

# The Spectrum of Ore Deposit Types, Volcanic Environments, Alteration Halos, and Related Exploration Vectors in Submarine Volcanic Successions: Some Examples from Australia

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## Abstract

Variations in shape, metal content, alteration mineralogy, and volcanic host rocks of the ore deposits in the two major volcanic-hosted massive sulfide (VHMS) districts of eastern Australia, the Cambrian Mount Read Volcanics and the Cambro-Ordovician Mount Windsor subprovince, strongly reflect their volcanic environment, conditions of ore formation, and hydrothermal alteration processes.

Lens and sheet-style polymetallic zinc-rich deposits such as Rosebery, Hellyer, Que River, and Thalanga are considered to have formed in moderate to relatively deep water environments (500–1,000+m). These deposits probably formed either on the sea floor (e.g., Hellyer, Que River) or by replacement of porous volcanoclastic units directly below the sea floor (e.g., Rosebery). The footwall alteration associated with these polymetallic VHMS deposits was controlled by host-rock permeability and porosity, which are in turn related to volcanic facies type, degree of fracturing, and synvolcanic structural architecture. Focusing of hydrothermal fluids along synvolcanic structures has resulted in well-zoned chlorite-sericite footwall alteration pipes within footwall lavas at Hellyer. On the other hand, diffuse fluid flow through very thick pumice breccia at Rosebery and Hercules has resulted in strata-bound, sericite-dominated footwall alteration zones parallel to the paleosea floor and the ore lenses.

Massive and disseminated, pyritic Cu-Au deposits, such as those in the Mount Lyell field and at Highway-Reward, formed by subsea-floor replacement and are associated with only minor zinc-lead massive sulfide ore. These deposits formed from higher temperature fluids (>300°C), in which copper transport is enhanced, and are commonly located in felsic volcanic centers dominated by shallow porphyritic intrusions (e.g., Highway-Reward). The Cu-An ore lenses may be strata-bound (e.g., Mount Lyell) or crosscutting pipes (e.g., Highway-Reward) depending on the structure and permeability characteristics of the felsic volcanic host rocks. The presence of high-sulfidation alteration minerals (e.g., pyrophyllite, zunyite) in some of the Cu-An deposits (e.g., Mount Lyell field) indicates that fluids were relatively acidic and suggests the possibility of magmatic fluid input into the hydrothermal system. Alteration zonation associated with the Cu-An VHMS deposits is more symmetrical than that of the Zn-rich deposits, with sericite-rich alteration extending into the hanging wall, in keeping with the subsurface replacement origin of these deposits.

Synvolcanic gold-rich deposits, with high gold/base metal ratios are less common than the Cu-Au and Zn-rich VHMS ore types. The gold-rich ores (e.g., Henty, South Hercules) are strata-bound in nature, have low sulfide contents, and are associated with central zones of intense silicification, surrounded by envelopes of sericite-pyrite and carbonate alteration. Volcanological and geochemical studies at Henty indicate the gold-rich ore formed by the replacement of particular volcanic units deposited in a relatively shallow water environment dominated by volcanoclastic facies, lavas, and limestones.

This spectrum of Cu-Au, Zn-rich, and Au-only deposits in the Mount Read Volcanics and the Mount Windsor subprovince is interpreted to represent a continuum from classic sea-floor VHMS ores toward those with features more akin to porphyry Cu-Au and epithermal Au-Ag deposits. This spectrum relates to the interplay between factors in the submarine volcanic environment and the character of the hydrothermal fluid as follows: (1) proportions of volcanoclastic, lava, and subvolcanic intrusive facies; (2) depth of seawater; (3) permeability and porosity of volcanic host rocks; (4) balance between magmatic components and seawater components in the ore fluid; and (5) temperature and acidity of the ore fluid.

Mineralogical, lithogeochemical, and isotopic studies have revealed a range of alteration vectors useful in exploration for both the Zn-rich and Cu-An VHMS deposits. Carbonate and white mica compositional variations are highlighted as important mineralogical vectors; thallium and antimony halos may be useful trace element vectors; and oxygen and sulfur provide important isotope vectors toward the center of the hydrothermal system.

## Introduction

THE TWO principal submarine volcanic successions in Australia that host volcanic-hosted massive sulfide (VHMS) deposits, the Cambrian Mount Read Volcanics in Tasmania and the Cambro-Ordovician Mount Windsor subprovince in

Queensland, contain a range of base metal and gold-bearing sulfide deposits (Table 1). The aims of this paper are to briefly review the geological features, volcanic environments, and genesis of the spectrum of deposit styles and, based on the contributions to this special issue, to compare their patterns of hydrothermal alteration. From this analysis we propose a series of alteration vectors useful for mineral exploration.

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TABLE 1. Tonnage-Grade Data for the Major Volcanic-Hosted Deposits in the Mount Read Volcanics and the Mount Windor Subprovince

Deposit type	Tonnage (Mt)	Zn (wt %)	Pb (wt %)	Cu (wt %)	Ag (ppm)	Au (ppm)	Form	Status	Location
Zn-Pb-Cu	16.2	13	7	0.4	160	2.3	Elongate MS lens	Mine closed	Mt. Read Volcanics
	3.1	13.5	7.5	0.6	200	3.4	Folded MS lens	Past producer	Mt. Read Volcanics
	31.7	14.3	4.4	0.6	146	2.3	Multiple MS sheets	Current mine	Mt. Read Volcanics
	3.4	17.3	5.4	0.4	169	2.8	Multiple MS lenses	Past producer	Mt. Read Volcanics
	6.6	8.4	2.6	1.8	69	0.4	Sheetlike MS lenses	Past producer	Mt. Windsor subprovince
	1.8	6.2	2.2	0.5	29	0.9	Sheetlike MS lenses	Prospect	Mt. Windsor subprovince
	312	1	6.2	0.3	Deformed stockwork	1.5	Subvertical pyritic pipes	Current mine	Mt. Read Volcanics
	3.7	6.2	1	6.2	11.3	Disseminated sulfides in	Current mine	Mt. Read Volcanics	Mt. Windsor subprovince
	1.7	11.3	11.3	11.3	11.3	Disseminated sulfides in	Current mine	Mt. Read Volcanics	Mt. Windsor subprovince
	Au only	1.7	11.3	11.3	11.3	11.3	Disseminated sulfides in	Current mine	Mt. Read Volcanics

Abbreviation: MS = massive sulfide

## Spectrum of Ore Deposit Types in the Mount Read Volcanics

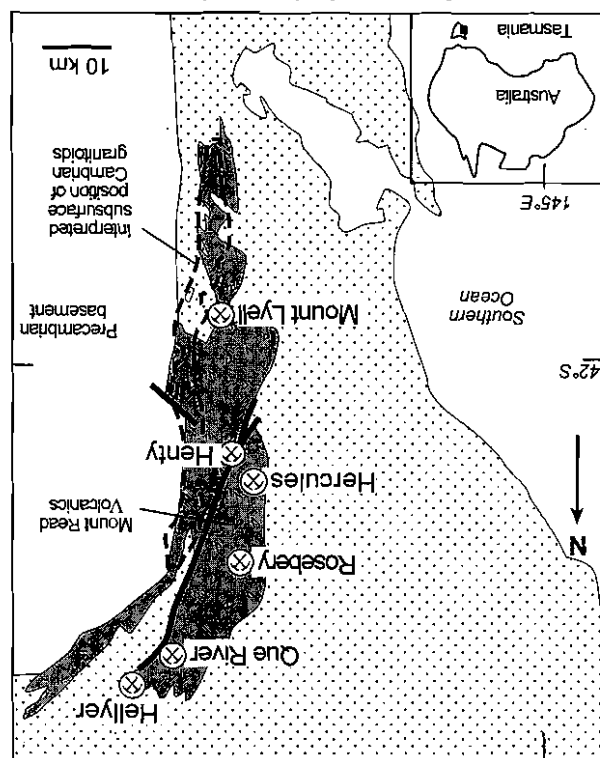
The spectrum of VHMS deposits in the Mount Read Volcanics (Fig. 1) includes lens and sheet-style massive polymetallic zinc-rich ores such as Hellyer and Rosebery, massive and disseminated pyritic copper-gold ores in the Mount Lyell field, and disseminated strata-bound gold-rich ores at Henty and South Hercules (Large, 1997).

