco; (10) Rosebery; (11) Hellyer; (12) Crandon. The *grey box* corresponds to the area of the plot where deposits <0.5 Mt of both Cu and Zn metals lie (in excess of 90% of the world's VHMS deposits, according to Gibson 1990)

interact with rocks, particularly at low temperature (e.g. Large 1992), leading to lower Cu ratios. Conversely, the same solubility relationship makes it difficult to enrich Cu relative to Zn during leaching unless the temperature is sufficiently high such that Zn is totally leached from the rock. Alternatively, high Cu ratios can also be achieved through the addition of an "independent" Cu-rich metal component. Hence, high Cu ratios for the underlined deposits in Fig. 2 are indicative of either high-temperature (>300–350°C) leaching or contribution of "independent" Cu.

Although hydrothermal leaching favours the enrichment of Zn relative to Cu, magmatic processes favour the enrichment of Cu over Zn in magmatic–hydrothermal fluids (Stanton 1991, 1994). During fractional crystallisation, Zn is preferentially sequestered into early-formed silicates (e.g. biotite and amphibole: Lukanin and Dernov-Pegarev 2004) and oxides, leading to the rapid enrichment of Cu relative to Zn in the residual melt. As crystallisation continues, both Zn and Cu partition into supercritical magmatic–hydrothermal fluid evolved by the exsolution of water dissolved in the magma. However, once again, the partitioning coefficient of copper is significantly higher than that of zinc, further enhancing Cu enrichment in magmatic–hydrothermal fluids (Candela and Piccoli 1995). Similarly, partitioning of metals such as Sn, Mo and W into supercritical fluids also results in the enrichment of magmatic–hydrothermal fluids in these elements (Heinrich et al. 1999; 1992). Hence, magmatic–hydrothermal fluids are possible sources of "independent" Cu as well as other less common elements in some VHMS deposits.

Yang and Scott (1996) have documented these processes in modern VHMS deposits in the Manus back-arc basin area. They documented a close association of ore/metal-rich fluids with melt inclusions from volcanic rocks associated with the deposits. However, Yang and Scott (1996) could not demonstrate a direct link between the magmatic brines they observed and the fluids that are forming the modern VHMS deposits.

In and of themselves, high 100Cu/(Cu+Zn) and enrichment in Sn, Mo or W are not sufficient evidence for a magmatic–hydrothermal contribution to VHMS ores. As discussed above, high hydrothermal temperatures could also result in an enrichment of Cu over Zn, and Brauhart (1999) and Huston et al. (2001) demonstrated evidence of the leaching of Mo in the Panorama VHMS district (see below). Hence, other evidence, such as alteration assemblages (see above) or mineral chemistry (see below) is required to demonstrate such a contribution.

Mass balance considerations

In one of the seminal early papers advocating a direct magmatic–hydrothermal contribution of metal to VHMS ores, Sawkins and Kowalik (1981) estimated that the concentration of Pb present in the large Buchans, New-foundland district required leaching of over 300 km³ of rock, a volume they considered excessive. Rather, they argued that a more realistic source was a ~50-km³ felsic magma chamber. Although changing Sawkins and Kowalik's (1981) assumptions (e.g. rock type leached and amount of metal deposited) could reduce the volume required for leaching substantially, similar calculations for even larger (e.g. Kidd Creek, Ontario or Brunswick No. 12, New Brunswick) deposits require leaching of extremely, possibly unrealistically, large volumes of rock.

Although leaching of metals of altered rocks in VHMS systems has been known for several decades, both from observational and theoretical grounds (e.g. Ohmoto et al. 1983), only recently have sufficiently detailed studies been undertaken to establish the location and extent of metal leaching in VHMS systems. Galley (1993) showed that in well-studied VHMS systems, granites generally intruded 1.3–3 km below the stratigraphic position of related VHMS deposits, with semi-conformable alteration zones developing in volcanic rocks above the granites. Studies of these semi-conformable zones indicate that they have lost significant metal. Losses of up to 90% copper, zinc and lead have been documented in the Troodos Ophiolite, Cyprus (Richardson et al. 1987; Jowitt et al. 2009), the Snow Lake district, Manitoba (Skirrow and Franklin 1994), and the Panorama district, Western Australia (Brauhart et al. 2001). The amount of metal lost generally exceeded that present in the deposits by up to an order of magnitude. This observation also extends to elements such as Ba, Mo and S, though not Sn (Brauhart 1999; Brauhart et al. 2001; Huston et al. 2001).

Hence, for the small- to moderate-sized districts in which sufficiently detailed studied have been undertaken, leaching of metals by evolved seawater more than accounts for known metal in the deposits. Even so, an input of magmatic/hydrothermal-derived metal into these systems cannot be excluded from these data, although it is not necessary. For larger, particularly giant, districts, the quantity of metal present in the deposits requires (possibly unrealistically) large leaching cells, leading Sawkins and Kowalik (1981) to suggest a magmatic–hydrothermal contribution to at least one system. However, for giant deposits, the size of the magma chamber required to provide sufficient magmatic–hydrothermal metal may also be unrealistically large. Hence, the formation of giant VHMS deposits may require special geological circumstances that allow the development of giant circulation cells or the involvement of large volumes of magma.

Composition of ore minerals: trace elements in cassiterite

Of the granitophile metals, Sn is most commonly concentrated in VHMS deposits, with the Neves Corvo (see

below) deposit being one of the largest known concentrations of Sn. However, the origin of Sn in VHMS and other deposits is controversial, with some authors advocating derivation by leaching of Sn-enriched host sequences. For instance, rocks in the stratigraphic footwall to the Sn-rich Kidd Creek can contain over 10 ppm Sn (Barrie et al. 1999), and a review by Mulligan (1975) concluded that the source of Sn in Sn-rich Canadian VHMS deposits was leaching of Sn-enriched rocks in the footwall stratigraphy. Collectively, these data indicate that in many Sn-bearing VHMS deposits, Sn could have been sourced via leaching of Sn-enriched sources during seawater circulation.

However, in carbonate replacement and skarn deposits, the close association of the deposits with Sn-enriched granites and ^{18}O enrichment of the ore fluids (Collins 1981; Layne et al. 1991) suggests a direct magmatic–hydrothermal origin of Sn, raising the possibility for a similar origin in some VHMS deposits. One possible method of assessing the origin of Sn is using the trace element characteristics of cassiterite, the most common Sn mineral, as a fingerprint of the geochemical affinities of the Sn-bearing fluids. The trace elements most widely used as diagnostic metal source indicators in cassiterite are Nb, Ta, Zr, Sc, Ti, W and Fe. Table 1 summarises the trace element composition of cassiterite from Sn deposits and occurrences in a wide range of geological settings.

Tin-bearing pegmatites, some greisens and stanniferous (W-poor) quartz veins are characterised by very high contents of Nb and Ta (and, to a lesser extent, Zr). Cassiterite from these deposits is also characterised by low W contents, as predicted by Baumann (1970) and Lehmann (1982), and high Ti and Fe contents. In contrast, cassiterite from sub-volcanic porphyry Sn deposits are characterised by low trace element contents, and cassiterite from other granite-related Sn deposits exhibit trace element compositional signatures that are intermediate between that of those two extremes. Hence, the trace element composition of many types of granite-related cassiterite may be strikingly different from that of pegmatitic cassiterite (cf. Hennigh 1993; Neiva 1996). This reflects variable "dilution" of the magmatic fluid either by longer transport processes (i.e. temperature decrease and chemical evolution through interaction with footwall rocks) or mixing with increasing proportions of surficial fluids. However, the granite-affiliated cassiterite is marked by high contents of Ti (± Sc), Fe and, in most cases, W.

This contrasts with the trace element composition of cassiterite from "typical" Sn-bearing VHMS deposits which are characterised by low overall trace element contents (Table 1: Hennig and Hutchinson 1999; Marcoux et al. 1996). This signature differs from granite-related deposits and is consistent with leaching of footwall rocks, as has been suggested by Mulligan (1975) and Barrie et al. (1999).

This interpretation is supported by the association of cassiterite with sphalerite in most VHMS deposits (Relvas et al. 2006a).

However, the highly Sn-enriched Neves Corvo deposit differs from typical Sn-rich VHMS deposits in having very high contents of Fe and W, and, possibly, Ti and Sc, and local enrichments of Ta and Nb (Table 1: Relvas 2000). These characteristics are similar to some granite-related cassiterite, suggesting a magmatic affiliation for the Sn-bearing fluid in this deposit. These studies indicate that the presence of Sn in VHMS deposits is not sufficient to infer a significant magmatic–hydrothermal contribution to these deposits. The trace element composition of cassiterite and the association of Sn-rich deposits with host sequences enriched in Sn suggest that in most cases, Sn was leached from the footwall sequence. The only exception appears to be the highly Sn-enriched Neves Corvo deposit where the trace element composition of cassiterite is similar to that of granite-related deposits.

Composition of ore minerals: Se/S ratios of sulphides

Auclair et al. (1987), Cabri et al. (1985) and Huston et al. (1995) demonstrated that the Cu-rich portions of VHMS deposits have higher Se/S values than Cu-poor, Zn-rich portions, based both on bulk ore analyses and microscopic analyses of individual minerals. Using existing thermodynamic data, Huston et al. (1995) estimated fluid Se/S ratios based on the Se content of pyrite, concluding that the Cu-rich zones in VHMS deposits were deposited from Se-rich fluids (Se/S ~ 10^{-5}–10^{-4}) relative to Zn-rich zones (<10^{-6}). These results were interpreted to indicate a dominant seawater source for sulphur in Zn-rich zones but a quantitatively important magmatic contribution in Cu-rich zones, either from leaching of volcanic rocks or a direct magmatic–hydrothermal contribution.

Subsequent studies have demonstrated additional complexity in interpreting Se/S. In particular, Layton-Mathews et al. (2008) demonstrated that the extremely high Se/S that characterise the Wolverine deposit are the consequence of interaction of the ore fluids with highly Se-enriched sediments stratigraphically below the deposit. However, they interpreted high, though not extreme, Se/S at the Kudz Ze Kayah deposit to be indicative of an input from leached volcanic rocks. Hence, as high Se/S could be produced either from direct magmatic–hydrothermal emanations or leached from volcanic rocks, high Se/S should not be considered suggestive of a magmatic–hydrothermal contribution to VHMS systems.

Ore fluid composition

Based upon a compilation of published fluid data from active VHMS deposits and fluid inclusion data from ancient

Table 1 Trace element composition of cassiterite from tin deposits from differing geological settings

	Sn-bearing pegmatites		Other granite-affiliated Sn deposits					Neves Corvo deposit			Other VHMS deposits
Nb	1,134–12,244 (6,383)	839–6,921 (3,006)	3,775–6,221 (4,998)	<3,000	70–1,678 (637)	23–3,855 (632)	0–1,623 (~158)	NR	<8	<10–20 (<10)	0–132 (<8)
Ta	2,876–18,758 (8,542)	737–6,961 (3,139)	10,810–14,577 (12,698)	<4,500	82–2,702 (955)	0–436 (48)	>26–282 (~57)	<16–98	<30–105 (~63)	<1–4 (~1)	<26–82 (~40)
Zr	481–1,138 (739)	NR	NR	50–700	NR	0–85 (45)	<5–332 (66)	NR	~0–40 (~19)	<10–94 (<10)	7–328 (37)
Sc	~0–8	NR	NR	50–700	NR	NR	NR	NR	NR	<1–182 (44)	NR except Kidd Creek (<10: Seifert et al. 1997)
Ti	109–3,247 (1,101)	180–4,016 (2,568)	(1,319)	280–4,400	2,517–5,215 (3,776)	0–1,393 (366)	NR	NR	NR	<100–12,100 (~2,100)	NR except Kidd Creek (<10: Seifert et al. 1997)
W	102–635 (292)	<50–793 (~524)	<50–79	1,000–6,000	317–1,110 (564)	NR	<23–5,885 (~1,027)	18–11,119	41–9,737 (2,099)	<120–3,000 (1,536)	<16–462 (<45)
Fe	1,651–5,090 (2,741)	466–3,032 (1,529)	4,355–4,589 (4,472)	NR	180–779 (413)	1,217–88,512 (12,057)	36–7,799 (2,179)	4,313–16,044	2,863–9,642 (5,436)	1,500–6,400 (4,308)	<21–5,071 (427)
Source	1	2	3	4	5	6	7	8	9	10	11

Data in parts per million; range indicated with average values in parentheses. Data sources as follows:

(1) Hennig (1993): Micro-PIXE trace element analyses of nine cassiterite samples from six Sn-bearing pegmatite deposits (Black Mtn., Coosa Co., Hill City, Kamativi, Tanco, Uis); Sc and Ti analysed using laser ablation microprobe analysis (six samples from three deposits)

(2) Neiva (1996): Electron microprobe analytical profiles (averaged and recalculated for element concentrations in ppm) of representative cassiterite crystals (n=6) from four occurrences of Sn-enriched granitic pegmatites from northern Portugal (Cabração, Bessa, Fental and Revel)

(3) Neiva (1996): Electron microprobe analytical profiles (averaged and recalculated for element concentrations in parts per million) of representative cassiterite crystals (n=2) from two Sn-bearing quartz vein systems in northern Portugal (Montezinho and Argozelo)

(4) Seifert et al. (1997) and references therein): Trace element concentration ranges characteristic of cassiterite from the granite-related tin deposits of the Erzgebirge district, Germany, the Cornwall district, UK, and the Mt. Pleasant deposit, Canada

(5) Neiva (1996): Electron microprobe analytical profiles (averaged and recalculated for element concentrations in parts per million) of representative cassiterite crystals (n=9) from W/Sn-bearing quartz veins from northern and central Portugal (seven deposits: Carris, Lombo de Boi, Linhares, Fonte Figueira, Vale de Gatas, Muralha, Carvalhal, and Panasqueira)

(6) Inverno (1991): Electron microprobe analyses (n=77) on 14 samples from the Mt. Pleasant endogranitic Sn deposit, Canada (ranges and averages calculated taking the mean composition of individual samples)

(7) Hennig (1993): Micro-PIXE trace element analyses of 24 cassiterite samples from 15 granite-affiliated tin deposits (Anchor, Belitung, Dolcoath, E. Kemptville, Franklin Mtns, Geyer, Hawyna, Llallagua, Mt. Pelion, N. Basset, Panasqueira, Rex Hill, Shin Kiura, Sleitat Mtn, Tingha)

(8) Serranti et al. (1997): Micro-PIXE trace element analyses of 11 selected grains of cassiterite from the Neves Corvo Deposit

(9) Hennig (1993): Micro-PIXE trace element analyses of nine cassiterite samples from the Neves Corvo Deposit

(10) Hennig (1996) and Hennig and Hutchinson (1997): Trace element analyses of pure cassiterite powders separated from 61 samples of Neves Corvo Sn-rich ores

(11) Hennig (1993): Micro-PIXE trace element analyses of 44 cassiterite samples from the Dickstone (4), Geco (2), Homestake (2), Kidd Creek (21), Kloof (1), Maranda (1), South Bay (2), Sullivan (6), United Verde (3), and Winston Lake (2) VHMS deposits

NR not reported

VHMS deposits, de Ronde (1995) demonstrated that most VHMS ore fluids had a relatively restricted range in composition, particularly with respect to salinity. Typical VHMS ore fluids have salinities between 1.9 and 9.1 eq wt. % NaCl, corresponding to levels 60–290% that of modern seawater (3.1% NaCl of 3.5% total salinity: Castro and Huber 2007). In addition, de Ronde (1995) also reported a subset of VHMS fluid data to indicate much higher salinities of up to 38 eq wt.% NaCl. More recent work on ancient deposits has indicated that deposits with higher salinities are more common in the rock record (see below; Solomon et al. 2004).