Rosebery and Hellyer are the best examples of lens and sheet-style polymetallic zinc-rich deposits, although smaller deposits at Que River and Hercules have been mined in the past. The Hellyer ore deposit consists of a single elongate 16 million ton (Mt) lens of massive sulfide at the contact between footwall andesitic lavas and volcanoclastic facies, and overlying pillow basalt intercalated with black mudstone (McArthur, 1989; Gemmell and Large, 1992; Gemmell and Fulton, 2001). Rosebery, on the other hand, although containing similar sulfide mineral assemblages and metal grades, consists of 16 separate ore lenses with a sheathlike morphology, located within a sequence of fine-grained volcanic and stone, black mudstone, and rhyolitic volcanoclastic units at the top of a thick regionally extensive succession of rhyolitic pumice-rich mass flows (Green et al., 1981; Allen, 1994a; Large et al., 2001). Both the Hellyer and Rosebery massive sulfide lenses show classic footwall to hanging-wall metal zonation: Fe → Cu → Pb, Zn, Ag → Au → Ba, although at Hellyer the zonation is within the single ore lens and at Rosebery successively stratigraphically higher lenses show higher Ba and lower Cu-Fe content.

Most previous workers agree that the massive sulfide ores at Rosebery and Hellyer formed at or just below the sea floor (e.g., Green et al., 1981; Gemmell and Large, 1992; Allen, 1994b; Solomon and Groves, 1994; McArthur, 1996; Khin Zaw et al., 1999). In both cases it is considered likely that the ores formed in sea-floor depressions or small basins adjacent to fault-controlled hydrothermal vents. However, the precise nature of sulfide deposition and ore deposit evolution has been the subject of considerable debate.

At Hellyer, McArthur (1989, 1996), Large (1992) and Gemmell and Large (1992), concluded that the massive sulfide orebody grew as a mound in a sea-floor depression, with a metal zonation developed by hydrothermal zone refining, in a similar fashion to that described for many Kuroko deposits by Eldridge et al. (1983). Solomon and Khin Zaw (1999), on the other hand, used fluid inclusion evidence to suggest that the ore fluid was too dense to enable mound growth and that the

FIG. 1. Location of Mount Read Volcanics and associated major mineral deposits, western Tasmania. The outline of the interpreted major mineral volcanic granitoid body is from Large et al. (1996).



metal sulfides precipitated within a brine pool ponded within a sea-floor depression. A potential problem with the brine pool model for Hellyer is the source of the high-salinity ore fluids. Solomon and Groves (2000) point out the lack of evidence for evaporitic sediments in the Cambrian and Precambrian basement source region and conclude that the most likely reason for the high salinities is the presence of significant magmatic fluid input, as previously suggested by Khin Zaw et al. (1996). However, no other evidence exists for the involvement of magmatic fluids at Hellyer.

Solomon and Walshe (1979) and Solomon and Groves (1994) considered that the sheetlike form, stratiform sulfide banding, large size, and high Zn-Pb metal content of the Rosebery deposit set it apart from the classical mound-style Kuroko massive sulfide deposits. They argue that Rosebery is more like the large VHMS deposits in the Bathurst district, Canada, than the smaller Kuroko deposits of Japan. In some respects Rosebery could be considered to possess some of the features of a SEDEX deposit (e.g., banded sheetlike form, high Zn/Cu ratio, high tonnage, lack of a well-developed stringer zone) located within a volcanic rather than a sedimentary setting.

Solomon and Groves (1994) proposed that Rosebery and similar sheetlike, banded, large tonnage and/or grade VHMS deposits formed within a brine pool from relatively high salinity fluids that underwent reverse buoyancy on mixing with seawater. In marked contrast to this model, Allen (1994a, b) provided volcanological and textural evidence to suggest that the sheetlike form and mineral banding in some of the Rosebery ore lenses are due to subsea-floor replacement of pumice-rich units below impermeable quartz-porphyritic rhyodacitic synvolcanic sills. A similar process of subsea-floor replacement was also proposed by Khin Zaw and Large (1992) for the South Hercules deposit, situated to the south of Rosebery.

In summary, the jury is still out on the exact process of the formation of Rosebery and Hellyer, but most workers agree that the ores are synvolcanic and formed on, or just below, the sea floor, from moderate- to high-salinity ore fluids (5–15 wt % NaCl and 160°–320°C; Khin Zaw et al., 1996).

#### *Massive and disseminated strata-bound pyritic Cu-Au deposits*

The Mount Lyell district (Fig. 1) contains 22 Cu-Au deposits with a total of 312 Mt of 1.0 percent Cu and 0.3g/t Au hosted within rhyolitic and dacitic volcanic facies. Previous studies (e.g., Cox, 1981; Walshe and Solomon, 1981; Large, 1992) considered the Cu-Au deposits to be largely subsea-floor replacement VHMS ores; however, recent research (Corbett, 2001; Huston and Kamprad, 2001) has demonstrated that the ores have mineralogical and alteration affinities with high-sulfidation epithermal deposits and may thus represent a hybrid type between VHMS and epithermal deposits, developed within a submarine volcanic succession. There is disagreement on the timing of the Cu-Au mineralization and high-sulfidation alteration event. Huston and Kamprad (2001) argue for an Ordovician age for the mineralization and alteration (~460 Ma), whereas Corbett (2001) provides convincing evidence for a Cambrian age similar to other deposits in the Mount Read Volcanics. Corbett (2001,

fig. 3) has recognized a zonation throughout the Mount Lyell district, from large disseminated pyrite-chalcopyrite ores at depth (with elevated magnetite-apatite-REE), passing upward to bornite-rich ores in a zone of intense massive and vuggy silica alteration (including enargite and pyrophyllite) below the paleosea floor, followed by an uppermost zone of small, massive sulfide Zn-Pb-Cu lenses interpreted as exhalative sea-floor deposits.

*Subvolcanic intrusions in the Mount Lyell district:* A series of granitic sill-like intrusions occur at depth along the eastern margin of the Mount Read Volcanics (Fig. 1). Research by Mike Solomon and his students (Solomon, 1976; Polya et al., 1986; Eastoe et al., 1987) proposed a relationship between synvolcanic granite emplacement, district-scale alteration, seawater circulation, and massive sulfide formation. More recently, Large et al. (1996) suggested the possibility of a direct input of magmatic fluids carrying gold, copper, iron, and phosphorous to form the copper-gold VHMS deposits in the Mount Lyell district. Geophysical evidence (magnetics and gravity) indicates that the granite(s) form a narrow discontinuous body or series of bodies about 60 km long and 2 to 4 km wide toward the base and eastern margin of the volcanic pile that hosts the deposits (Large et al., 1996, fig 4). The two outcropping parts of the elongate composite granite body (the Murchison and Darwin granites) are strongly altered, high K, magnetite series granites. The Murchison granite varies in composition from diorite to granite (58–78 wt %  $\text{SiO}_2$ ; Polya et al., 1986), whereas the Darwin granite is composed of two highly fractionated phases (Jones, 1993) with an  $\text{SiO}_2$  content from 74 to 78 wt percent. The depth of the granite below the lowest VHMS horizon is difficult to determine due to later structural events. Various reconstructions place the granites at a depth of 3 to 7 km below the ore horizon.

The coeval and comagmatic nature of the granites and volcanics is based on geology (Polya et al., 1986; Corbett, 1992; Jones, 1993), geochemistry (Crawford et al., 1992; Wyman, 2000), and geochronology (Perkins and Walshe, 1993). Radiometric dating gives an age of  $508 \pm 6$  Ma compared to the range of the Mount Read Volcanics of  $501$  to  $510 \pm 7$  Ma (Perkins and Walshe, 1993). The dating is not sufficiently precise to establish the exact timing of the Cambrian granite intrusion with respect to Cu-Au mineralization at Mount Lyell.