As discussed by de Ronde (1995), the range in salinity of the majority of VHMS fluids can be explained mostly by phase separation at depth in the hydrothermal system (cf. Butterfield et al. 1990), possibly in combination with subsidiary processes such as rock hydration or dissolution of Cl-bearing minerals (e.g. Seyfried et al. 1986). Another factor that may contribute to the range of measured salinities from the geological record could be temporal variations in the salinity of seawater. Knauth (2005) suggested that the salinity of seawater in the Archean and Paleoproterozoic was significantly higher (by up to a factor of 2 or more), decreasing only after the development of long-lived major continental landmasses allowed extensive deposition of evaporites and formation of basinal brines. Drieberg (2003) suggested that Mesoarchean seawater may have been up to a factor of 3 more saline than modern seawater. This variability and processes such as deep phase separation probably account for the variability in salinity of most VHMS ore fluids.

However, a significant minority of VHMS ore fluids are characterised by much more saline fluids: the Windy Craggy (Peter and Scott 1993), Hellyer (Zaw et al. 1996), Neoarchean Mattagami Lake deposits (Costa et al. 1983) and some deposits in the Iberian Pyrite Belt (Sánchez-España et al. 2000; Nehlig et al. 1998). The authors of studies identifying high-salinity fluids in VHMS systems may not ascribe an origin, although de Ronde (1995) suggested that a magmatic–hydrothermal origin could account for elevated salinities.

de Ronde (1995) also documented systematic variations in the amount and ratios of gases dissolved in fluids venting from modern VHMS systems. He observed that venting fluids from back-arc systems generally have higher total gas concentrations than those from mid-ocean ridges. Volcanic-hosted massive sulphide deposits from the Hokuroku district also have high gas contents, similar to those venting from the Okinawa back-arc system (de Ronde 1995). However, in modern systems, isotopic data suggest that carbonic gases are sourced from organic matter (Gamo et al. 1991).

Data from fluid inclusions and actively venting fluids indicate large variations in the composition of VHMS ore fluids. However, in most cases, these variations can be caused by processes, such as boiling, that are known to occur in modern systems dominated by evolved seawater or by variations in seawater through time. Hence, in most cases, variable salinity or elevated gas contents should be viewed as permissive and not diagnostic evidence of magmatic–hydrothermal contributions to VHMS systems. However, the presence of salinities that are consistently above coeval seawater, such as those at the Windy Craggy deposit (Peter and Scott 1999) is difficult to account for in seawater-dominated systems and may be more consistent with a major magmatic–hydrothermal contribution to the hydrothermal system.

Isotopic criteria

In many hydrothermal systems, stable isotope characteristics have been a key piece of evidence to demonstrate magmatic–hydrothermal contributions to the ore fluids (e.g. Taylor 1987). The power of stable isotopes lies in the contrasting isotopic properties of magmatic–hydrothermal fluids relative to surficial fluids such as seawater or meteoric water. However, water–rock reactions and other hydrothermal processes can complicate these signatures, making isotopic fingerprinting less diagnostic. Radiogenic isotopes, when used as tracers, can constrain sources of ore metals and related elements; however, additional data are generally required to identify the origin, be it leaching of underlying rocks or magmatic–hydrothermal.

Sulphur

Sangster (1968) originally observed that $\delta^{34}S$ values of sulphide minerals from Phanerozoic VHMS deposits were ~17‰ lower than those of coeval seawater sulphate. Four decades later, this fundamental observation applies for most VHMS deposits of this age, with $\Delta^{34}S_{seawater\ sulphate–ore\ sulphide}$ having a mean value of 16.5±5.4‰. Moreover, sulphate minerals in most Phanerozoic VHMS deposits (including modern systems) have similar values to coeval seawater sulphate, with $\Delta^{34}S_{seawater\ sulphate–ore\ sulphate}$ having a mean value of 0.5±2.9‰ (n=9; from data tabulated in Huston 1999; excludes three outliers ranging between 10.0‰ and 17.6‰). Ohmoto et al. (1983) and Solomon et al. (1988) interpreted these relationships to indicate that a significant proportion of reduced sulphur in VHMS ores was derived from partial inorganic reduction of marine sulphate as seawater convected through the volcanic pile underlying VHMS deposits. The other major source of reduced sulphur was interpreted to be rock sulphur dissolved from the volcanic pile. Such sulphur would have a very similar sulphur isotope signature to that of sulphur derived from H_2S-dominated magmatic–hydrothermal fluids.

In contrast, ore sulphides in Paleoproterozoic to Paleoarchean deposits have a more restricted range (1.0 ± 2.6‰, $n=17$), interpreted to indicate that dissolved rock sulphide or magmatic–hydrothermal H_2S were the dominant source of ore sulphide. This dominance was inferred to be the consequence of very low total sulphur concentrations in seawater (2 ppm) during this period (Huston 1999).

As discussed above, disproportionation of magmatic SO_2 to form aqueous sulphate and H_2S is one process by which the highly acidic fluids responsible for advanced argillic alteration assemblages could form. This reaction, which becomes important below 400°C in oxidised magmatic–hydrothermal fluids, also involves significant sulphur isotope fractionation: $\Delta^{34}S_{sulphate–H2S}$ varies from 18 at 400°C to 29 at 200°C (Ohmoto and Rye 1979). In high-sulphidation epithermal deposits, disproportionation of magmatic–hydrothermal fluids resulted in $\Delta^{34}S_{sulphate–sulphide}$ of 20–30‰, with sulphide minerals commonly having $\delta^{34}S$ values between −10‰ and 0‰ (Arribas 1995).

Although negative $\delta^{34}S_{sulphide}$ values are present in many VHMS systems, these values are rarely dominant (cf. Huston 1999). Rather, very negative values are mostly outliers and rarely form significant populations. In many cases, these values are from pyrite in the host sedimentary units and may be the result of bacterial sulphate reduction (cf. Ohmoto and Rye 1979). However, a few deposits, such as black smoker deposits in the Lau back-arc and the Mount Lyell district (see below), are characterised by major populations with low (less than −3‰) $\delta^{34}S$ and advanced argillic alteration assemblages. The presence of a major population of anomalously low $\delta^{34}S_{sulphide}$ can be suggestive of disproportionation of magmatic–hydrothermal SO_2, particularly if $\Delta^{34}S_{sulphate–sulphide}\sim20$–30‰, $\Delta^{34}S_{seawater\ sulphate–ore\ sulphate}$ is non-zero (i.e. $|\Delta^{34}S_{seawater\ sulphate–ore\ sulphate}|>5$‰) and, most importantly, advanced argillic alteration assemblages are present.

Oxygen and hydrogen

At first glance, large differences between the isotopic compositions of oxygen and hydrogen between seawater and magmatic–hydrothermal fluids (cf. Sheppard 1986; Taylor 1992: Fig. 3) suggest that these two isotopic systems could effectively establish the presence of magmatic–hydrothermal fluids in VHMS ore systems. However, processes such as water–rock reaction and phase separation modify the initial seawater isotopic signature as seawater passes through the volcanic pile such that the isotopic differences between evolved seawater and magmatic–hydrothermal fluids are muted (Fig. 3).

Figure 3 also shows the isotopic compositions of ore fluids from VHMS deposits relative to the fields of magmatic–hydrothermal fluids and seawater. With a few
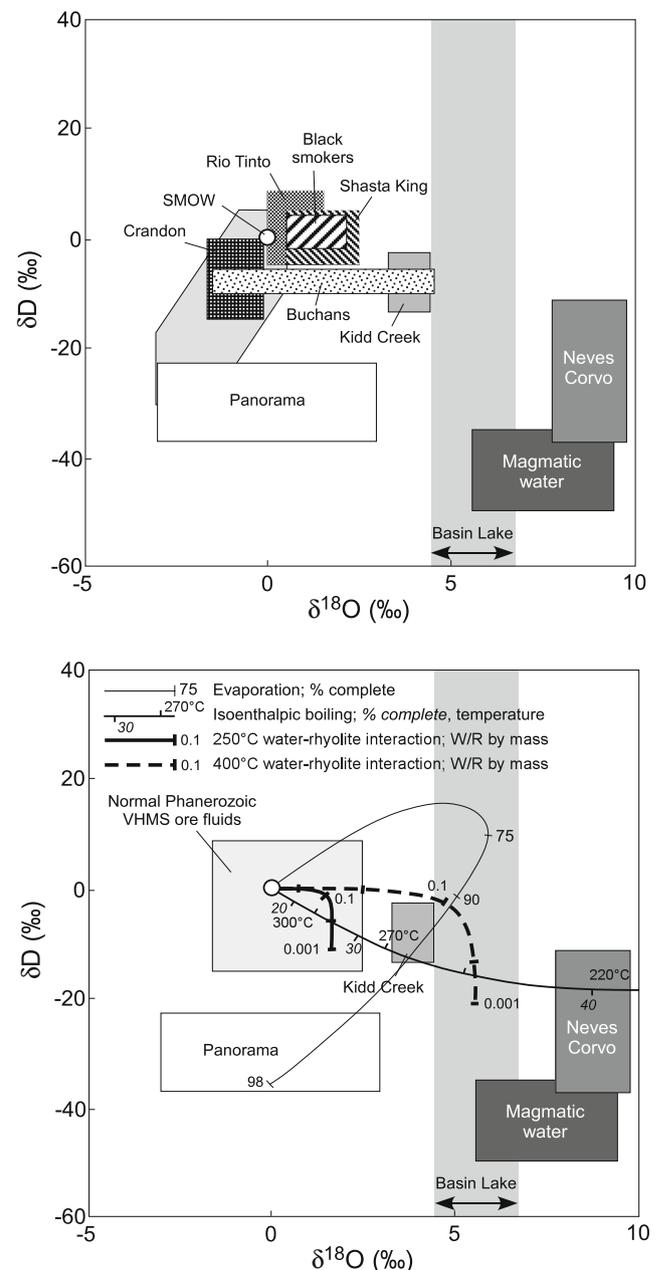
Fig. 3 $\delta^{18}O$ versus δD diagrams showing the fields of selected VHMS ore-forming fluids, the fields of seawater and magmatic–hydrothermal fluids, and paths showing the evolution of seawater undergoing open-system water–rock interaction, adiabatic boiling and mixing with magmatic–hydrothermal fluid. Diagram modified after Huston (1999) to include new data from Panorama (Drieberg 2003), Neves Corvo (Relvas et al. 2006b) and Basin Lake (Williams and Davidson 2004)

exceptions, VHMS ore fluids range in $\delta^{18}O_{fluid}$ from −2% to 4‰ and in δD_{fluid} from −40% to 5‰ (cf. Huston 1999). These variations can easily be accounted for by water–rock interactions (Munhá et al. 1986), deep-seated phase separation (Huston 1999) or secular variations in $\delta^{18}O$ and δD of seawater (Sheppard 1986). Hence, for most

VHMS deposits, we do not consider existing oxygen or hydrogen isotopic evidence to be sufficient evidence to advocate magmatic–hydrothermal contributions to VHMS ore systems. However, in deposits characterised by high $\delta^{18}O_{fluid}$ (>5‰), a significant magmatic–hydrothermal contribution cannot be excluded.

A few VHMS deposits have been interpreted to have $\delta^{18}O_{fluid}$ above 5‰ (cf. Huston 1999). Most of these deposits are from high-grade metamorphic terrains, raising the possibility that the apparent $\delta^{18}O_{fluid}$ values reflect overprinting metamorphic conditions and not the primary ore fluid characteristics. An important exception is the low greenschist facies Neves Corvo deposit where $\delta^{18}O_{fluid}$ has been estimated at ~8.5‰ (Relvas et al. 2006b; see below), a value difficult to produce with processes known to occur in VHMS circulation cells. Reliable estimates of primary $\delta^{18}O_{fluid}$ above 5‰ may be a diagnostic criterion for magmatic contribution into a VHMS system. Another exception is the Basin Lake high-sulphidation prospect in the Mount Read Volcanic Belt where Williams and Davidson (2004) inferred that the ore fluid had $\delta^{18}O$ values of 4.4–6.7‰.

Radiogenic isotopes

Like stable isotopes, radiogenic isotopes can be used as tracers to constrain the origin of some elements. This is done by establishing isotopic ratios at the time of mineralisation ("initial" ratios) and comparing these ratios to the ratios in the source at the time of mineralisation. As an example, initial Pb isotope ratios in many ore types are determined in Pb-rich minerals such as galena. The Pb system has a great advantage over other isotopic systems in that Pb is a major ore metal in most VHMS deposits. Other isotopic systems that have been used as a proxy to trace the origins of ore components include Nd–Sm, Rb–Sr, Re–Os and He.

A number of studies have identified the presence of multiple sources of ore components in VHMS systems. One of the better examples was that of Fehn et al. (1983) who documented district-scale heterogeneity, though deposit-scale homogeneity, of Pb isotopes in Zn/Pb-rich black ores from the Hokuroku district of Japan. The lead isotopic compositions of these ores were intermediate between those of less radiogenic volcanic rocks that underlie the deposits and the more radiogenic rocks that underlie the volcanic rocks, leading Fehn et al. (1983) to conclude that the Pb in the ores was sourced from both of these sources, with intra-district heterogeneity caused by variations in the proportions of the two sources. However, in all deposits studied, Cu-rich yellow ores had Pb isotopic compositions significantly less radiogenic than the Zn/Pb-rich ores. These differences were interpreted by Fehn et al. (1983) to

indicate a greater input of less radiogenic volcanic rocks as the individual hydrothermal systems waxed, although they are permissive of a direct contribution of magmatic–hydrothermal Pb from a less radiogenic magmatic source.

As discussed below, Pb and Sm–Nd isotopic studies in the Iberian Pyrite Belt (Relvas et al. 2001) and Mount Read Volcanic Belt (Gulson and Porritt 1987) also indicate isotopic heterogeneity at various scales and indicate the presence of multiple metal sources. However, like the Hokuroku study (Fehn et al. 1983), the data cannot be used to demonstrate the presence of a magmatic–hydrothermal metal source, although they are permissive of such a source.

Helium and Sr isotope studies of modern vent systems suggest that both elements were derived from underlying volcanic and, in some cases, sedimentary rocks, with minimal input from seawater (de Ronde 1995; Hannington et al. 2005). In most cases, Sr isotope studies of ancient VHMS systems also indicate derivation from underlying rock units (e.g. de Ronde 1995; Relvas et al. 2001), although the data do not exclude a magmatic–hydrothermal source component.

Radiogenic isotope data have been used to identify (and exclude) sources of components in hydrothermal systems. In some cases, they indicate multiple sources and are permissive of contribution of metals from both magmatic–hydrothermal and leached country rock sources.

Case studies

To assess the role of granites in the metallogenesis of VHMS deposits, we describe below the geology, alteration assemblages and isotopic geochemistry of selected deposits in line with the criteria outlined above. We have chosen these deposits as they span almost the entire period of geologic time during which VHMS deposits formed. They formed in a wide range of geodynamic environments and they illustrate a wide variety of geological and geochemical characteristics, including alteration and metallogenic assemblages. These case studies include both deposits with which the authors are familiar and others based on descriptions in the literature. Three of these case studies (Iberian Pyrite Belt, Mount Read Volcanics and Blake River Group) involved VHMS provinces with a wide variety of characteristics, implying that granites may have played quite different metallogenic roles even within districts or provinces.

Modern systems

Following the classification of Sillitoe et al. (1996), modern VHMS systems (Fig. 1) have been divided into high-sulphidation and low-sulphidation (i.e. quartz–chlorite–

sericite) systems. Low-sulphidation systems are most common, with examples including the deposits in the North Fiji Basin and most sites along mid-ocean spreading ridges. Sites of high-sulphidation mineralisation and alteration include Okinawa Trough, Palinuro Seamount, Lau Basin and DESMOS (Sillitoe et al. 1996; Hannington et al. 1999a, 2005). Examples discussed below in detail include Conical Seamount and DESMOS, which are examples of high-sulphidation systems. In addition, we describe sulphur isotope systematics of modern systems as a whole as these data provide important constraints on the extent of magmatic–hydrothermal contributions.

Conical Seamount, Tabar–Feni Island Chain, Papua New Guinea

Conical Seamount is a submarine alkali basalt volcano situated 10 km south of Lihir Island in the Tabar–Feni island chain, Papua New Guinea (Petersen et al. 2002). Polymetallic (Zn–Pb–Ag–Au–As–Sb) veins, pyritic stock-work and hydrothermally altered rocks discovered on the summit represent an unique example of submarine Au mineralisation with mineralogical, chemical and textural characteristics common to some subaerial epithermal systems (Herzig et al. 1998b, c; Petersen et al. 2002). The giant Ladolam epithermal gold deposit (42 Moz Au) is situated in the crater of an alkali stratovolcano on Lihir Island. Portions of the mineralisation and alteration assemblages at Ladolam are similar to those observed on Conical Seamount (Gemmell et al. 2004). Importantly, this deposit is the first known example of a modern system developed in an island arc setting (Herzig et al. 1994; Herzig and Hannington 1995; Petersen et al. 2002).

Conical Seamount consists of vesicular, coherent and brecciated pyroxene–phyric, alkali–olivine basalt and tra-chybasalt. Polymetallic (Zn–Pb–Ag–Au–As–Sb) veins, pyritic stockwork and hydrothermally altered rocks at the summit of Conical Seamount provide an example of submarine Au-rich mineralisation. Gold concentrations in samples from Conical Seamount reach 230 ppm, with an average of 25 ppm ($n=40$), and are the highest reported on the modern seafloor (Herzig et al. 1999; Petersen et al. 2002). Three stages of mineralisation are observed: (I) stockwork veins, veinlets and disseminations; (II) veins and disseminations; and (III) fracture fillings and vesicle infill (Petersen et al. 2002; Gemmell et al. 2004). The stage I assemblage consists of pyrite with variable marcasite associated with an alteration assemblage of illite/smectite and amorphous silica, with variable amounts of chlorite, kaolinite and alunite, and with trace aluminium phosphate minerals. The stage II assemblage contains chalcopyrite, galena, pyrite, Cu–Pb–As–Sb sulfosalts and native gold associated with an alteration assemblage of amorphous

silica–chalcedony, illite, smectite, adularia, secondary Na–K plagioclase, chlorite, kaolinite, barite and trace apatite. Stage III has realgar, alacranite, orpiment, stibnite, pyrite and overgrowths amorphous silica, but is not associated with obvious alteration assemblages (Petersen et al. 2002; Gemmell et al. 2004).

Conical Seamount has the lowest hydrothermal $\delta^{34}S_{sulphide}$ values (−17.5‰ to 6.1‰) known from modern seafloor hydrothermal systems (Petersen et al. 2002; Gemmell et al. 2004). Analyses of stage I pyrite varies from −17.5‰ to 6.1‰ (mean=−1.6‰), whereas $\delta^{34}S$ values of stage II base metal sulphide are more restricted, with a range of −9.5‰ to 3.9‰ (mean=−2.1‰: Gemmell et al. 2004). There is a systematic increase in $\delta^{34}S$ with successive paragenetic stages and with distance from the core of the hydrothermal system. A model by Petersen et al. (2002) suggested a contribution of magmatic volatiles in the earliest stages of mineralisation (stage I), followed by a combination of sulphur leached from the underlying volcanic rocks and reduced seawater sulphate during the main base and precious metal precipitating event (stage II). However, new sulphur isotope data of Gemmell et al. (2004) suggested a greater input of magmatic volatiles, plus boiling, throughout both stage I and II assemblages. The sulphur isotope data from Conical Seamount suggest that magmatic volatiles have contributed a significant amount of sulphur to this Au-rich, subaqueous hydrothermal systems (Gemmell et al. 2004).

DESMOS, Eastern Manus Basin, Papua New Guinea

The DESMOS caldera (Fig. 1) in the eastern Manus Basin, Papua New Guinea, contains a subaqueous, actively forming high-sulphidation system (Gamo et al. 1997; Gena et al. 1997, 1998; Gemmell et al. 1999). DESMOS is located in a 60-km-wide extensional zone of submarine volcanism between two transform faults in a back-arc environment to the north of the New Britain island arc (Binns and Scott 1993). The eastern Manus Basin contains three known active hydrothermal zones (PACMANUS, SuSu and DESMOS) and is becoming recognised as a regional-scale modern analogue for volcanic-hosted mineral districts in ancient back-arc environments (Gemmell 1995; Binns et al. 1997).

In 1990, hydrothermal activity was discovered at DESMOS, a mafic volcano that contains a north/north-west-trending 250-m-deep, 1.5×2.0-km summit caldera. Lavas at the caldera are basaltic andesites. A small but very active hydrothermal field, called Onsen, was discovered on the northern wall of the caldera at 1,930-m depth (Gamo et al. 1997). Extensive silicic and argillic alteration, with disseminated pyrite, is associated with hydrothermal vent-ing, but no massive sulphides were observed. In 1995, active white smokers were found to be venting extremely

acid (pH 2), sulphate-rich fluids at 88–120°C (Gamo et al. 1997). Hydrothermal plumes rich in CH_4, Mn and Al are present in the water column above DESMOS (Gamo et al. 1997). The presence of abundant SO_4 in combination with low δD and $δ^{34}S$ in the vent fluids, as well as total C/S and $CO_2/^3He$ values in the range of island arc magmatic fluids, led Gamo et al. (1997) and Ishibashi et al. (1998) to suggest that these fluids were of magmatic derivation. Subsequent alteration studies (Gemmell et al. 1999) identified advanced argillic alteration assemblages characterised by quartz, alunite, kaolinite–dickite, diaspore, native sulphur, pyrite and pyrophyllite.

Native sulphur occurring in vesicles and fractures in the DESMOS samples have $δ^{34}S$ values between −5.9‰ and −6.8‰ ($n=6$), making them the lowest $δ^{34}S$ values yet reported for native sulphur from the modern seafloor. These values are much lower than magmatic values and, in the

absence of biogenic sulphur and/or boiling, indicate a ^{34}S-depleted source of magmatic origin (Herzig et al. 1998a, b, c), possibly the consequence of SO_2 disproportionation. The DESMOS alteration assemblage (quartz, kaolinite–dickite, native sulphur, alunite, diaspore, pyrophyllite and pyrite) is a classic advanced argillic assemblage characteristic of high-sulphidation environments (Heald et al. 1987; Hedenquist and Lowenstern 1994; White and Hedenquist 1995).

Sulphur isotope systematics of modern systems

Sulphur isotope data for sulphide minerals and native sulphur from modern seafloor hydrothermal sites have a wide range of values (Fig. 4). $δ^{34}S$ values for sulphides for unsedimented mid-ocean ridges range from −1‰ to 11‰, whereas the range for sedimented mid-ocean ridges is −4‰
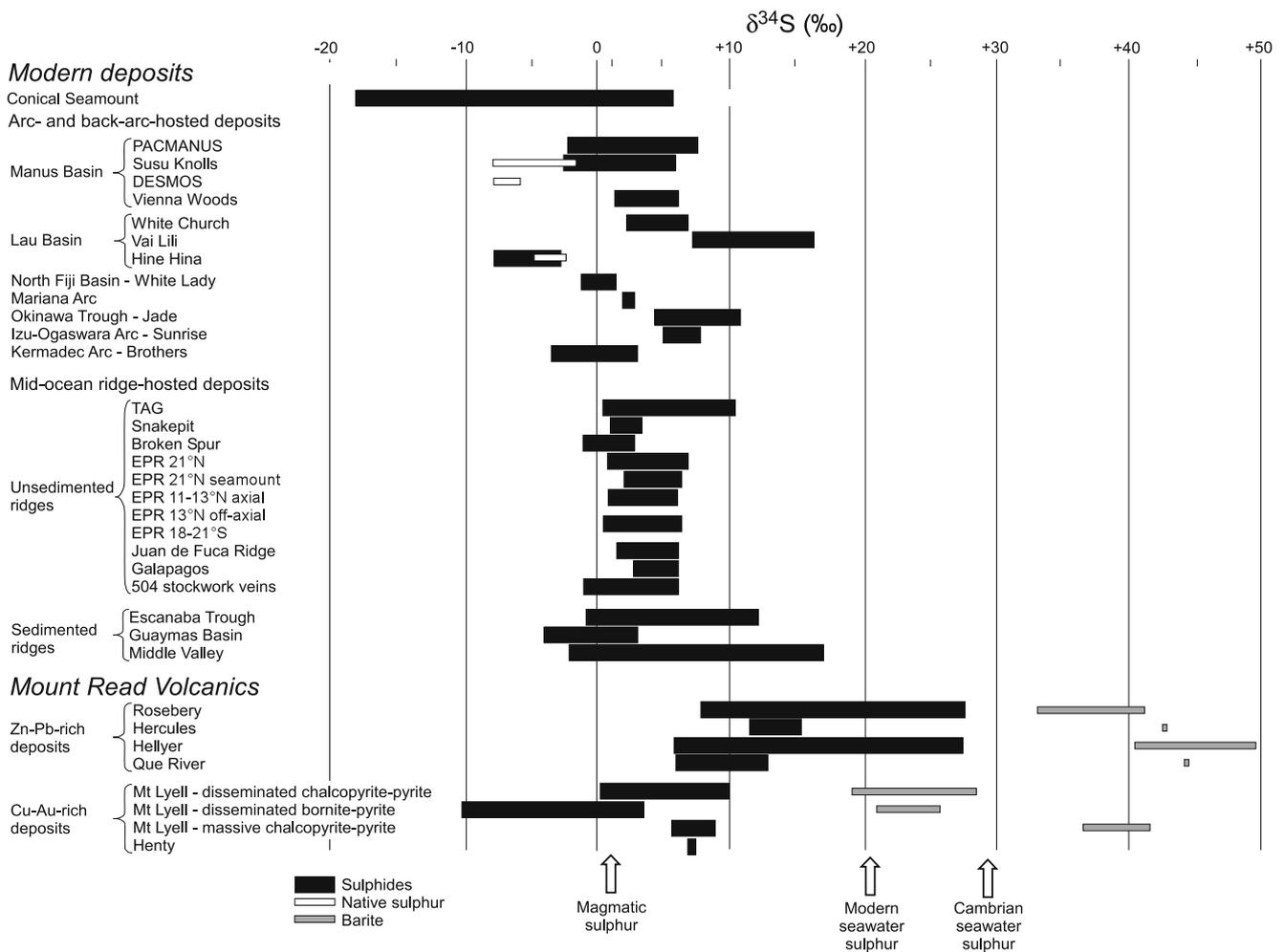
Fig. 4 Comparison of $δ^{34}S$ values for hydrothermal sites on mid-ocean ridges and arc environments on the modern seafloor and for deposits from the Cambrian Mount Read district, Tasmania. Diagram modified from Gemmell and Sharpe (1998) with additional data from Gemmell et al. (1999), Goodfellow et al. (1999), Iizasa et al. (1999), de Ronde et al. (2000), Solomon et al. (1969, 1988), Green et al. (1981) and Walshe and Solomon (1981)

to 17‰ (Shanks et al. 1995; Goodfellow et al. 1999). For mid-ocean ridge hydrothermal systems, Shanks et al. (1995) concluded that $\delta^{34}S$ values of vent fluid H_2S indicate that mid-ocean ridge basalt (MORB) sulphur is the principal sulphur source, with a small contribution from inorganically reduced seawater sulphate. For hydrothermal systems in the sedimented ridge environment, the sources of sulphur include MORB, inorganic reduction of seawater sulphate and a minor component of organically reduced seawater sulphate (Goodfellow and Franklin 1993; Shanks et al. 1995; Goodfellow et al. 1999).

Sulphides from seafloor hydrothermal systems forming in arc environments of the western Pacific have $\delta^{34}S$ values that range from −8‰ to 16‰ (Fig. 4). Herzig et al. (1998c) suggested that the light sulphur in sulphides ($\delta^{34}S=-7.3‰$ to −2.8‰, $n=12$) and native sulphur ($\delta^{34}S=-4.8‰$ to −2.4‰, $n=3$) from the Hine Hina site in the Lau basin implied a ^{34}S-depleted source of probable magmatic origin. Similar values from DESMOS caldera, as discussed above,

and somewhat higher values from the PACMANUS, SuSu Knoll and Brothers Volcano sites are also interpreted to indicate a magmatic–hydrothermal origin (Gamo et al. 1997; Gemmell et al. 1996, 1999; de Ronde et al. 2000; J.B. Gemmell, unpublished data).

These variations in $\delta^{34}S$ indicate that the sulphur in modern VHMS systems has a variety of sources, including reduced seawater sulphate, sulphide leached from volcanic and sedimentary rocks in the substrate and magmatic–hydrothermal sulphur. Of these, the first two appear to be most important in mid-ocean ridge-hosted systems, whereas in many systems currently forming in modern arc environments, magmatic–hydrothermal contributions could be more important.

Iberian Pyrite Belt

The Iberian Pyrite Belt (Fig. 5) is one of the most richly mineralised metallogenic provinces in the world, with
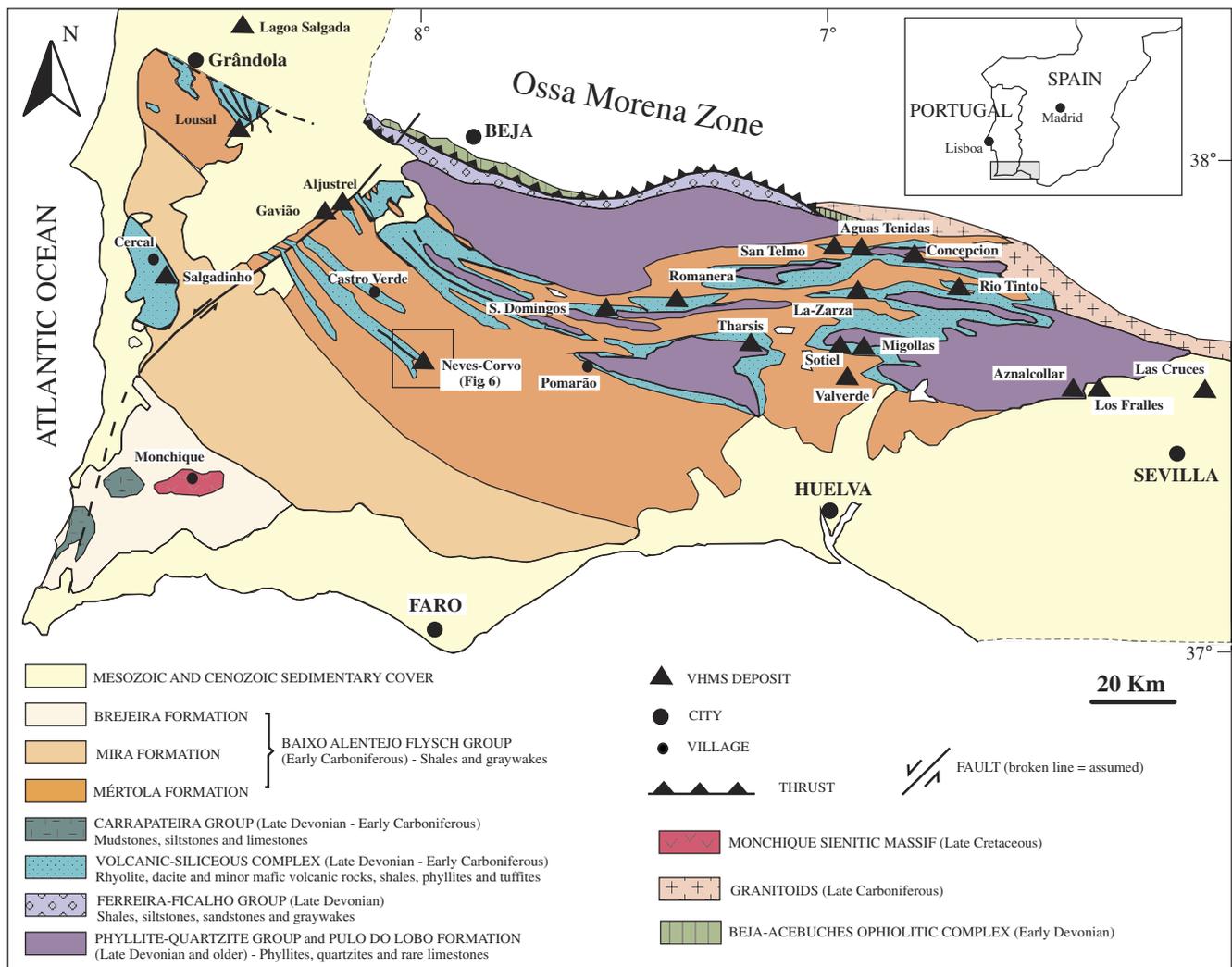
Fig. 5 Geology of the Iberian Pyrite Belt showing the location of deposits discussed in the text

global resources totalling over 21 Mt Cu, 34 Mt Zn, 12 Mt Pb and 0.8 kt Au contained in about 2,500 Mt of massive and stringer sulphides from 88 deposits (Tornos 2006). These deposits formed over a period of up to six million years during the Late Devonian (356–350 Ma: Tornos 2006; Barrie et al. 2002 and references therein). Ore formation was associated with left-lateral strike-slip faulting induced by an oblique collision that created locally extensional conditions and allowed the opening of an ensialic marine basin. Crustal thinning and magma under-plating provided long-lasting high heat flow and high regional geothermal gradients (Silva et al. 1990; Quesada 1998; Tornos et al. 2005), and extension favoured the rise and shallow emplacement of high-temperature, dominantly felsic magmas (Munhá 1983; Mitjavilla et al. 1997). These magmas drove hydrothermal fluid flow, including seawater convection and the dewatering of shale-dominated footwall sequences, resulting in up flow of brines along syn-depositional faults, focussing fluid flow and deposition upon mixing with seawater (Marcoux 1998; Sáez et al. 1999; Relvas 2000; Tornos et al. 2005).