Based on regional alteration studies, complimented by gravity and magnetic patterns, Large et al. (1996) suggested that the Mount Lyell hydrothermal alteration system was connected to a deep-seated magmatic-hydrothermal alteration system related to the elongate Cambrian granite(s) that crop out south of Mount Lyell in the Jukes and Darwin areas. Low-grade porphyry Cu-style mineralization has been recognized in places surrounding the Cambrian granites (Hums, 1987; Doyle, 1990; Large et al., 1996), where it is associated with magnetite-chlorite and tourmaline-quartz veins that overprint early K feldspar alteration (Wyman, 2000).

Convincing evidence for magmatic fluid and metal input into the hydrothermal system at Mount Lyell is difficult to document, probably because the system has been swamped by seawater convection over the life of the hydrothermal cell. However, evidence in favor of the Cambrian granites acting as a thermal source and contributing a magmatic component to the ore fluid includes (see also Solomon and Groves, 2000):

(1) the whole-rock and trace element geochemistry indicates the granitoids are comagmatic with the suite 1 volcanics that host and underlie most of the deposits (Crawford, et al. 1992); (2) the presence of alteration minerals (e.g., pyrophyllite, alunite types) adjacent to the ores indicates a very acidic hydrothermal fluid (Huston and Kamprad, 2001); (3) the presence of magnetite-apatite + pyrite assemblages at Prince Lyell and a correlation between Cu, P, and Fe in the ores (Large et al., 1996); (4) the  $O^{18}$ -enriched hydrothermal magnetite of about 4 per mil at Prince Lyell indicates a magmatic origin (Raymond, 1992); (5) the Nd-Sm isotope data support a link between apatites in the magnetite-apatite assemblages at Prince Lyell and the Cambrian granites (Wyman, 2000); (6) the recent fluid inclusion studies by Khin Zaw et al. (in press) in the Western Tharsis deposit, Mt. Lyell, indicate salinities much higher than seawater—in the range 6 to 34 wt percent NaCl; and (7) the high  $(Cu + Au)/(Zn + Pb + Ag)$  ratios in the ores are compatible with high-temperature, acidic ore fluids of magmatic origin.

Our current model for the Mount Lyell field (Fig. 2) depicts the major disseminated Cu-Au ores, such as Prince Lyell and Western Tharsis, as hybrid VHMS-high-sulfidation

epithermal style ores with a connection to a low-grade porphyry environment at depth (e.g., Jukes Pty. prospect) and an exhalative Zn-Pb massive sulfide at the sea floor above (e.g., Comstock deposit). The formation processes and geological environment of Cu-Au deposits in the Mount Lyell field may be similar to that suggested by Sillitoe et al. (1996, fig. 2) for high-sulfidation volcanogenic massive sulfide deposits.

#### Disseminated strata-bound gold-rich ores

There are several synvolcanic gold-rich deposits in the Mount Read Volcanics that contain a high gold/base metal ratio and are composed principally of disseminated mineralization rather than massive sulfide lenses. The Henty deposit (Halley and Roberts, 1997; Callaghan, 2001), a current producing mine (1.7 Mt at 1.1 g/t Au), is the best known example, but others include South Hercules (Khin Zaw and Large, 1992) and the footwall precious metal zone at Que River (McGoldrick and Large, 1992).

Henty is a low-sulfide strata-bound gold deposit within an intensely silicified zone adjacent to the regionally extensive Henty fault system. Although the deposit is synvolcanic and, based on Pb isotope and stratigraphic evidence (Halley and

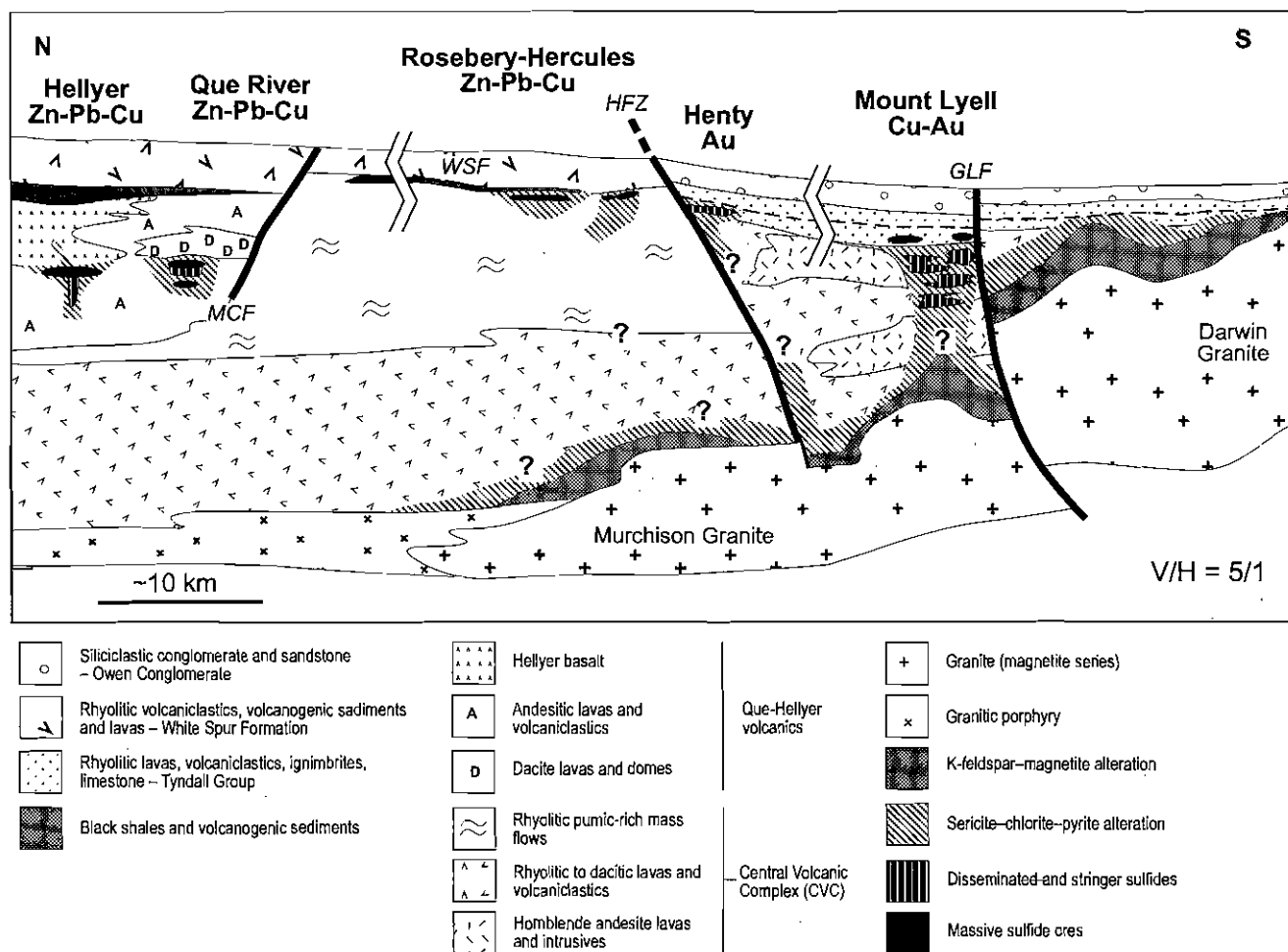


FIG. 2. Schematic long section for the Mount Read Volcanics showing the interpreted locations and morphologies of VHMS deposits and their associated alteration zones (based on Large et al., 1996; Halley and Roberts, 1997; Callaghan, 2001; Corbett, 2001).