Although the average Iberian Pyrite Belt deposit is strongly pyritic (28.4 Mt at 0.84% Cu, 1.36% Zn and 0.48% Pb: calculated from data in Tornos 2006), some deposits possess moderate to high base metal contents (e.g. Neves Corvo and Las Cruces). Most orebodies have lensoid morphology, although many of them were tectonically disrupted and/or stacked. Stratabound (e.g. Tharsis: Tornos et al. 1998; Neves Corvo: Relvas et al. 2006a) to cone-shaped (e.g. Rio Tinto: Garcia Palomero 1980; Aljustrel: Barriga and Fyfe 1988; Valverde: Toscano et al. 1993) ore-related hydrothermal alteration assemblages are classically zoned, with a chlorite (and local pyrophillite and/or donbasite) and/or quartz-rich core that is successively enveloped by sericite- and paragonite-rich zones. Typical IPB deposits formed from low to moderate temperature (70–270°C), low to moderate salinity (3–12 eq wt.% NaCl) and mildly acid fluids (Relvas 1991; Barriga and Relvas 1993; Leistel et al. 1998; Sánchez-España et al. 2000, 2003; Almodóvar et al. 1998). North to south variations in the relative abundances of volcanic to sedimentary rocks in the host sequences appear to have constrained the style of mineralisation within the Iberian Pyrite Belt (Tornos 2006).

With the exception of the Neves Corvo deposit, radiogenic isotopes (Pb, Nd, Sr and Os) indicate that the ore metals were derived from a homogeneous, relatively evolved crustal source (Relvas et al. 2001; Tornos and Spiro 1999; Tornos 2006; Mathur et al. 1999; Munhá et al. 2005). Similarities in lead isotopic compositions of the ores to both felsic volcanic and metasedimentary rocks strati-graphically below the host sequence (Marcoux 1998; Relvas et al. 2001; Jorge et al. 2007) suggest that these rocks or basement sourced the ore metals. Radiogenic

isotopic data are consistent with commonalities observed in metal ratios between these rocks and typical sulphide ores in the province (e.g. Tornos and Spiro 1999; Relvas et al. 2006a; Tornos 2006). Although oxygen and hydrogen isotopic signatures of the Iberian Pyrite Belt ore fluids are shifted relative to contemporary seawater values (e.g. Barriga and Kerrich 1984; Munhá et al. 1986; Sánchez-España et al. 2003; Relvas et al. 2006b), in most cases, these shifts are interpreted as a consequence of water–rock interaction, requiring no intervention of fluids other than deeply circulated seawater, connate waters equilibrated with the PQ siliciclastic sediments, low-grade dewatering fluids or combinations of these (e.g. Carvalho et al. 1999; Tornos and Spiro 1999; Relvas 2000; Tornos 2006; Tornos and Heinrich 2009).

In contrast to most Iberian Pyrite Belt deposits, the Neves Corvo deposit (Fig. 6) is enriched in both Sn and Cu, with Cu ratios of 50 significantly higher than the typical VHMS range of 15–25. Total Sn metal content totals 0.3 Mt, with extremely high Sn grades attained in stringer and massive cassiterite ores (to 60% Sn). Although these features make the Neves Corvo deposit truly unique among known Iberian Pyrite Belt deposits, the host sequence to the deposit is similar to that elsewhere in terms of geochem-istry, lithology and volcanology (Munhá et al. 1997; Rosa et al. 2008; Jorge et al. 2007). Given the similarity in geological setting but major differences in metal content, Relvas et al. (2006a, b) highlighted the "exotic" character of Sn, both with respect to other deposits in the Iberian Pyrite Belt and other Sn-bearing massive sulphide deposits, including Kidd Creek.

Although accessory cassiterite is present in a number of Iberian Pyrite Belt deposits, especially in the central and southernmost parts of the belt (e.g. Aljustrel, Aznalcollar, Romanera, Los Silos, Tharsis, Torrerera, Rio Tinto and Sotiel: Barriga 1983; Leistel et al. 1994; Marcoux et al. 1996), the cassiterite in these deposits is practically devoid of HFSE and occurs as very small inclusions in sphalerite. Collectively, these features suggest a metal-leaching origin for the tin in these deposits.

In contrast, at Neves Corvo, about two thirds of the tin occurs as relatively low-grade disseminated cassiterite associated with high-temperature Cu-rich ore, suggesting a link between Sn- and Cu-bearing ore fluids. The remainder occurs in an early (pre-main massive sulphide stage) generation of massive and stringer cassiterite, which was fed by independent Sn stockworks related to synvolcanic growth-faults (e.g. "tin corridor" of the Corvo orebody: Relvas et al. 2006a). To our knowledge, the massive and stringer cassiterite ores from the Neves Corvo tin corridor possess the highest tin grades (to 60% Sn; often above 25% Sn) ever reported in primary tin deposits in the world.
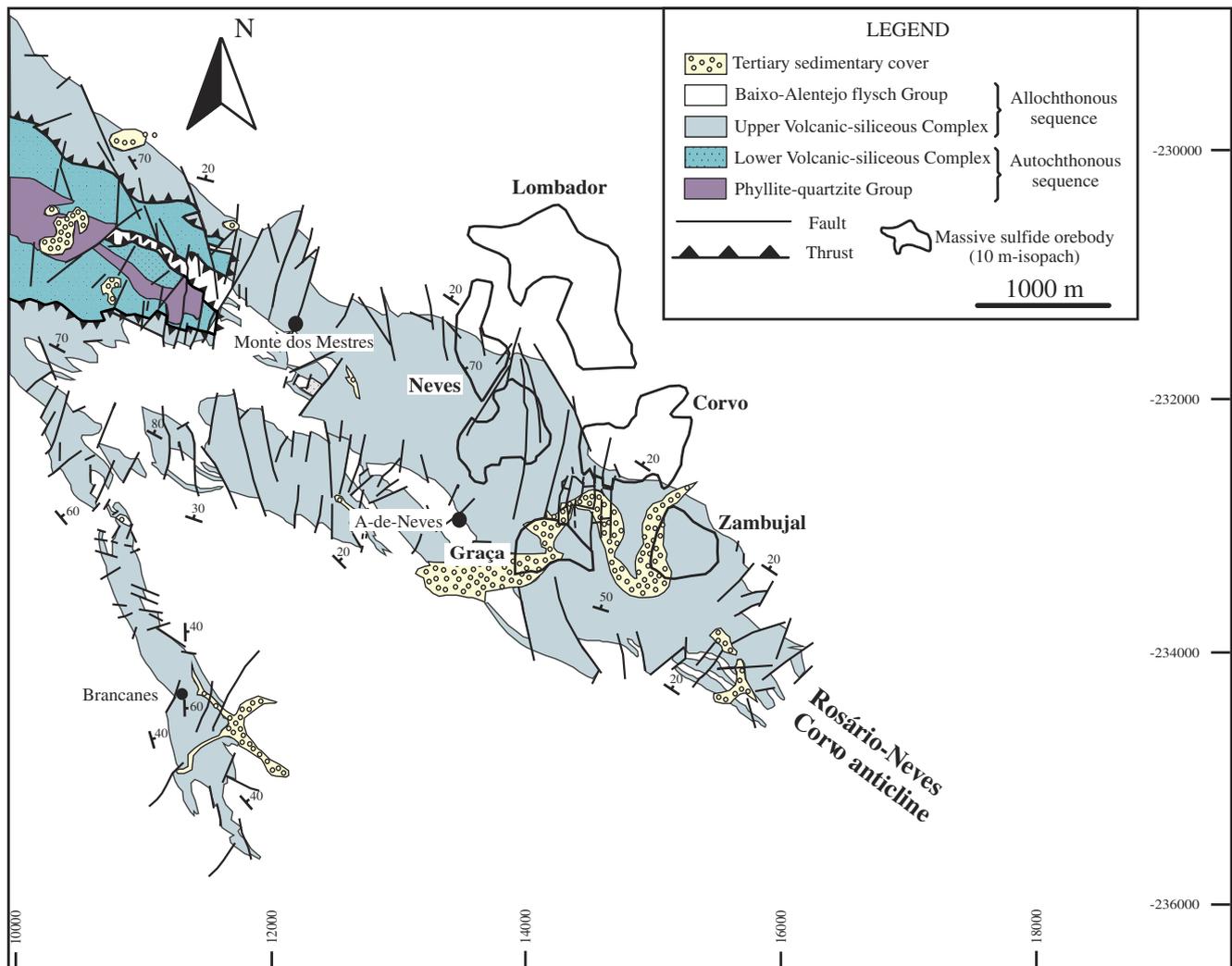
Fig. 6 Geologic map of the Rosário-Neves-Corvo anticline. The projection on surface of the massive sulphide ore 10-m isopach contour indicates location of the five Neves-Corvo orebodies (modified after Leca et al. 1983; Relvas et al. 2006a)

The origin of Sn in the Neves Corvo orebodies has not been convincingly determined, partly as a consequence of the absence of regional exposure. With the possible exception of intrusive bodies in the Campo Frio Complex, Spain, no plutonic rocks have been unequivocally established as being linked to Iberian Pyrite Belt felsic volcanism: The oldest exposed plutonic rocks in the Iberian Pyrite Belt postdate volcanism (Sáez et al. 1996 and references therein). However, Munhá et al. (1997) showed that the most differentiated Neves Corvo felsic volcanic rocks may be the surficial expression of a Sn-enriched granitic pluton at depth. This is supported by melt inclusions in quartz phenocrysts from felsic volcanic rocks, which raise the possibility of Sn-rich granites at depth (Tornos et al. 2004; Marques et al. 2008). None of these data, however, allow distinction between direct and indirect (wall rock pre-enrichment) magmatic contributions.

Fluid temperatures estimated by Relvas et al. (2006b) on the basis of oxygen isotope geothermometry for the massive sulphide stockwork at Corvo decrease from as high as 400°C in the central stockwork to <200°C in the periphery. These data indicate that the highest temperature part of this zone was characterised by ^{18}O-rich ore fluids with $\delta^{18}O_{fluid}$ of 8.3±1.5‰ and δD_{fluid} of −37‰ to −11‰ (Fig. 3; Relvas et al. 2006b). These values are most consistent with magmatic–hydrothermal fluids and are difficult to produce from seawater through known processes such as water–rock reaction or evaporation. As indicated by Fig. 3, the boiling curve does intersect the Neves Corvo field, but at a very low temperature, which is inconsistent with the known fluid temperatures of the Sn-rich central stockwork zone. The interpretation of a magmatic origin for these fluids is supported by the HFSE-rich character of Neves Corvo cassiterite, which is similar to cassiterite

from magmatic–hydrothermal Sn deposits, as discussed previously.

Mixing arrays in $\varepsilon_{Nd(350\ Ma)}$–Sm/Nd and $^{206}Pb/^{204}Pb$–$^{207}Pb/^{204}Pb$ diagrams indicate that sulphide and tin ore deposition involved ore-forming solutions with two distinct isotopic sources (Fig. 7). Relvas et al. (2001) interpreted one of these sources, characterised by less radiogenic Pb and less evolved Nd, to have been derived from sedimentary and volcanic rocks that stratigraphically underlie the ores. Relvas et al.

(2001) interpreted the second source, which is preserved in the Sn-rich ores and was characterised by highly radiogenic Pb and evolved Nd, to have been derived from an external source. This source, which is not present in other Iberian Pyrite Belts ores, is interpreted to be magmatic–hydrothermal fluids, basinal brines or metamorphic fluids that have circulated deeply through older basement rocks.