Roberts, 1997), roughly the same age as the other felsic volcanic-hosted deposits at Rosebery and Mount Lyell, features which make it significantly different from the other VHMS deposits in the belt include the following: (1) it is a low sulfide disseminated style with only minor lenses of massive polymetallic sulfide; (2) it is hosted by a relatively shallow water facies association, including ignimbrite and limestone, at the base of the Tyndall Group (White and McPhie, 1996); and (3) the gold-silver-tellurium-rich core of the deposit is surrounded by a zone of copper-lead-bismuth and an outer halo of zinc (Callaghan, 2001).

Halley and Roberts (1979) compared Henty to other gold-rich massive sulfides described by Poulsen and Hannington (1995) and concluded that Henty was a shallow-water exhalative VHMS deposit with high gold and low base metal grades related to boiling of the hydrothermal fluid. Recent work by Beckton (1999) and Callaghan (1998, 2001) has shown that the strata-bound gold ores formed by replacement rather than exhalation. Callaghan (2001) argues that the metal association (Au-Cu-Bi-Te), extensive carbonate alteration halo, and replacement textures suggest that the deposit formed by subsea-floor replacement of particular volcanic and carbonate-rich units during mixing of a magmatic-hydrothermal fluid with seawater.

In most respects Henty has little in common with typical VHMS deposits, such as Hellyer and Rosebery, and is more akin to a shallow marine strata-bound epithermal Au-Ag replacement deposit (Fig. 2). Previous workers (e.g., Corbett,

1992; Callaghan, 2001) have noted that Henty and the Comstock deposits at the top of the Mount Lyell system lie at the same stratigraphic level at the base of the Tyndall Group. A number of other Cu-Au and Zn-Pb prospects lie at this stratigraphic position between Henty and Mount Lyell, suggesting the possibility that the gold-rich ores at Henty represent the top of a magmatic-hydrothermal system similar to the copper-gold system at Mount Lyell (Fig. 2).

#### *Comparisons to deposits in the Mount Windsor subprovince: Queensland*

Three significant massive sulfide deposits (Thalanga, Highway-Reward, and Liontown) and another five small massive sulfide lenses (Waterloo, Argincourt, Magpie, Handcuff, and Warrawee) are known from the Cambro-Ordovician Mount Windsor subprovince (Fig. 3). Except for Highway-Reward, all the deposits are stratiform polymetallic (Zn-Pb-Cu-Au-Ag) massive sulfide lenses, showing some similarities to the Rosebery and Hellyer deposits in the Mount Read Volcanics. In contrast, Highway-Reward consists of several discordant massive pyritic Cu-Au pipe-shaped bodies and has some features in common with the Mount Lyell deposits in Tasmania. For the purposes of this comparison we will discuss the characteristics and origin of the two principal deposits at Thalanga and Highway-Reward.

**Thalanga deposit:** Thalanga comprises several sheetlike, steeply dipping, sulfide lenses extending over about 3 km of

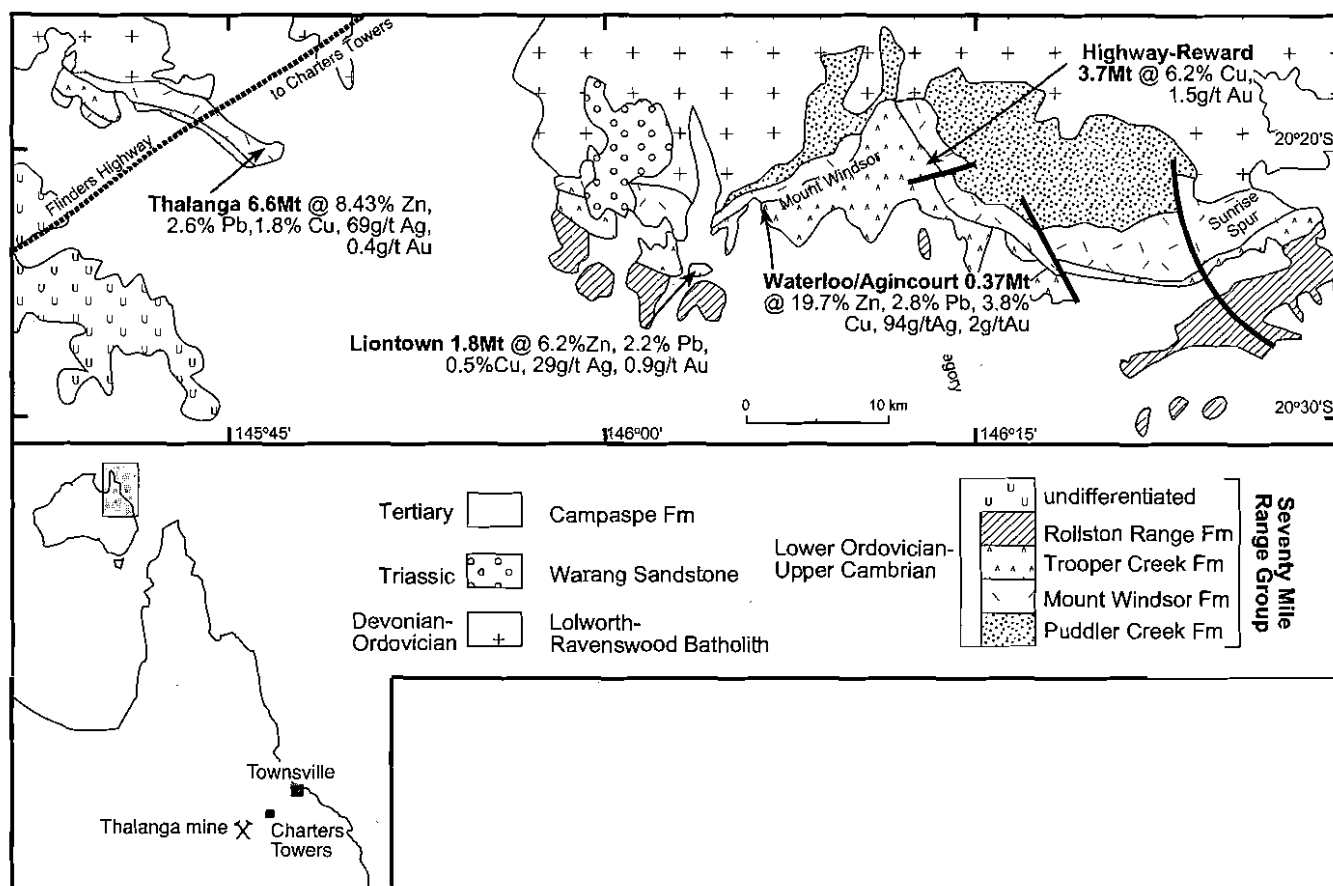


FIG. 3. Locations of VHMS deposits in the Mount Windsor subprovince, eastern Queensland.

strike and containing a total of about 7 Mt of ore. The ore lenses are strata bound within a single stratigraphic interval that is dominated by coarsely volcanoclastic facies and sills with quartz phenocrysts above a thick footwall sequence of rhyolitic lavas and intrusions and beneath a hanging-wall sequence of dacitic lavas and volcanoclastic units. The ore lenses and enclosing rocks were deformed and metamorphosed to upper greenschist-grade assemblages during the Mid-Late Ordovician period (Berry et al., 1992). Remobilization has complicated metal zonation in the sulfide lenses, but they are generally pyritic and copper rich at the stratigraphic base and zinc-lead rich elsewhere. Semimassive barite  $\pm$  magnetite exists in the lateral and upper fringes of some ore lenses. The sheetlike morphology and metal zonation at Thalanga are similar to that exhibited by the Rosebery deposit in the Mount Read Volcanics.

An extensive, feldspar-destructive sericite-chlorite-pyrite alteration zone stratigraphically underlies the deposit. Within this pervasive alteration zone are discrete quartz-pyrite  $\pm$  chlorite stringer zones of intense alteration that appear to represent discordant hydrothermal feeders leading obliquely up to the sulfide lenses (Paulick et al., 2001). Thin strata-bound zones of chlorite-tremolite-carbonate associated with ore in the western lenses represent metamorphosed chlorite-carbonate alteration assemblages (Herrmann and Hill, 2001). Dacitic volcanic facies in the hanging wall immediately above the ore are essentially unaltered.

The deposit is interpreted to have formed in a moderate to deep marine setting, probably in sea-floor depressions on the crest of a rhyolite lava-dominated volcanic center (Paulick and McPhie, 1999). Sulfur isotope data from barite and sulfides are consistent with sulfur derivation from Cambro-Ordovician seawater and igneous rocks (Hill, 1996). Several lines of evidence indicate that the sulfide lenses formed directly on the sea floor and partly by replacement of volcanoclastic facies in the upper few meters of the substrate. The evidence includes: (1) the strata-bound distribution of lenses immediately above zones of intense alteration in the footwall; (2) the presence of clasts of massive sulfide in polymictic volcanic breccias; and (3) the immobile element composition of ore-related chlorite-tremolite-carbonate rocks, which indicates that these units formed by replacement of volcanic rocks (Herrmann and Hill, 2001).

**Highway-Reward deposit:** The Highway-Reward deposit comprises three subvertical pipelike bodies of massive pyrite and minor chalcopyrite totaling about 10 Mt and including a premining resources of 3.7 Mt grading 6.2 percent Cu and 1.7g/t Au (Craig Miller, pers commun., 2000). The massive pyrite pipes have a vertical extent of up to 250 m, discordant with the shallowly dipping volcanic host sequence. They are surrounded by a broad low-grade halo of sphalerite  $\pm$  galena  $\pm$  barite in disseminations and veinlets. A small strata-bound lens of sphalerite-pyrite-galena-chalcopyrite-barite exists about 50 m above the southern edge of the Reward pipe. The host rocks comprise numerous small (tens of meters in diameter) domelike bodies of felsic porphyritic intrusive rocks separated by intervals of volcanic siltstone, sandstone, and pumiceous and polymictic breccia (Doyle and McPhie, 2000; Doyle, 2001). Doyle and Huston (1999) concluded that the massive pyrite pipes, although essentially synvolcanic, formed

mainly by subsea-floor replacement of the permeable margins of adjacent felsic cryptodomes.

### Spectrum of Volcanic Environments Hosting VHMS Deposits

The Cambrian Mount Read Volcanics in western Tasmania and the Cambro-Ordovician Mount Windsor subprovince Queensland host important massive sulfide deposits that display a range of textural, mineralogical, and compositional characteristics. Both of these successions comprise complex assemblages of texturally and compositionally diverse volcanic facies that also illustrate a wide spectrum in the volcanic environments of massive sulfide ore formation. Research combining volcanic facies analyses and alteration studies has been undertaken at Rosebery (Allen, 1994a; Large et al., 2001) and Hellyer (Waters and Wallace 1992; Gemmell and Fultz 2001) in the Mount Read Volcanics, and at Thalanga (Paulick and McPhie 1999; Paulick et al., 2001) and Highway-Reward (Doyle and McPhie, 2000; Doyle, 2001) in the Mount Windsor subprovince. These deposits serve to demonstrate much of the spectrum, in some cases being hosted by lavas or synvolcanic intrusions and others by volcanoclastic successions. They also show marked variations in the geometry and style of both of the massive sulfide orebodies and related hydrothermal alteration halos.

In this section, the principal facies characteristics of the host successions to these four massive sulfide deposits are summarized. We also briefly consider how primary facies characteristics of the host volcanic successions, especially porosity, permeability, and the presence of volcanic glass, have influenced the distribution and texture of alteration facies. This subject is examined in detail in Giffkins and Allen (2001) on Rosebery in the Mount Read Volcanics and in Doyle (2001) on Highway-Reward in the Mount Windsor subprovince.

### *Facies architecture of the Mount Read Volcanics*

The regionally mappable lithostratigraphic units within the Mount Read Volcanics each comprise a varied assemblage of volcanic facies types, in some cases together with nonvolcanic principally sedimentary facies. The principal lithostratigraphic units are the Central Volcanic Complex, Eastern quartz phenocryst sequence, Western volcano-sedimentary sequence (Yolande River sequence, Dundas Group, Mount Charter Group), and the Tyndall Group (Corbett 1992). Although felsic compositions dominate the volcanic facies of all lithostratigraphic units, intermediate to mafic volcanic facies are locally important, especially within the Central Volcanic Complex and the Western volcano-sedimentary sequences. The lithostratigraphic units can be mapped on the basis of the dominant facies types present and provide a framework for the volcanic facies architecture. Essential elements of the facies architecture are a volcanic facies association comprising lavas and domes, diverse volcanoclastic facies, and synvolcanic intrusions; and a sedimentary facies association comprising black pyritic mudstone, micaceous mudstone, and basement-derived sandstone (McPhie and Allen, 1992).

Lava flows and domes consist of both coherent and autoclastic (autobreccia, hyaloclastite, resedimented hyaloclastite, and intrusive hyaloclastite) facies. Flows and domes commonly occur in association with synvolcanic intrusions, mainly sills

and cryptodomes. Margins of the extrusions and intrusions are typically glassy and in some cases, pumiceous; formerly glassy domains are commonly perlitic. Interiors are typically microcrystalline, spherulitic, or micropoikilitic. Although the volcanoclastic facies range widely in textural characteristics, there are four particularly common types: (1) very thick (tens of meters), massive to graded beds of rhyolitic pumice breccia; (2) very thick, massive to diffusely stratified units of crystal-rich (feldspar, quartz, clinopyroxene) sandstone; (3) thick to very thick, massive to graded beds of polymictic volcanic conglomerate or breccia; and (4) pale, massive or laminated shard-rich mudstone.

The facies architecture of the Mount Read Volcanics shows distinct regional variations in the proportions of volcanic versus sedimentary facies. The volcanic facies association locally dominates the succession, but elsewhere the volcanic facies are interbedded with, or subordinate to, sedimentary facies. For example, sections about 800 m thick through the Mount Read Volcanics at Mount Black near Rosebery are composed almost entirely of volcanic facies (felsic lavas, intrusions, pumice breccia), whereas at Hellyer sedimentary facies (black mudstone and micaceous mudstone) up to 700 m thick dominate hanging-wall sections.

The volcanic facies association exhibits considerable diversity in eruption and emplacement processes. The spectrum ranges from the products of exclusively effusive, intrabasinal eruptions, such as the andesitic lavas and domes in the footwall of the Hellyer massive sulfide orebody, to the products of explosive eruptions, possibly from vents located at the basin margin, such as the pumice breccia units in the hanging wall at Hellyer. Among the volcanoclastic facies, there is a spectrum from facies that are clearly syneruptive, having been generated by a coeval explosive eruption, to posteruptive facies that exhibit evidence for temporary storage and reworking prior to redeposition. Syneruptive facies are characterized by the dominance of unmodified juvenile components of uniform composition and very thick, mass-flow sedimentation units. The very thick rhyolitic pumice breccia units of the footwall to the Rosebery and Hercules massive sulfide orebodies are excellent examples of syneruptive facies that record a major explosive eruption. Massive to graded beds of polymictic volcanic conglomerate with significant proportions of rounded clasts occur in the Rosebery-Hercules hanging wall and are good examples of volcanoclastic facies thought to be posteruptive, generated by more complex and lengthy transport and reworking histories.

The volcanic facies association in the Mount Read Volcanics also displays marked regional variations in the proportions of magma compositions represented. Much of the succession is dominated by rhyolite and dacite. For example, primary and syneruptive volcanic facies in the host succession to the Rosebery and Hercules massive sulfide deposits are almost exclusively rhyolitic to dacitic. However, intermediate to mafic volcanic facies are important at several locations, some of which host massive sulfide deposits. For example, at Hellyer, the volcanic facies in the footwall are mainly andesitic, facies coeval with the orebody are dacitic, and the hanging wall includes thick (~100 m) basaltic sills.