As described in other sections of this paper, most VHMS deposits with significant magmatic–hydrothermal contribu-

Fig. 7 Radiogenic isotopes diagrams for Neves Corvo (after Relvas et al. 2001). a $\varepsilon_{Nd}(T=350\ Ma)$ versus Sm/Nd diagram comparing the IPB "fresh" volcanic rock compositions (Mitjavilla et al. 1997) with those of Neves Corvo ores. The linear arrays illustrate the development of hydrothermal fluid source heterogeneities and (distinct) fluid mixing processes involved in Neves Corvo ore genesis. b, c Diagrams illustrating lead isotopic compositions for Neves Corvo cassiterites. Representative data of typical IPB sulphides is shown on the inset of c for comparison (small dots: $^{206}Pb/^{204}Pb = 18.133 \pm 0.021$, $^{207}Pb/^{204}Pb = 15.622 \pm 0.015$, $^{208}Pb/^{204}Pb = 38.191 \pm 0.049$; Marcoux 1998). The lead isotopic composition of typical IPB ores is similar to that of their felsic volcanic (VSC unit; Marcoux 1998) and metasedimentary (PQ unit; Jorge et al. 2007) host rocks. Neves Corvo copper ores (squares); Neves Corvo copper–tin ores (triangles); Neves Corvo stringer tin ores (circles); Neves Corvo massive cassiterite (stars)
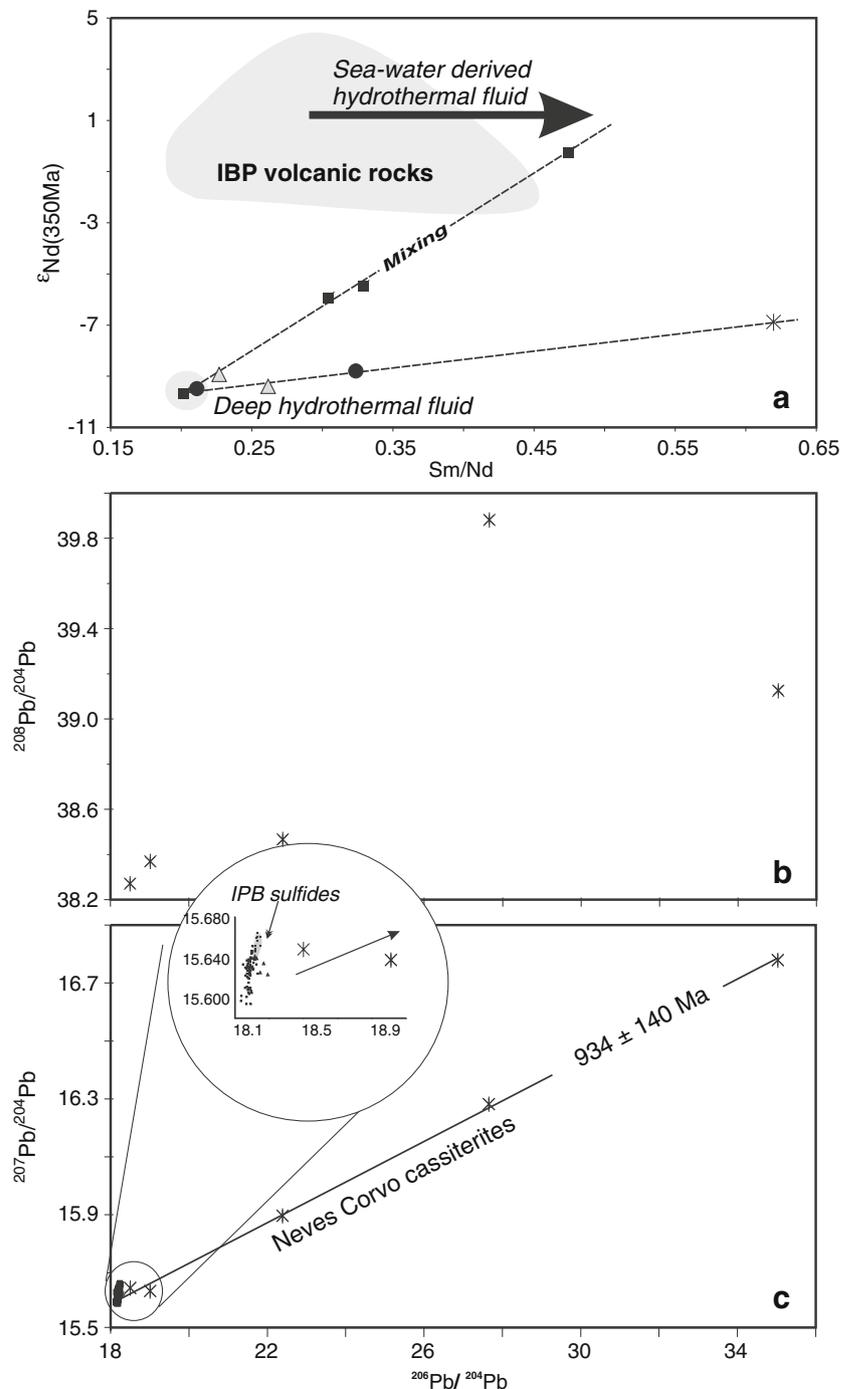
tions are characterised by advanced argillic alteration assemblages that are interpreted to have been caused by disproportionation of SO_2 in magmatic–hydrothermal fluids derived from oxidised magmas. The Neves Corvo lacks both of these characteristics. Unlike in typical porphyry–copper and epithermal systems, where magmatic SO_2 may dominate over H_2S (Ishihara 1981; Hedenquist 1995; Bodnar 1995; Candela and Piccoli 1995), magmatic fluids associated with Sn-rich granitic plutons are always reduced and contain H_2S as the dominant sulphur species (Heinrich et al. 1992; Hedenquist and Lowenstern 1994), which accounts for the lack of advanced argillic assemblages associated with the Neves Corvo deposit.

On balance, the metallogeny, alteration mineralogy and ore metal assemblages of most Iberian Pyrite Belt deposits is best accounted by hydrothermal systems dominated by seawater or expelled connate brines. There is no strong, unequivocal evidence of a magmatic–hydrothermal contribution to these systems. However, the unusually high Cu (relative to Zn) and Sn grades and the close association of Sn with Cu at the Neves Corvo deposit is strongly suggestive of a significant magmatic–hydrothermal component to the ore fluids. This inference is supported by the ^{18}O-rich character of the highest temperature ore fluids. Based on these data and the HFSE-rich character of Neves Corvo cassiterite, we consider that this deposit had a significant magmatic–hydrothermal component during formation. Importantly, as magmatic–hydrothermal Sn deposits are most commonly associated with reduced granites, advanced argillic alteration assemblages are not a necessary characteristic to infer a magmatic–hydrothermal component in VHMS systems.

Mountt Read Volcanics, Tasmania

The Cambrian Mount Read Volcanic Belt in western Tasmania (Fig. 8) is Australia's most significant VHMS province, with pre-mining global resources of 8.1 Mt Zn, 3.0 Mt Pb, 3.3 Mt Cu, 9.1 kt Ag and 278 tonnes Au (Seymour et al. 2007). The Mount Read deposits can be split into two groups according to their metallogeny: Zn–Pb and Cu–Au. Differences between these two groups extend beyond metallogeny to include differences in the form and style of the ore, in associated alteration assemblages, and in sulphur and lead isotope systematics.

In addition to having low Cu/(Cu+Zn) ratios, deposits of the Zn–Pb group, which includes the Hellyer, Que River, Rosebery, Hercules, South Hercules, Mt Charter and Tasman/Crown Lyell deposits, are characterised by massive stratiform ores that are dominated by pyrite, sphalerite, galena and barite and are confined to breaks in volcanic activity, as marked by fine-grained siliciclastic rocks and/or changes of volcanic composition

(Fig. 9a, b). These deposits are interpreted to have formed either at or just below the seafloor in response to the mixing of upwelling ore fluids with cold seawater (Green et al. 1983; Gemmell and Large 1992). The alteration zones associated with these deposits are dominated by quartz–chlorite±carbonate (e.g. Hellyer: Gemmell and Large 1992; Gemmell and Fulton 2001) and quartz–sericite–pyrite (e.g. Rosebery: Green et al. 1983; Large et al. 2001) assemblages. The form and associated alteration assemblages of these Zn/Pb-rich deposits are typical of "normal" VHMS deposits worldwide.

In contrast, the Cu–Au group of deposits, which include those in the Mount Lyell field, and the Garfield, Basin Lake and Henty–Mt Julia deposits (Fig. 8), are characterised mostly by disseminated stratabound ores that have replaced volcanic rocks. Important exceptions to this generalisation are the Blow and South Lyell deposits, the only stratiform massive sulphide bodies in the Mount Lyell field (Walshe and Solomon 1981). The most striking differences between the Cu–Au group and the Zn–Pb group are the ore and, particularly, alteration assemblages. Although most deposits of the Cu–Au group are dominated by a chalcopyrite–pyrite ore assemblage, zones within many orebodies contain significant bornite that is associated with minor to trace chalcocite, mawsonite, molybdenite, hematite, enargite and barite (Walshe and Solomon 1981; Manning 1990; Huston and Kamprad 2001). As first recognised by Cox (1981), many of the deposits in the Mount Lyell field contain significant pyrophyllite and topaz in alteration assemblages. After documenting the zonation of pyrophyllite and topaz (Fig. 9c) and recognising the presence of woodhouseite and zunyite at the Western Tharsis deposit, Huston and Kamprad (2001) initially suggested that the minerals were part of an advanced argillic alteration assemblage and that the Mount Lyell field was in part a high-sulphidation Cu–Au system. Since then, studies of the deeper parts of the Henty–Mt Julia gold system have documented similar advanced argillic alteration assemblages (Callaghan 2001), and K. Denwar (2007, personal communication) has documented similar alteration zonation in other deposits in the Mount Lyell field, suggesting that the Mount Lyell field and the Henty–Mt Julia deposit are expressions of the same high-sulphidation hydrothermal system, with the latter having formed in the upper levels of the system. The Basin Lake system, midway between the Henty deposit and the Mount Lyell field, is also characterised by advanced argillic assemblages (Williams and Davidson 2004).

In addition to the geological differences described above, the Zn–Pb and Cu–Au groups have systematic differences in stable and radiogenic isotopes. In general, sulphide minerals from the Zn–Pb group have significantly higher $\delta^{34}S$ values (8–19‰; ~15‰ depleted relative to coeval seawater) than those from the Cu–Au group (−11‰ to
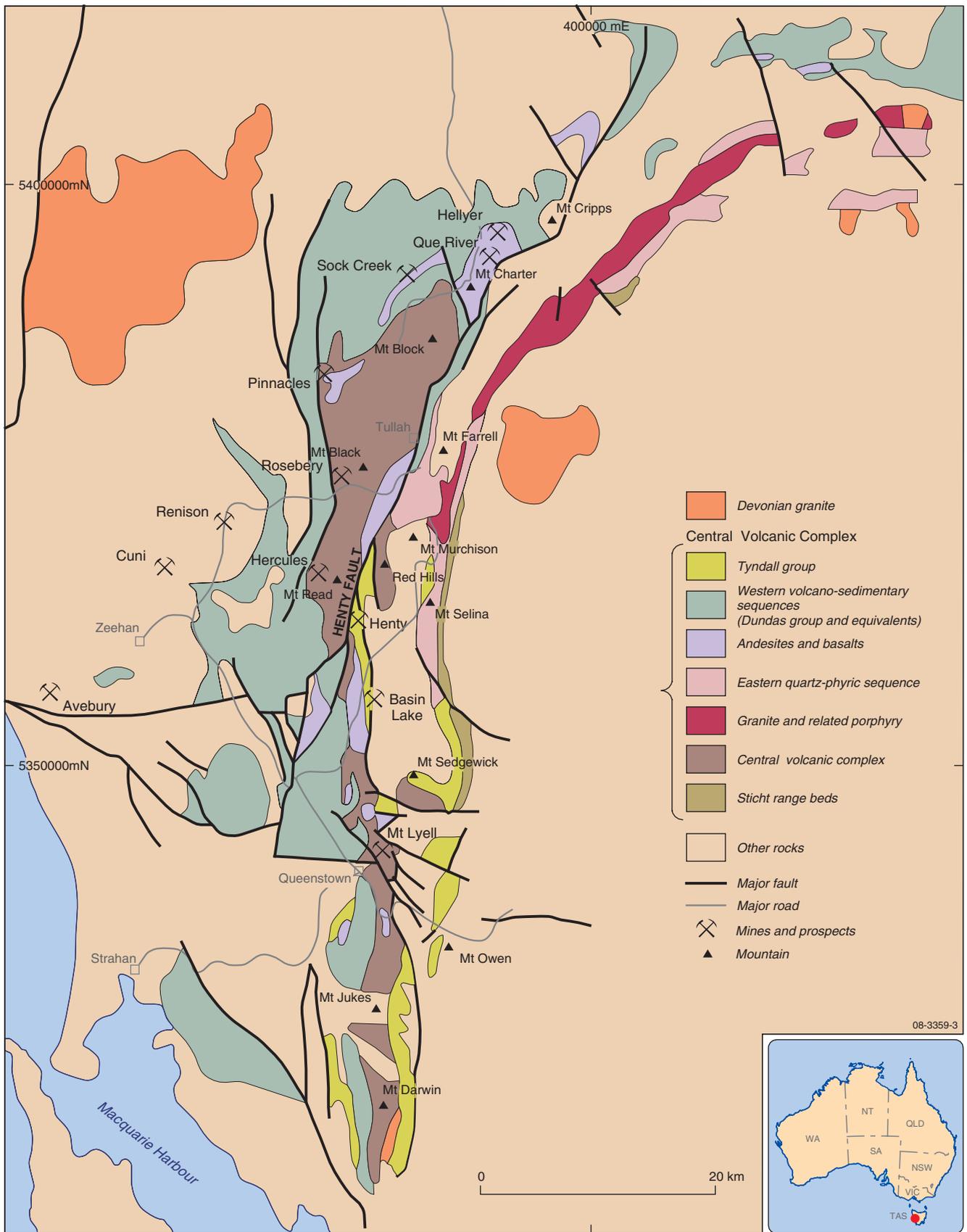
Fig. 8 Geology of the Mount Read Volcanics, western Tasmania, showing the location of major VHMS and related deposits and selected other deposits
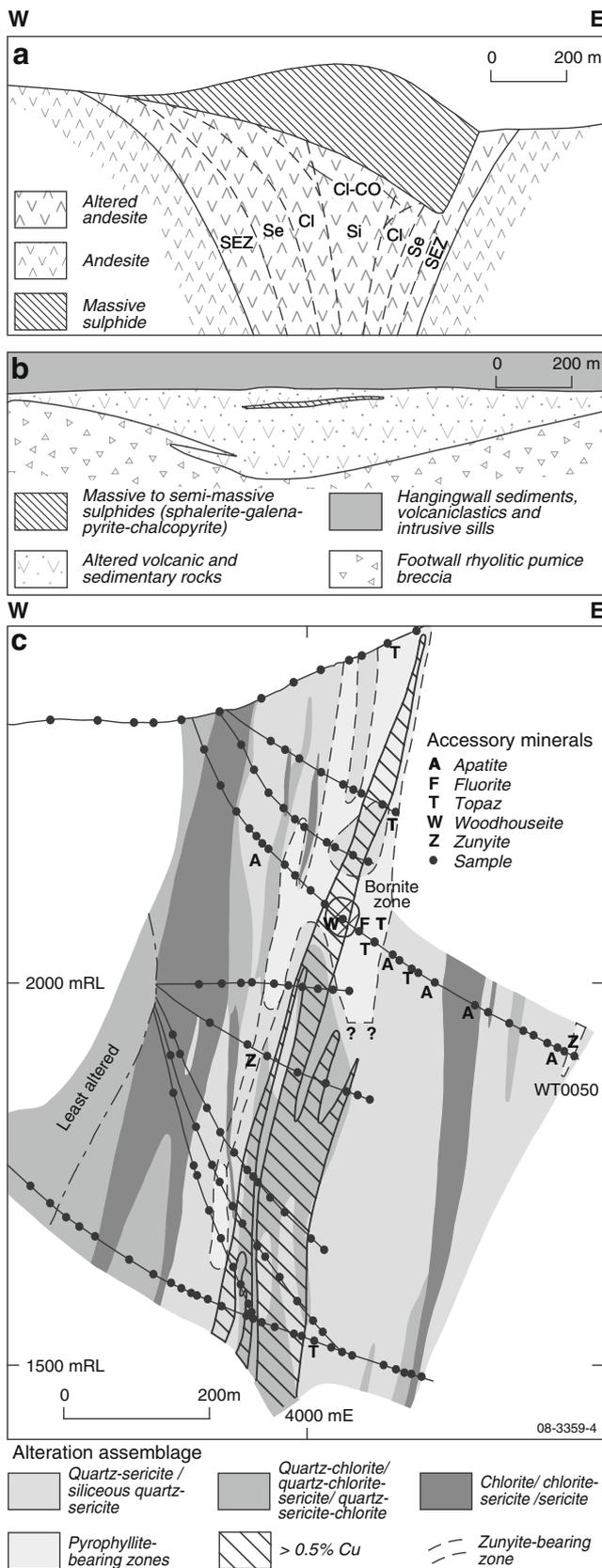
◀ **Fig. 9** Cross-sections of the Hellyer (after Gemmell and Large 1992) (**a**), Rosebery (after Large et al. 2001) (**b**) and Western Tharsis (after Huston and Kamprad 2001) (**c**) deposits. For (**a**), *SEZ* indicates the stringer envelope zone, *Se* indicates sericite-altered zones, *Cl* indicates chlorite-altered zones, *C–CO* indicates chlorite/carbonate-altered zones, and *Si* indicates the siliceous core

10‰). In the Cu–Au group, bornite-bearing assemblages tend to have lower values (−11‰ to 4‰, mostly −8‰ to 2‰; ~30‰ depleted relative to coeval seawater) than assemblages that lack bornite (5–10‰; Solomon et al. 1969, 1988; Green et al. 1981; Walshe and Solomon 1981). Moreover, barite from Zn–Pb group deposits tends to have significantly higher $\delta^{34}S$ values (33–47‰) than barite from Cu–Au group deposits (19–30‰). The only exception is The Blow deposit which has barite $\delta^{34}S$ (37–41‰) more similar to those of Zn–Pb group deposits. These data suggest two discrete sulphur sources for the Zn–Pb and Cu–Au deposits.