Another aspect of the geology of the Mount Read Volcanics that shows important variation is the inferred water depth at

the time of emplacement. A below wave base, moderate to relatively deep submarine setting is inferred to have prevailed for most of the succession and is indicated by the presence of trilobite and other marine fossils, turbidites, and black pyritic mudstone in the sedimentary facies association. This interpretation is consistent with the presence of very thick volcanoclastic mass-flow units, hyaloclastite, peperite, and pillow lava in the volcanic facies association. The Rosebery, Hercules, Hellyer, and Que River orebodies probably all formed in such moderate- to deep-water environments. No conclusive evidence for the exact water depth at the time of mineralization is available, but based on the lack of evidence of boiling in fluid inclusions at Hellyer and Rosebery (Khin Zaw, 1991; Khin Zaw et al., 1996) and by analogy with present-day sea-floor massive sulfides, it is speculatively assumed that the depth ranged from about 500 to greater than 1,000 m. In contrast, a shallower water setting, at or just below storm wave base, is most likely to have existed for much of the region during deposition of the youngest lithostratigraphic unit, the Tyn-dall Group, when the Au-rich Henty deposit and the uppermost parts of the Cu-Au Mount Lyell deposits were formed. The evidence for a shallower setting at Henty includes the local presence of limestone that contains a shallow-water fauna and in situ welded ignimbrite (White and McPhie, 1997).

#### *Setting of Hellyer*

The Hellyer massive sulfide orebody occurs within a substantial, intermediate to mafic volcanic succession known as the Que-Hellyer Volcanics, which is part of the Mount Charter Group (Corbett and Komyschan, 1989). The massive sulfide occurs above a footwall comprising andesitic and basaltic lava and sills with quartz phenocrysts, together with associated autoclastic breccia (mainly hyaloclastite) and peperite (Waters and Wallace 1992; Fig. 4a). The hanging wall is dominated by basalt (Hellyer Basalt). The abundance of basalt-mudstone peperite indicates that most of the basalt units are sills that intruded black mudstone (Que River Shale). Very thick, graded units of rhyolitic pumiceous and volcanic lithic breccia interbedded with turbidites and mudstone occur in the upper parts of the hanging wall (Southwell Subgroup). Along strike from the massive sulfide, the ore position is marked by coarse polymictic volcanic breccia, sandstone, and mudstone, and dacitic lavas and domes.

Trilobites in the Que River Shale, very thick sections of black mudstone, and the abundance of graded mass-flow units collectively indicate that the Hellyer massive sulfide formed in a moderate to deep (>1,000 m?) submarine setting. The volcanic facies association indicates proximity to intrabasinal vents for effusive basaltic and andesitic eruptions and synvolcanic intrusions.

The hydrothermal system responsible for the Hellyer massive sulfide was hosted by a lava- and intrusion-dominated volcanic succession. In such successions, permeability can be very high but is commonly fracture controlled and is also strongly influenced by facies geometry, especially the margins of lavas or domes. These controls are reflected in the well-defined and pipelike footwall alteration (Gemmell and Large, 1992) that suggests fluid flow was strongly focused by a vertical synvolcanic fault.

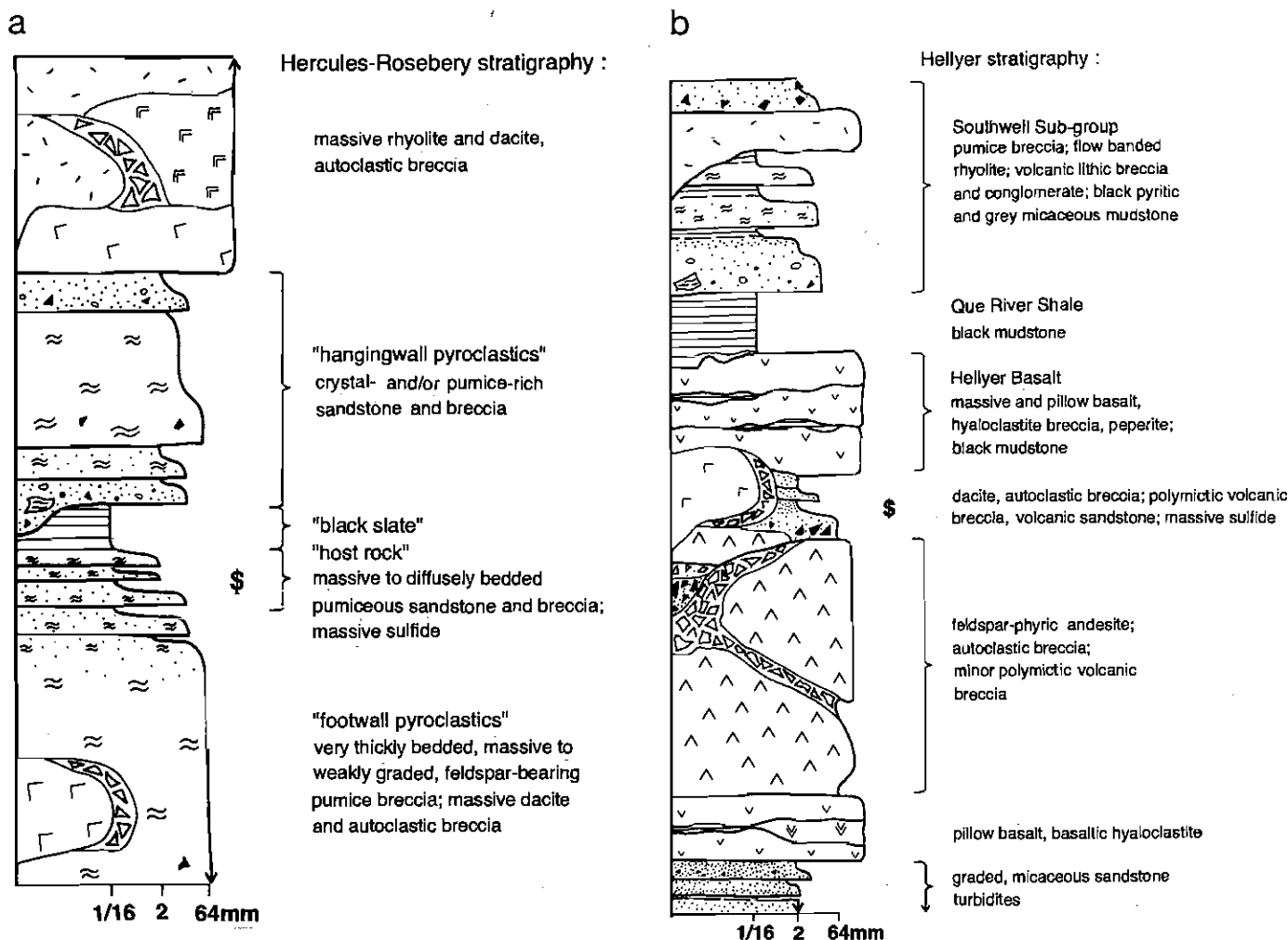


FIG. 4. Stratigraphic columns showing volcanic facies relationships in the (a) Rosebery-Hercules, and (b) Hellyer-Que River areas of the Mount Read Volcanics. The \$ sign denotes the stratigraphic position of massive sulfide deposits.

### Setting of Rosebery and Hercules

The Rosebery and Hercules massive sulfide lenses occur in part of the Central Volcanic Complex that is dominated by very thick, weakly graded units of feldspar-porphyrific rhyolitic pumice breccia. The ore lenses are located in the stratified pumiceous sandstone and mudstone top (host rock, Fig. 4b) of very thick pumice breccia that forms most of the footwall (Allen, 1994a; Large et al., 2001). The hanging wall comprises thick graded beds of variably crystal-rich and pumiceous sandstone (hanging-wall pyroclastics) interbedded with black mudstone.

A below-wave base submarine setting for the Rosebery-Hercules succession is clear from the presence of very thick graded beds and black mudstone, but there are no features that provide more precise constraints. The volcanic facies association is dominated by syneruptive pumiceous mass-flow deposits generated by a voluminous rhyolitic explosive eruption. The vent position has not been identified but was probably not within the area encompassed by existing exposures.