Gulson and Porritt (1987) recognised systematic differences in lead isotope ratios of Zn–Pb and Cu–Au deposits in the Mount Read Volcanics. Of the major deposits, Rosebery and Hercules had the least radiogenic lead, whereas the Mount Lyell and Henty deposits had the most radiogenic lead, with the Que River and Hellyer deposits having intermediate, though possibly slightly more primitive, compositions (Fig. 10). Importantly, small Zn–Pb orebodies in the Mount Lyell field differed from the Cu–Au orebodies in having similar lead isotope characteristics to the Rosebery and Hercules deposits. This suggests that
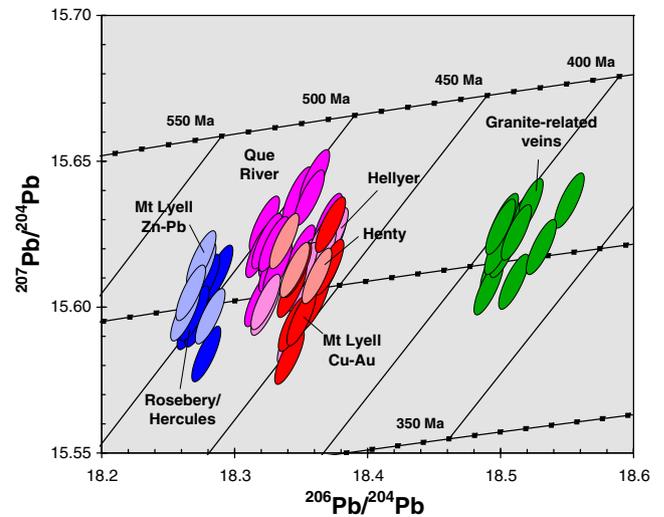
Fig. 10 $^{206}Pb/^{204}Pb$ versus $^{207}Pb/^{204}Pb$ diagram showing lead isotope characteristics of selected deposits from the Mount Read Volcanics, western Tasmania (data from Gulson and Porritt 1987), and lead isotope evolution curves. The evolution curved were calculated for μ of 12.10, 12.25 and 12.40 using a modified Cumming and Richards (1975) model fitted using the Rosebery deposit as a pinning point ($\varepsilon = 0.07985 \times 10^{-9}$). Isochrons are shown as *light lines*. *Ellipses* indicate 2σ analytical error

either the Cu–Au deposits were either younger or had a different lead source to the Zn–Pb orebodies, both in the Mount Lyell field and more generally in the Mt Read volcanic belt.

Geological, geochemical and isotopic data all point to major genetic differences between Zn–Pb and Cu–Au group deposits in the Mount Read Volcanics. The forms, metal associations and alteration assemblages of Zn–Pb group deposits are fairly typical of "normal" VHMS deposits worldwide. Sulphur isotope values of sulphide minerals have been interpreted as a mixture between reduced Cambrian seawater sulphate and sulphur dissolved from underlying volcanic rocks, and the barite $\delta^{34}S$ values have been interpreted as sourced from Cambrian seawater (Solomon et al. 1988). As there is no a priori reason to invoke a magmatic–hydrothermal component to account for the metal association, alteration assemblages or sulphur isotope systematics, we interpret the Zn–Pb group of the deposits in the Mount Read Volcanics to have formed by circulation of (evolved) seawater, without a significant magmatic–hydrothermal component.

In contrast, the alteration assemblages associated with the Cu–Au group of deposits are not typical of VHMS assemblages, having more in common with advanced argillic assemblages associated with high-sulphidation epithermal deposits. Moreover, sulphur and lead isotope data suggest that these components of the hydrothermal system had a different source to Zn–Pb group deposits. In particular, the barite $\delta^{34}S$ values are not compatible with a Cambrian seawater source. An alternative source, which is also compatible with $\delta^{34}S_{sulphide}$ values, is a disproportion-ation from SO_2, a mechanism that would also have produced the highly acidic fluids required to form the advanced argillic alteration assemblages in the Mount Lyell field and at the Henty–Mt Julia deposit. The fractionation between sulphate and sulphide minerals in the Mount Lyell system is broadly compatible with that noted between these minerals in porphyry copper deposits (12–20‰: Ohmoto and Rye 1979). More radiogenic lead isotopes in the Cu–Au orebodies relative to those in small Zn–Pb orebodies are consistent with two different lead sources in the Mount Lyell field, with the source of the Rosebery-like Zn–Pb orebodies most likely leaching of volcanic rocks, as discussed above. The other source could possibly have been a magmatic source, although the data are not diagnostic. Hence, lead and, particularly, sulphur isotope data, when combined with the advanced argillic alteration assemblages, suggest a significant magmatic–hydrothermal component for the Mount Lyell Cu–Au and, by analogy, the Henty–Mt Julia Au deposits. These results are compatible with the results of Large et al. (1996) who suggested a magmatic–hydrothermal component to the Mount Lyell system based on the presence of magnetite–apatite assemb-

lages in the ores and a similar assemblage spatially associated with Cambrian granites (see above).

Blake River Group, Abitibi Suprovince, Québec

The ~2700 Ma Blake River Group in western Quebec contains two well-studied VHMS districts, the Noranda and Doyon-Bousquet-LaRonde districts (Fig. 11), that are characterised by major differences in metallogeny, alter-ation assemblages and structural overprinting.

The ~2702 Ma Noranda district contains 18 small to medium deposits and one large deposit (Horne) that are hosted by rhyolitic, andesitic and basaltic volcanic rocks that form the Noranda cauldron (Kerr and Gibson 1993: Fig. 11, inset A). Other than contact metamorphic effects associated with emplacement of the Lac Dufault Granodi-orite, the Noranda district is characterised by greenschist or lower facies metamorphism; hence, many of the original volcanic, alteration and ore textures are preserved. The smaller deposits tend to be associated with coherent lavas, whereas the larger deposits (e.g. Horne and Mobrun) tend to be spatially associated with volcaniclastic rocks (Kerr and Gibson 1993; Larocque et al. 1993). Proximal alteration assemblages associated with Noranda VHMS deposits tend to form pipe-like chloritised and/or sericitised zones (Kerr and Gibson 1993). Regional hydrothermal alteration assemblages, which include chlorite-bearing, epidote/quartz-bearing and silica-rich assemblages, form semi-conformable zones that can be traced for tens of kilometres from proximal alteration zones associated with VHMS deposits (Gibson 1990; Paradis et al. 1993). These assemblages are typical of regional and proximal alteration assemblages associated with "typical" VHMS deposits (cf. Galley 1993).

The Noranda Cauldron is associated with the Flavrian-Powell Intrusive Complex, a polyphase sill complex that both accompanied and postdated the development of the cauldron. Galley (2003) documented six intrusive phases and, based on geological and isotopic data, suggested that VHMS formation was temporally associated with the earliest quartz diorite phase. Geological relationships suggest that emplacement of the trondjhemitic phase, which comprises the majority of intrusive complex, postdated VHMS deposition (Galley 2003). Sub-economic porphyry-related (Don-Rouyn) and breccia-hosted (St Jude) Cu–Mo deposits are associated with the later trondjhemitic phase and therefore postdate VHMS mineralisation (Galley 2003).

In contrast, the ~2698 Ma Doyon-Bousquet-LaRonde district contains only four VHMS deposits (Fig. 11, inset B), but these deposits are larger than the deposits in the Noranda district. The deposits in this district are also highly strained and have undergone higher grade metamorphism (upper greenschist to lower amphibolite) relative to the
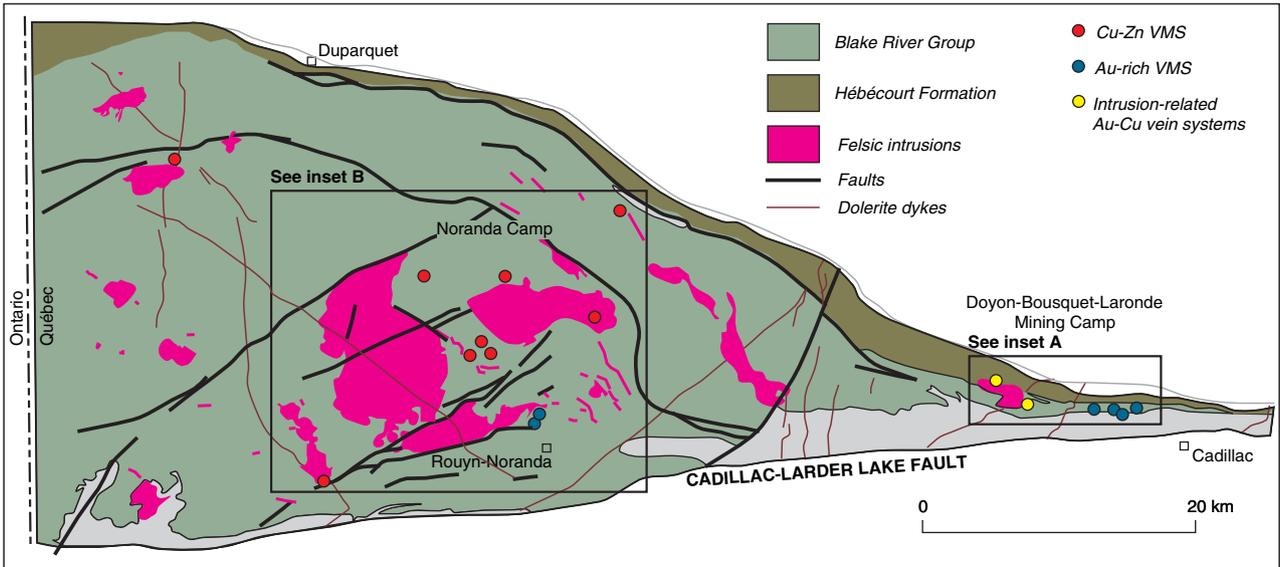
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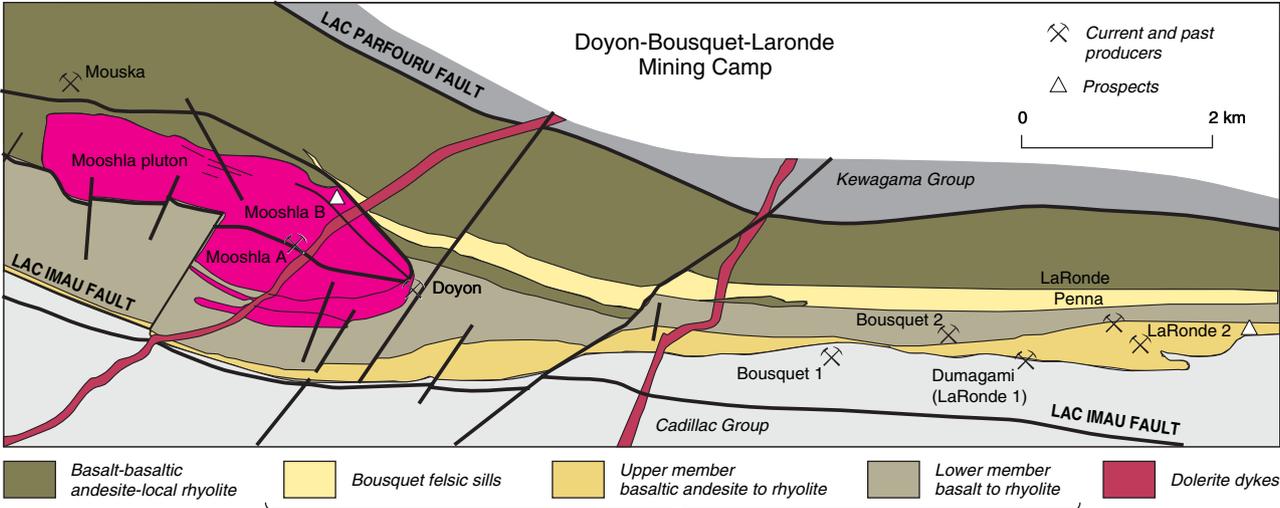
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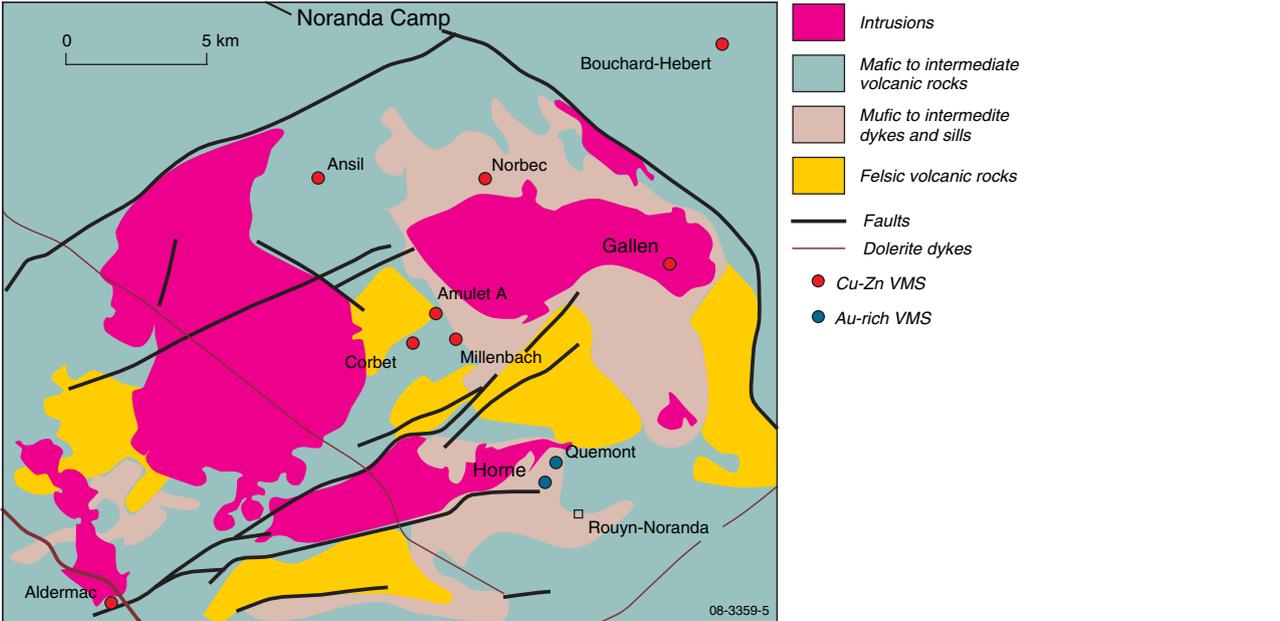
deposits in the Noranda district (Mercier-Langevin et al. 2007a). The deposits are relatively base metal-poor (0.3–0.6% Cu; 0.4–2.2% Zn), but tend to be Au-rich (4.3–8.1 g/t: Mercier-Langevin et al. 2007a; Franklin et al. 2005), contrasting with higher base metal (0.1–7.2% (mostly 0.8–5.0%) Cu; 0.0–8.6% (mostly 0.8–8.6%) Zn: Franklin et al. 2005) and more variable Au (0.03–6.9 g/t: Franklin et al. 2005) grades in the Noranda district.

The VHMS deposits in the Doyon-Bousquet-LaRonde district are hosted by the upper part of the basaltic to rhyolitic lower member or in the andesitic to rhyolitic upper member of the Bousquet Formation, which overlies mafic-dominated volcanic rocks of the Hébécourt Formation. The boundary between these two units is the contact between underlying tholeiitic and overlying calc-alkaline volcanic rocks (Mercier-Langevin et al. 2007b).

The intrusion-related Doyon deposit (Gossselin 1998; Galley and Lafrance 2007) consists of stockwork Au-rich chalcopyrite–pyrrhotite–quartz veins hosted mostly by volcanic rocks of the lower member of the Bousquet Formation. As these stockworks are cut by chloritic dikes related to the latest phase of the Mooshla intrusive complex (Gossselin 1998), they were emplaced during the late phase of this intrusive complex (Galley and Lafrance 2007). Like the VHMS deposits, alteration zones associated with the Doyon deposit are characterised by metamorphosed, aluminous advanced argillic alteration assemblages (now quartz–kyanite–andalusite assemblages). In the VHMS deposits, proximal aluminous assemblages (Tourigny et al. 1989; Marquis et al. 1990; Dubé et al. 2007) grade outward to quartz-muscovite±garnet-bearing assemblages. These aluminous alteration assemblages differentiate deposits of the Doyon-Bousquet-LaRonde district from the Noranda district and the vast majority of other VHMS deposits worldwide.

The sub-volcanic Mooshla intrusion comprises phases with a compositional range from gabbro to tonalite (Galley and Lafrance 2007). Compositionally, the tholeiitic early and intermediate phases are compatible with the Hébécourt Formation and lower member of the Bousquet Formation, whereas the late tonalitic and calc-alkaline phases are compatible with the upper member of the Bousquet Formation (Lafrance et al. 2003; Galley and Lafrance 2007). As noted by Mercier-Langevin et al. (2007b), the upper member of the Bousquet Formation is characterised by type FII (Lesher et al. 1986) rhyolites, which differ from the type FIII rhyolites characteristic of the Noranda district. Galley and Lafrance (2007) found that the late phases of the Mooshla intrusive complex were characterised by miarolitc

cavities that contain pyrite and chalcopyrite, suggesting that these phases were volatile-rich.

Despite their spatial (40 km) and temporal (coeval, within error) proximity, the Noranda and Doyon-Bousquet-LaRonde districts differ substantially in terms of metallogeny, alteration assemblages and, probably, location within the tectonic setting. Moreover, geological and geochemical evidence suggests that deposits of the Doyon-Bousquet-LaRonde district had a significant magmatic–hydrothermal contribution, whereas those in the Noranda district did not. Evidence favouring a magmatic–hydrothermal contribution to the Doyon-Bousquet-LaRonde district includes metamorphosed aluminous, advanced argillic alteration assemblages and the transition from an intrusion-related deposit through increasingly Zn-rich Au/Cu-rich VHMS deposits stratigraphically and laterally away from the Mooshla intrusive complex. In contrast, the relatively Zn-rich VHMS deposits of the Noranda district are characterised by chlorite-bearing alteration assemblages, with no evidence in the ores or alteration assemblages of a significant magmatic–hydrothermal contribution to the hydrothermal system. Moreover, magmatic–hydrothermal Cu–Mo deposits hosted by the Flavrian-Powell intrusive complex postdate the VHMS ores.

Kidd Creek, Abitibi Subprovince, Ontario

The ~2714 Ma Kidd Creek deposit in the Abitibi-Wawa Subprovince of eastern Canada is one of the largest known VHMS deposits, with global resources of 148 Mt grading 6.18% Zn, 0.22% Pb, 2.31% Cu and 87 ppm Ag, with significant Sn (~0.14%: Hennig and Hutchinson 1999) and In credits (Franklin et al. 2005). The ore lenses overlie an extensive zone of "cherty breccia", highly silicified rhyolitic rock with minor chlorite. However, as the ore zone is approached, the amount of chlorite increases. The hanging wall rocks to the ore lenses are typically quartz–sericite altered (Koopman et al. 1999). Aside from the highly siliceous character of the altered rocks, this alteration assemblage is typical of VHMS deposits as a whole.

However, parts of the Kidd Creek orebodies have quite unusual geochemical assemblages. In particular, the core of the South orebody is characterised by a bornite-rich replacive zone marked by a complex Cu–Co–Bi–Se–Ag–As–Ni assemblage. Hannington et al. (1999b) interpreted that this zone formed under peak hydrothermal conditions during the influx of high-temperature (350–400°C), Cu-rich fluids. They suggested that possible sources of metals comprising the bornite zone include (1) leaching of country as the hydrothermal circulation cell deepened, (2) condensation of a metal-rich brine during deep-level phase separation or (3) direct magmatic–hydrothermal contributions. Although they noted that the most likely source of Se was magmatic–hydrothermal fluids, the lack of a nearby

intrusion combined with the structural dismemberment of the hydrothermal system precluded a definitive assessment of the role of magmatic–hydrothermal fluids.

Huston and Taylor (1999) also suggested that the Kidd Creek ore fluids could have contained at most 20% magmatic–hydrothermal fluids based on δD_{fluid} estimated from δD values of chlorite closely associated with chalcopyrite-rich stringers. However, this assumes that the δD of Archean seawater was similar to that of modern day seawater, an assumption that may not hold.

Hence, at Kidd Creek, geological and geochemical data are compatible with a significant contribution (to 20%) of magmatic–-hydrothermal fluid. However, the data are not definitive of such a contribution as the data can be interpreted in other ways or later structural complexity precludes resolution of possible magmatic contributions. We consider Kidd Creek to be an example of a system dominated by evolved seawater with a possible small, though significant, magmatic–hydrothermal contribution to account for the Se-rich character of the bornite zone.

Panorama, East Pilbara Province, Western Australia

The Panorama district in the East Pilbara province of Western Australia, the oldest significant VHMS district known (~3240 Ma), is one of the best exposed and well-documented VHMS hydrothermal system in the world. The nearly unique combination of extensive exposure of the hydrothermal system, including the coeval Strelley Monzogranite (Fig. 12), and low metamorphic grade have
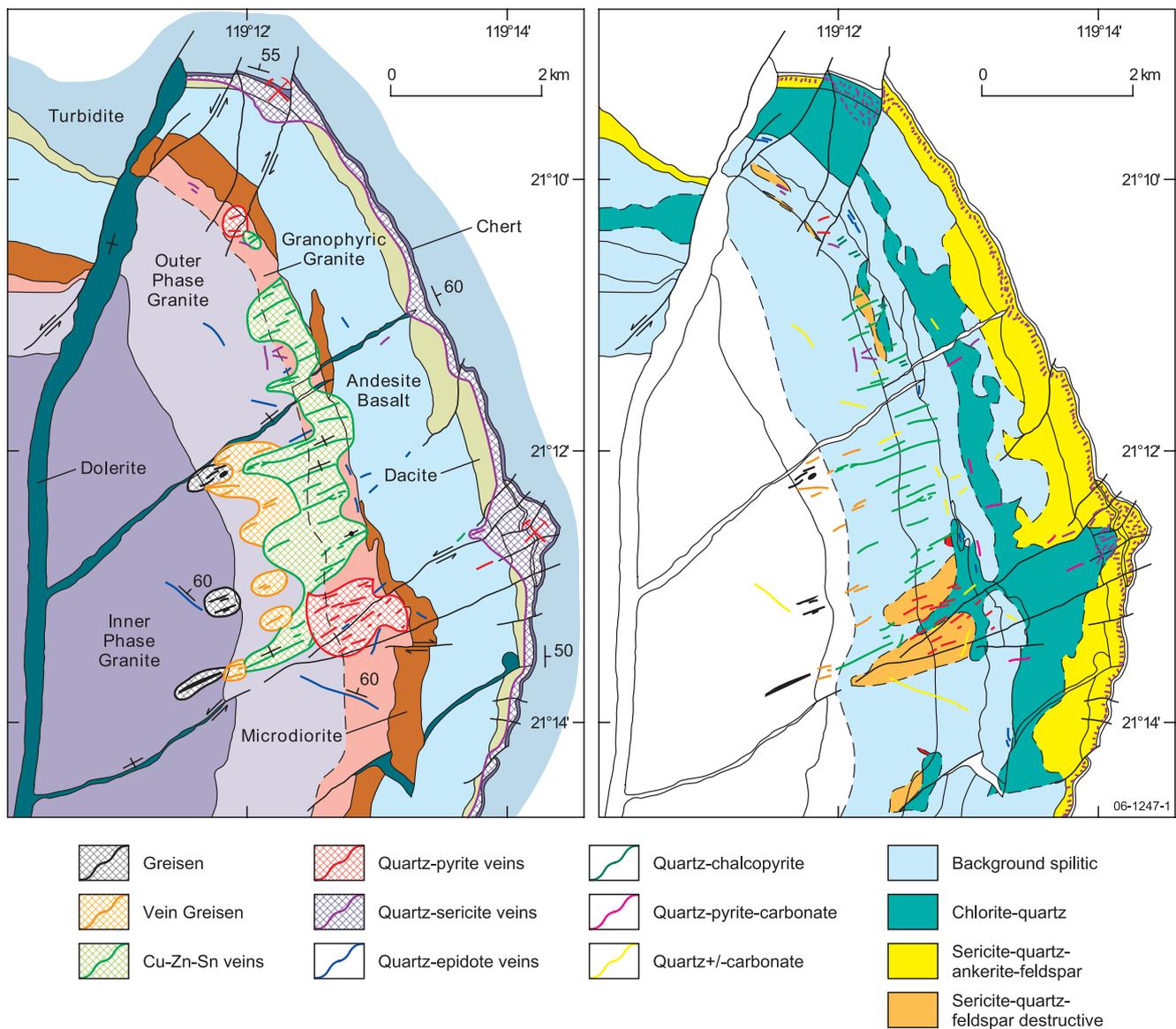
Fig. 12 Maps showing the distribution of alteration assemblages and veins in the Pilbara VHMS district, Pilbara, Western Australia

allowed Brauhart et al. (1998, 2000, 2001), Huston et al. (2001) and, particularly, Drieberg (2003) to document the interplay between magmatic–hydrothermal fluids and evolved seawater.

Drieberg (2003) used a combination of geological observations, fluid inclusion data and stable isotope data to distinguish fluid types and their origins. She recognised two periods of magmatic–hydrothermal activity that were spanned by convective flow of evolved seawater. The first magmatic–hydrothermal event involved devolatilisation of the slightly older outer phase monzogranite to form miarolitic cavities, aplite dikes and pegmatites. Fluids associated with these magmatic–hydrothermal manifestations were highly saline (31–65 eq wt.% NaCl), ^{18}O-rich ($\delta^{18}O_{fluid} \sim 9$‰) and enriched in zinc, lead and copper (Drieberg. 2003). Drieberg (2003) also interpreted quartz chalcopyrite veins near the upper contact with the volcanics as related to this magmatic–hydrothermal event, noting that the fluids that formed these veins were saline (4–9 eq wt.% NaCl) and ^{18}O-rich ($\delta^{18}O_{fluid} \sim 4$–5‰). However, the rarity of quartz–chalcopyrite veins and the lack of these fluids in the overlying volcanic pile suggest that the amount of magmatic–hydrothermal fluid was limited and did not egress into the evolved seawater-dominant hydrothermal system in the volcanic pile.

Magmatic–hydrothermal activity associated with the inner phase monzogranite was more extensive, producing vertically extensive, well-zoned vein alteration systems that can be traced from the inner phase into the outer phase granite, but generally not into the volcanic pile. Pod-like to linear zones of quartz–topaz, quartz–fluorite and quartz–muscovite greisen are localised below the inner–outer phase contact, and this system extends into the lower part of the outer phase where it is characterised by quartz greisen with malachite staining at surface. Quartz–chalcopyrite–sphalerite–cassiterite veins also initiate at the base of the outer phase granite and extend to the base (and locally into) the base of the volcanic pile. Drieberg (2003) interpreted these greisens and veins as a zoned hydrothermal system associated with the emplacement of the inner phase monzogranite. Fluids that formed greisens within the inner phase monzogranite were highly saline (30–58 eq wt.% NaCl) and ^{18}O-rich ($\delta^{18}O_{fluid} \sim 6$–9‰). Both salinity and δ^{18}O decrease upwards through the outer phase granite, with fluids that formed the quartz–sulphide–cassiterite veins having salinities of 3–14 eq wt.% Nacl and δ^{18}O ~ 2–6‰. Drieberg (2003) interpreted these variations to indicate progressive mixing of magmatic–hydrothermal fluids with evolved seawater.

Importantly, Drieberg (2003) did not find evidence of a significant magmatic–hydrothermal component in the overlying volcanics. Rather, she documented lower salinity fluids (5–11 eq wt.% NaCl) with lower δ^{18}O (−3‰ to 3‰)

in the volcanic pile, consistent with evolved Archean seawater. This result is also consistent with whole rock δ^{18}O patterns of Brauhart et al. (2000) that suggest that hydrothermal circulation in the volcanic pile was dominated by evolved seawater. The Panorama δD (−36‰ to −23‰) values of fluids within the volcanic pile are significantly lower than those for Phanerozoic VHMS ore fluids; however, this could be due to secular variation in $\delta D_{seawater}$ (Drieberg 2003).

Hence, in the Panorama district, which is characterised by "normal" metal (Zn–Cu–Pb–Ag±Au) and alteration assemblages (quartz–chlorite and quartz–sericite), the magmatic–hydrothermal system appears to have been separate to the seawater-dominated hydrothermal system, even though apparently coeval. These results suggest either that the magmatic–hydrothermal system was vastly smaller than the convecting seawater system or that the two systems were physically separated. Drieberg (2003) found that the density of the magmatic–hydrothermal fluid (1.4 g/cm^3) was significantly greater than the fluids in the volcanic pile (0.9–1.0 g/cm^3), suggesting that although density contrasts allowed magmatic–hydrothermal fluid to ascend through the inner and outer phase monzogranites, it would have been too dense to mix extensively with the overlying evolved seawater convective system.

These interpretations are supported by whole rock geochemical analyses of Brauhart et al. (2001) and Huston et al. (2001) who documented a zone of Zn, Cu, Pb and S leaching at the bottom of the volcanic pile that is spatially associated with quartz–chlorite alteration assemblages formed by the passage of high-temperature evolved seawater. These workers demonstrated that the total amount of metal lost in these zones greatly exceeds the amount of metal present in the deposits, suggesting that a magmatic–hydrothermal input of metal, even Cu and Mo, is not required to form the deposits. These data, combined with the fluid inclusion and isotopic data of Drieberg (2003), suggest a separation of magmatic–hydrothermal activity from evolved seawater circulation that resulted in the Panorama VHMS deposits.

An assessment of criteria used to postulate magmatic–hydrothermal contributions to VHMS deposits

Our analysis of criteria that have been used to advocate major magmatic–hydrothermal contributions to VHMS deposits indicates that in many cases, these criteria are equivocal. Moreover, criteria used to exclude a major magmatic–hydrothermal component in VHMS systems are also generally equivocal. However, there does seem to be overwhelming evidence in many VHMS systems, from

both geochemical and isotopic studies, that evolved seawater was the main ore fluid component and ore metals and sulphur were stripped as it circulated within the rock pile below the ore position. These processes account for the characteristics of "typical" VHMS deposits, that is those associated with proximal quartz–chlorite–sericite–pyrite alteration assemblages that formed from low- to moderate-salinity (0.5–3.0 times that of modern seawater) fluids with $\delta^{18}O < 4‰$. Formation of these deposits does not require a significant magmatic–hydrothermal component, as demonstrated in the Panorama district.

Deposits that are most likely to have a significant magmatic–hydrothermal component are those that deviate significantly from this norm. The most compelling criteria for such a component are evident in the hydrothermal system for the disproportionation of magmatic SO_2. This evidence includes the presence of aluminous (meta-)advanced argillic alteration assemblages and sulphur isotope characteristics, including $\delta^{34}S_{sulphide}$ consistently <0‰, $\delta^{34}S_{sulphate}$ different from that of coeval seawater sulphate and $\Delta^{34}S_{sulphate–sulphide} \sim 20$–30‰. We interpret these characteristics as compelling evidence of a major magmatic–hydrothermal component in VHMS systems, particularly if most or all are present. Deposits with these characteristics correspond to high-sulphidation-type VHMS deposits, which Sillitoe et al. (1996) also interpreted as having a major magmatic–hydrothermal component.