The hydrothermal system that produced the Rosebery and Hercules ore lenses operated in a volcanoclastic succession

with, at least initially, very high permeability and porosity. As a result, hydrothermal alteration of the footwall and host rocks is pervasive, widespread, conformable, and of variable intensity (Large et al., 2001). In addition, it is likely that the highly permeable host facies inhibited venting of hydrothermal fluids at the sea floor and instead favored a subsea-floor replacement origin for some of the ore lenses (Allen, 1994b).

### Facies architecture of the Mount Windsor subprovince

The regional lithostratigraphy of the Mount Windsor subprovince was described by Henderson (1986) and refined by Berry et al. (1992). There are four formations: the Puddler Creek Formation at the base, the Mount Windsor Formation, the Trooper Creek Formation, and the Rollston Range Formation at the top (Fig 4). The middle two formations (Mt. Windsor Formation and Trooper Creek Formation) are dominated by volcanic facies, whereas the lowest and topmost formations are dominated by sedimentary facies, principally turbidite and pelagic mudstone. The assemblage of volcanic facies is typical of submarine volcanic successions elsewhere in comprising lava flows and domes, synvolcanic intrusions, and diverse volcanoclastic facies. The Mount Windsor Formation is



composed of quartz-porphyritic rhyolitic lavas and intrusions, together with minor felsic volcanoclastic facies. The Trooper Creek Formation is more varied in the volcanic facies types (lavas, sills, and cryptodomes and a wide variety of volcanoclastic facies) and in the compositions (basalt through to rhyolite). The presence of turbidite, suspension-settled mudstone and graptolite, and pelagic trilobite fossils (Henderson 1986) implies that most of the succession was deposited in a below-wave base, probably moderately deep marine environment. However, shallow-water facies have recently been identified (Doyle 1997), indicating that water depths varied spatially and temporally.

Studies of the volcanic facies in the Mount Windsor subprovince are limited to detailed research at the Thalanga and Highway-Reward massive sulfide orebodies. These two examples extend the spectrum of volcanic environments in which massive sulfides form and show interesting and important differences from Rosebery-Hercules and Hellyer in the Mount Read Volcanics. Both deposits occur at felsic volcanic centers, on one hand dominated by lavas and domes (Thalanga) and on the other by synvolcanic intrusions (Highway-Reward). However, the two deposits contrast markedly in geometry in relationship to the host succession and in the pattern of hydrothermal alteration. Thalanga formed at or very close to the sea floor from exhaling hydrothermal fluids (Hill, 1996), whereas Highway-Reward formed by subsea-floor replacement, hydrothermal fluids being focused along the steep margins of shallow intrusions (Doyle and Huston, 1999).

#### Setting of Thalanga

The Thalanga massive sulfide lenses occur more or less conformably within a felsic lava- and dome-dominated

succession close to the contact between the Mount Windsor Formation and the Trooper Creek Formation. The footwall succession is dominated by strongly quartz- and feldspar-porphyritic rhyolitic lavas, including both coherent and autoclastic facies (hyaloclastite, resedimented hyaloclastite, auto-breccia) on the order of 1,000 m thick. Despite strong alteration, diverse original textures (including perlite, spherulites, microplitic texture, flow banding) and separate units have been identified (Paulick and McPhie 1999). The massive sulfide lenses occur in a complex succession of quartz- and feldspar-bearing, crystal-rich sandstone and breccia, quartz- and feldspar-porphyritic rhyolitic lavas and synvolcanic sills, and peperite. The hanging-wall volcanic succession is about 200 m thick and dominated by feldspar-porphyritic dacitic lavas with that include significant volumes of autoclastic facies (hyaloclastite, resedimented hyaloclastite), polymictic felsic volcanic breccia, feldspar crystal-rich sandstone, feldspar- and pyroxene-porphyritic andesitic sills, and nonvolcanic mudstone and sandstone. Importantly, quartz-rich sandstone and rhyolite with quartz phenocrysts previously thought to be restricted to the ore horizon are now known to occur in the hanging-wall succession as well (Paulick and McPhie 1999).

The Thalanga massive sulfide deposits formed at a submarine volcanic center dominated by the products of effusive rhyolitic eruptions, comprising lavas and domes, together with lava- or dome-derived, mass-flow-emplaced clastic units and synvolcanic intrusions (Fig. 5). The crest of this volcanic center could have been up to 500 m above the surrounding area, probably reflecting the constructional relief of the high-aspect ratio lavas and domes. This setting resembles that of the PACMANUS hydrothermal field in the eastern Manus

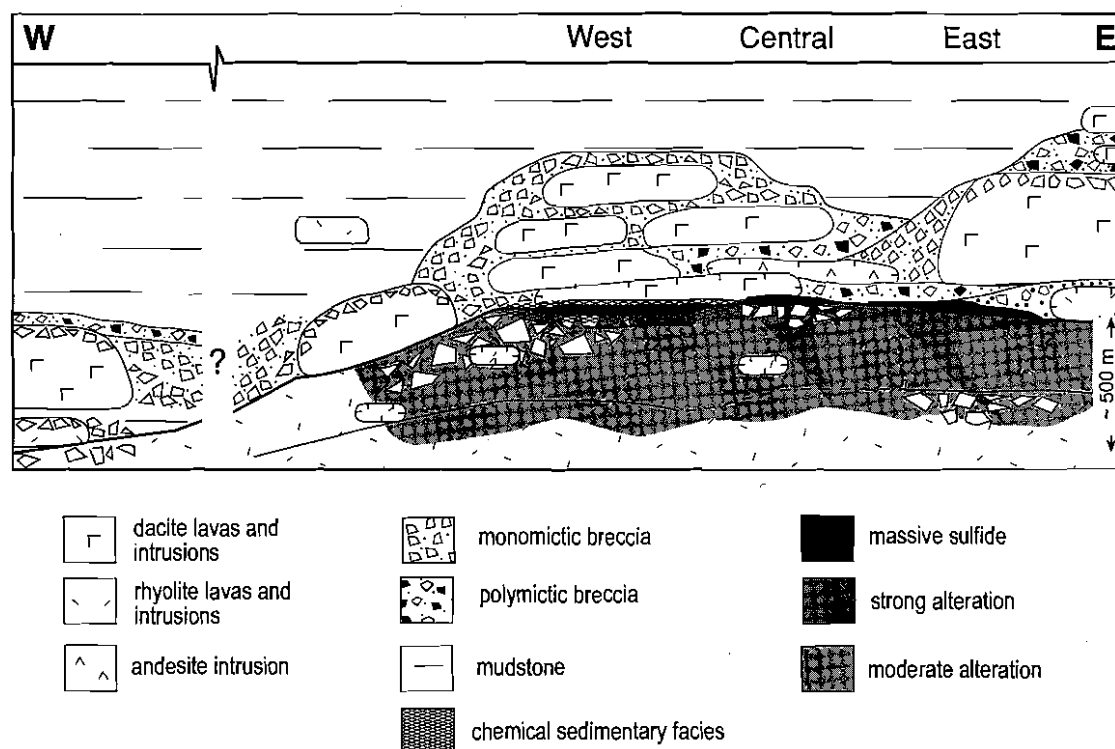


FIG. 5. Volcanic facies reconstruction of the environment of the Thalanga massive sulfide deposit, Mount Windsor subprovince, Queensland (after Paulick and McPhie, 1999).

basin (Papua New Guinea), which occurs at ~1,600 m below sea level on the top of a 400- to 600-m-high ridge composed predominantly of dacitic lava (Binns and Scott, 1993). After ore formation, the Thalanga mine area remained a center of effusive volcanism and topographically high, although compositions of lava flows and domes shifted to dacite. The massive sulfides at Thalanga were buried by dacite lavas, synvolcanic intrusions, and thick, mass-flow-emplaced volcanic breccias composed of locally derived clasts. Hemipelagic mudstone and turbidite sand, partly derived from an unknown possibly distal source, accumulated in surrounding lower lying areas.