Other, less compelling, evidence for magmatic–hydrothermal contributions to VHMS deposits include enrichment of Cu relative to Zn, high Sn abundances combined with magmatic trace element characteristics of cassiterite, extreme enrichment of ore fluids in ^{18}O ($\delta^{18}O >$ 5‰) and consistently elevated ore fluid salinities relative to modern seawater (more than three times). As these latter two characteristics are difficult to produce from known processes that modify seawater in VHMS systems, they are considered to be strong evidence for the incorporation of magmatic–hydrothermal fluids, particularly when supported by other evidence. The former two characteristics, which reflect the metallogeny of the system, are considered permissive of magmatic–hydrothermal contributions, although they could reflect high-temperature, seawater-dominated systems. However, the combination of Sn enrichment, a Sn-only or Cu–Sn association for Sn and magmatic-like trace element characteristics of cassiterite is considered strong evidence of a magmatic–hydrothermal contribution. To our knowledge, only one VHMS deposit, Neves Corvo, has these characteristics, which are supported by the presence of highly ^{18}O-enriched ore fluids.

We do not consider the presence of magmatic–hydrothermal prospects or deposits within VHMS districts as diagnostic of a magmatic–hydrothermal contribution to the VHMS system. In two districts where this has been

proposed, the magmatic–hydrothermal and VHMS systems were not coeval, and in another system where magmatic–hydrothermal occurrences were coeval with VHMS deposits, the magmatic–hydrothermal contribution, if any, was swamped by the evolved seawater contribution. Only in cases where contemporaneity and a direct link between the magmatic–hydrothermal and VHMS deposits can be demonstrated do we consider this association to be definitive, as in the Doyon-Bousquet-LaRonde district. Unless extreme ^{18}O enrichment is identified, we do not consider O–H isotope systematics to be definitive. Similarly, with the exception of the characteristics described above, sulphur isotope systematics are also not definitive, and radiogenic isotopes and gas compositions of ore fluids are not diagnostic and need to be supported by other data. Many of these data sets have also been used by previous workers as evidence of a lack of magmatic–hydrothermal contributions to the system. However, our analysis indicates that virtually no objective data can be used to exclude small magmatic–hydrothermal contributions to VHMS systems, although in most cases such a contribution is not necessary.

Geodynamic controls on magmatic–hydrothermal contributions to VHMS systems

Our assessment of existing evidence suggests that a minority of VHMS deposits have significant magmatic–hydrothermal contributions. These can be split into two groups: (1) Cu-Au-rich deposits characterised by advanced argillic alteration assemblages and sulphur isotope evidence of disproportionation of magmatic SO_2, and (2) Sn-rich deposits in which the Sn is associated with high-temperature assemblages, cassiterite has magmatic-like trace element signatures and the Sn-bearing ore fluids were ^{18}O-enriched. Of these, the first group is reasonably common, whereas only one example of the second group is documented.

Studies of well-established magmatic–hydrothermal deposits such as porphyry Cu, high-sulphidation epithermal and skarn/carbonate replacement Sn deposits, indicate that these deposits formed from volatile-rich magma bodies that were commonly emplaced as dykes, cylindrical stocks or as cupolas or apophyses developed along the upper contacts of large intrusive bodies (Seedorf et al. 2005; Çerny et al. 2005). Moreover, comparisons of magmatic–hydrothermal deposits suggest that porphyry and epithermal deposits form under quite different geodynamic environments to Sn skarn/carbonate replacement deposits (Seedorf et al. 2005; Meinert et al. 2005; Çerny et al. 2005).

Over the last two decades, tectonic and chemical controls on magmatic–hydrothermal ores systems have been increasingly recognised. Lehmann (1990) and Blevin

and Chappell (1995) demonstrated that metal associations in magmatic–hydrothermal systems are controlled by both the oxidation state and relative fractionation or evolution of the progenitor magma: Cu–Au deposits such as porphyry Cu and high-sulphidation epithermal deposits are favoured by oxidised, relatively primitive magmas, whereas Sn±W deposits are favoured by more reduced and fractionated magmas. Tectonically, porphyry Cu±Au±Mo and related magmatic–hydrothermal deposits are restricted to magmatic arcs where they are associated with volatile-rich magmas formed by the melting of metasomatised mantle wedge above the subducting slab (Candela and Piccoli 2005). In contrast, Sn-bearing magmatic–hydrothermal deposits are closely associated with crustal melts that were produced after a major period of subduction or during rifting of previously stable cratons (Meinert et al. 2005). These environments are not only quite different from each other, but also different from the back-arc rift setting typical of most VHMS deposits.

Tectonic setting of high-sulphidation VHMS deposits

High-sulphidation VHMS deposits in the LaRonde-Doyon-Bousquet deposits are associated with FII-type (classification of Lesher et al. 1986) felsic volcanic rocks that formed from magmas produced by high-pressure melting followed by fractional crystallisation and/or crustal contamination during magma ascent (Mercier-Langevin et al. 2007b). This contrasts with FIII-type felsic volcanic rocks, which dominate the Noranda district and formed from magmas produced by low-pressure, high-temperature melting of a basaltic protolith (Hart et al. 2004). The FII-type magmas at LaRonde-Doyon-Bousquet most likely formed by the (relatively deep) partial melting of a volatile-rich metasomatised mantle wedge, possibly just inboard of a volcanic arc (e.g. Mercier-Langevin et al. 2007b). In contrast, the FIII-type magmas in the Noranda district most likely were formed by decompression melting associated with back-arc rifting.

In the Mount Read Volcanics, high-sulphidation Cu–Au deposits are mostly localised to the east of the Henty Fault where they are hosted within the Tyndall Group or in the Central Volcanic Complex just below the Tyndall Group (Fig. 8; Huston and Kamprad 2001). In most cases, these deposits are located within a kilometre of the Great Lyell Fault. The Zn–Pb deposits are located further to the west and are hosted entirely within the Central Volcanic Complex. Geochemical studies by Crawford et al. (1992) indicated that most rocks within the Mount Read Volcanics are medium- to high-K calc-alkaline rocks, with localised shoshonites and tholeiites. Crawford and Berry (1992) proposed a model in which the Mount Read Volcanics formed after the collision between a continental fragment to

the west and an island arc to the east. Subduction associated with convergence between these two blocks was initially east-dipping, but following collision, the direction of subduction flipped, with the Mount Read Volcanics forming above a west-dipping subduction zone.

Crawford et al. (1992) record an increase with time from medium-K through high-K to shoshonitic compositions of calc-alkaline volcanic rocks in the Mount Read Volcanics, suggesting that these rocks were derived from the melting of an increasingly large ion lithophile element (LILE)-enriched source. The most likely source of these melts was the mantle wedge above the west dipping slab, with the LILE enrichment with time due to continued introduction of these elements into the wedge from the slab. Emplacement of the tholeiitic dykes late in the evolution of the Mount Read Volcanics suggests possible initiation of a back-arc basin. Crawford and Berry (1992) suggested that although the west-dipping subduction that formed the Mount Read Volcanics was relatively short-lived, this subduction may have stepped east to generate Ordovician volcanic arcs that contain shoshonite-related porphyry Cu–Au and associated high-sulphidation Cu–Au deposits in New South Wales.

Spatial and temporal relationships suggest that in the Mount Read Volcanics, high-sulphidation Cu–Au deposits, such as those at Mount Lyell, formed closer to the convergent margin and at a later time than the more "typical" Zn–Pb deposits. Both of these trends are consistent with an increase in input of LILE and, probably, volatiles to the melts that formed the volcanic pile. Similarly, in the Blake River Group, the LaRonde-Doyon-Bousquet deposits are localised closer to the inferred arc and higher in the stratigraphy relative to the Noranda deposits, and a modern submarine high-sulphidation system has been documented in the Tabar–Feni island arc off of Papua New Guinea (Petersen et al. 2002; Gemmell et al. 2004).

Based on these temporal and spatial relationships, Fig. 13a illustrates our model for the formation of magmatic–hydrothermal, high-sulphidation Cu–Au deposits on or near the seafloor relative to "normal" VHMS systems that formed mostly from circulating seawater. Magmas involved in the high-sulphidation Cu–Au deposits are interpreted to be flux melts derived from the metasomatised mantle wedge above a subducting slab. Such melts will be volatile-rich, oxidised and form closer to the convergent margin than the decompression melts formed in back-arcs that typically host VHMS deposits. The volatile-rich, oxidised and arc-proximal character of the flux melts favours significant magmatic–hydrothermal contributions of Cu and Au into VHMS systems owing to the high water content of the melts and, possibly, the geometry of the intrusions. In contrast, "normal" VHMS

a)

Continental crust — Back-arc Basin — Arc — Fore-arc

"Normal" VHMS system

Porphyry-epithermal system

0   50 km

Decompression melting: High-T, anhydrous mantle melts

Flux melting: Volatile-rich, oxidised melts

Metasomatism of mantle from subducted slab

0   2 km

Seawater circulation   Zn-rich VHMS deposits

Cu-Sn Veins

Sn-Mo bearing greisan   Magmatic-hydrothermal fluids

Polyphase sill

"Normal" VHMS system

0   2 km

Cu-Au-rich VHMS deposit

Seawater circulation   Disseminated and stockwork Cu-Au associated with advanced argillic alteration assemblages

Magmatic-hydrothermal fluids

High sulphidation VHMS system

▬ *Continental crust*	▬ *Arc-related volcanics*	▬ *Mantle*	▬ *Water*
▬ *Back-arc volcanics and sediments*	▬ *Oceanic crust*	▬ *Magma*	

b)

"Normal" VHMS system

0   50 km

Decompression melting of lower crust: Hydrous, reduced melts

Decompression melting: High-T, anhydrous mantle melts

0   2 km

Cu-Sn-rich VHMS deposit

Seawater circulation

Apophysis on highly fractionated pluton

Magmatic-hydrothermal fluids

▬ *Continental blocks*	▬ *Mantle*
▬ *Volcanics and sediments*	▬ *Magma*
▬ *Oceanic crust*	▬ *Water*

Fig. 13 Inferred tectonic environments in which VHMS deposits with significant magmatichydrothermal contributions relative to "normal" deposits: **a** Cu-Au-rich deposits with aluminous alteration assemblages; **b** Sn-rich Neves-Corvo-type deposits (inset in lower right is plan view schematically indicating inferred tectonic setting)

systems are associated with granites derived from decompression melting during back-arc extension that produced less volatile-rich melts.

As described by Galley (1993, 2003), most known intrusions associated with VHMS systems are sill-like with high aspect ratios, features that are not conducive to focussing of magmatic–hydrothermal fluids. This contrasts with porphyry Cu±Au±Mo deposits in which plug-like intrusions focussed magmatic–hydrothermal to deposit and concentrate metals within or in the immediate wall rocks to the intrusions. Hence, empirically and intuitively, granites and other melts associated with "normal" VHMS deposits are not likely to contribute significant quantities of magmatic–hydrothermal fluids into the system. However, if mineralising intrusions in near-arc environments have a plug-like shape more like those associated with porphyry Cu±Au±Mo deposits in the arcs, this may enhance the propensity for major magmatic–hydrothermal contributions in high-sulphidation VHMS systems. At present, there are insufficient data to assess this hypothesis.

Tectonic setting of Sn-rich, magmatic–hydrothermal VHMS deposits

Magmatic–hydrothermal Sn deposits such as greisens, skarn and carbonate replacement deposits are associated with apophyses or cupolas developed over large, volatile-rich, reduced and evolved crustal melts emplaced either after a period of subduction or during extension of continental crust. Although most Sn-rich VHMS deposits appear to have derived Sn by leaching of the underlying pile, reasonably strong evidence exists for a significant magmatic–hydrothermal contribution to the Sn-rich Neves Corvo deposit. Currently, the Iberian Pyrite Belt is thought to have formed in a series of trans-tensional pull-apart basins developed in the allochthonous South Portuguese Zone as a consequence of oblique convergence with the Iberian Massif. These pull-apart basins are interpreted to have formed as ensialic basins within continental crust based on radiogenic isotopes (Tornos et al. 2005). This environment is not dissimilar to the environment in which granite-related Sn deposits formed. Mafic underplating and decompression melting may have generated felsic peraluminous magmas that most likely evolved the Sn-rich magmatic–hydrothermal fluids that formed the Neves Corvo deposit.

Although based on one deposit, this analysis suggests that the incorporation of magmatic–hydrothermal Sn into VHMS systems is most likely to occur where the VHMS systems form in ensialic basins within thick continental crust along convergent zones (Fig. 13b). The role of subduction is open in the Iberian Pyrite Belt: Tornos et al. (2005) note the lack of a magmatic arc and regional metamorphism unlike that associated with subduction and collision and suggest that these effects have been masked by transpressional deformation if they were present. Perhaps decompression melting associated with transtensional extension can produce reduced granites that contribute magmatic–hydrothermal Sn to VHMS systems in limited cases.

Conclusions

Our analysis of data used to infer the presence or lack of a significant magmatic–hydrothermal contribution to VHMS systems suggests that in many cases, the evidence is equivocal. Although a small magmatic–hydrothermal contribution to VHMS systems is hard to eliminate, metal leaching of underlying rocks has been documented in a number of VHMS systems, suggesting that a magmatic–hydrothermal contribution of metals is not necessary. As a consequence, we consider that in most VHMS systems, magmatic–hydrothermal contribution to the metal budget was not significant. These systems are characterised by proximal alteration zones characterised by quartz–chlorite and quartz–sericite assemblages.

However, we also consider evidence for disproportionation of magmatic SO_2 to indicate a significant magmatic–hydrothermal contribution to some VHMS systems. Such evidence includes extensive (meta-) advanced argillic alteration systems and certain sulphur isotope characteristics. Other evidence that, in some cases, could indicate a magmatic–hydrothermal contribution include ore fluids enriched in ^{18}O (i.e. $\delta^{18}O>5$) and consistent highly saline ore fluids (>15 eq wt.% NaCl). However, apparent ^{18}O-enriched ore fluids may be a reflection of metamorphic overprinting, and hydrothermal processes and likely secular variations in seawater salinities can also produce high salinities noted in some VHMS ore fluids. We do not consider the presence of enriched Sn in VHMS deposits to be sufficient evidence for a significant magmatic–hydrothermal contribution unless independent supporting evidence is present, such as certain trace elements in cassiterite and ^{18}O-enriched ore fluids.

Volcanic-hosted massive sulphide deposits for which we confidently ascribe a magmatic–hydrothermal contribution include high-sulphidation Cu/Au-rich deposits and the Neves Corvo Sn-rich deposit. Although we consider it likely that magmatic–hydrothermal fluids were important in deposits such as Mt Morgan, the evidence is equivocal. It has been argued that a magmatic–hydrothermal source is

required to produce giant VHMS deposits; however, mass balance calculations suggest that typical VHMS-related granites may also have difficulty in providing sufficient metal. The source of metals in large VHMS deposits is a problematic issue that may require very special conditions.

Magmatic–hydrothermal contributions are favoured in near-arc environments where the melting of metasomatised mantle above downgoing subducted slabs produces volatile-rich, oxidised melts to form high–sulphidation hydrothermal systems. Such contributions may also be favoured later in the evolution of convergent margins. Back-arc environments are less favourable for magmatic contributions as decompression melting is less likely to produce volatile-rich magmas. Magmatic–hydrothermal contributions may also be favoured by phallic-shaped intrusions or cupolas developed over larger magma bodies.

The tectonic environment of magmatic–hydrothermal contributions of Sn to VHMS systems is less clear. The only example formed in pull-apart basins developed in continental crust as a response to oblique convergence. The role of subduction is unclear in these systems. However, the requirement of continental crust is similar to that for other granite-related Sn systems.

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