Mapping of alteration in the footwall at Thalanga (Paulick 1999) has shown that the zones of intense alteration do not coincide either with particular facies boundaries or facies types and, instead, clearly crosscut the facies arrangement (Fig. 5). Thalanga is important in this regard, illustrating a case where the facies architecture apparently had minimal influence on the ore-forming hydrothermal system.

#### *Setting of Highway-Reward*

The Highway-Reward massive sulfide pipes occur in a shallow intrusion-dominated felsic volcanic center (Doyle and McPhie, 2000; Fig. 6). The intrusions are interleaved with pumice breccia, crystal-rich sandstone, turbidites, and suspension-settled mudstone. Contact relationships and phenocryst populations (mineralogy, size, and percentages) indicate the presence of at least 13 distinct porphyritic units in a volume of  $1 \times 1 \times 0.5 \text{ km}^3$ . More than 75 percent of the units

have peperitic upper margins that demonstrate their emplacement into wet unconsolidated sediment as shallow sills and cryptodomes. A single partly extrusive cryptodome emerged at the sea floor, but the presence of additional lavas or partly extrusive cryptodomes is indicated by resedimented autoclastic breccia units.

Paleosea-floor positions at Highway-Reward are difficult to assign and in any case, they do not appear to have been favored locations for massive sulfide formation. Instead, hydrothermal fluids were constrained by the steep contacts of intrusions and focused within the porous and permeable, glassy, brecciated margins, promoting the formation of sub-sea-floor massive sulfide pipes (Doyle and Huston, 1999). This distinctive style of massive sulfide is also reflected in the distribution of alteration, zones of strong hydrothermal alteration, and pyrite-quartz-sericite stringer veins extending 150 m into the footwall and at least 60 m above the sulfide pipes.

#### *Volcanic influences on VHMS style*

Patterns shown by the deposits described above allow speculation that volcanic setting may be a significant influence on the style and metal content of VHMS deposits. In simple terms the more copper rich deposits appear to be associated with felsic volcanic centers dominated by subvolcanic intrusions (e.g., Highway-Reward), whereas the more zinc rich deposits are associated with both felsic (e.g., Rosebery, Thalanga) and mafic-intermediate (e.g., Hellyer, Que River) volcanic centers dominated by lavas and/or volcanoclastic facies. Studies by Arnold and Sillitoe (1989) and Messenger et

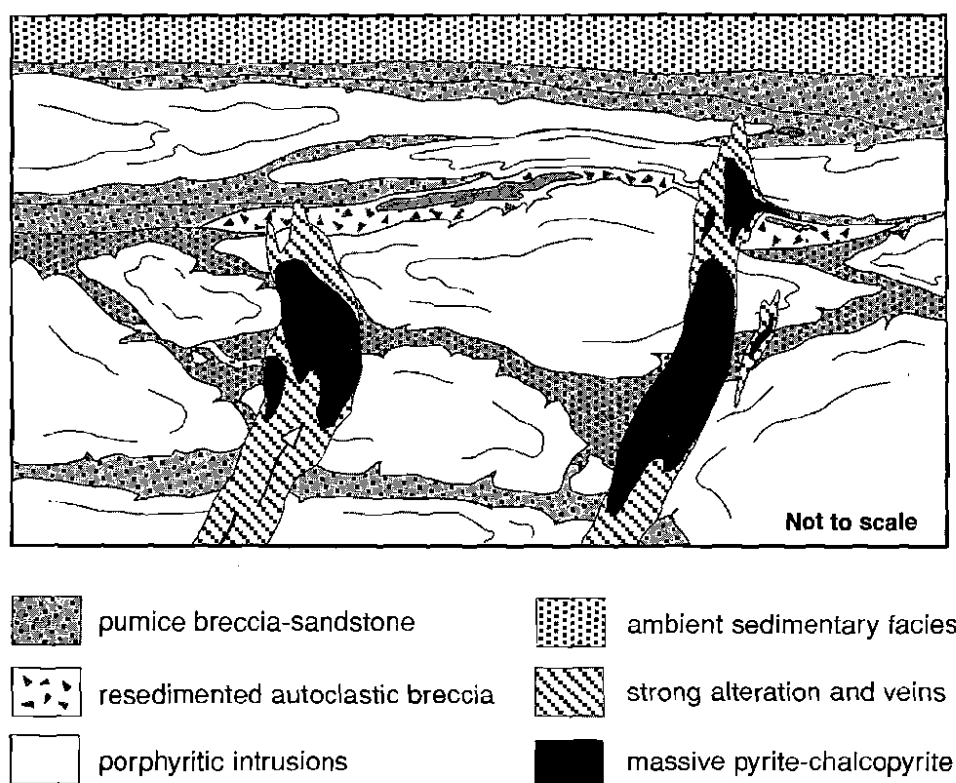


FIG. 6. Volcanic facies reconstruction of the environment of the Highway-Reward massive sulfide deposit, Mount Windsor subprovince, Queensland (after Doyle and McPhie, 2000).

al. (1997) at Mount Morgan support this proposed relationship between Cu-Au pyritic pipe ores and intrusion-related volcanic centers; however, the volcanic environment of Mount Lyell is too poorly understood to confirm the pattern.

Previous workers (e.g., Poulson and Hannington, 1995; Halley and Roberts, 1997) have demonstrated that the water depth can be an important control on gold/base metal ratio; gold-rich, base metal-poor deposits such as Henty typically form in shallow-water volcanic settings, whereas the base metal-rich deposits (e.g., Hellyer, Rosebery, Thalanga) are confined to deeper water volcanic settings (Fig. 3). The primary shape of the deposit may also be influenced by volcanic setting. Elongate mound-shaped deposits (e.g., Hellyer) form above major synvolcanic structures, in low-permeability volcanic facies that have focused hydrothermal fluid flow to the sea floor (Large, 1992). Multiple stratiform sheetlike lenses (e.g., Rosebery) are more likely to develop within permeable volcanoclastic facies, in which hydrothermal fluids are less focused and spread out laterally either below or onto the sea floor, forming thinner sheetlike lenses at various stratigraphic levels.

The relationship between ore metal ratios and nature of the volcanic center probably relates to the temperature of the associated hydrothermal system. Thermodynamic modeling studies (e.g., Sato, 1973; Large, 1977, 1992; Ohmoto et al., 1983) and measurements of temperature of black smoker vents on the sea floor (e.g., Goldfarb et al., 1983; Scott, 1992) have shown that copper mineralizing vents are typically associated with higher temperature fluids (>300°C) than the zinc mineralizing vents. Hydrothermal systems developed above or closer to synvolcanic intrusions are more likely to be hotter, and thus generate Cu-Au-rich ores, compared to the hydrothermal systems associated with lavas and volcanoclastic

facies or located on the cooler flanks of volcanic edifices and distal from synvolcanic intrusions.

#### Spectrum of Deposits in the Mount Read Volcanics and the Mount Windsor Subprovince

The deposit descriptions and genetic interpretations presented above suggest that the ores of the Mount Read Volcanics and the Mount Windsor subprovince do not all belong to the same VHMS class. Rather, there is a continuum or spectrum from classical VHMS deposits (e.g., Hellyer, Thalanga), which formed on the sea floor in a moderate- to deep-water environment, to replacement, intrusion-related, copper-gold deposits, which appear to be transitional between VHMS and high-sulfidation epithermal (e.g., Mount Lyell and Highway-Reward), to shallow-water gold-rich strata-bound replacement deposits that have some features akin to low-sulfidation epithermal ores. This spectrum is shown in a triangular diagram (Fig. 7) where the deposits have been plotted in terms of their attributes relative to end-member VHMS, porphyry Cu-Au-Mo, and epithermal Au-Ag ores. The spectrum encompasses deposit styles that we might expect in a submarine volcanic setting, from shallow-water (epithermal) to moderate- to deep-water (VHMS), and from subvolcanic intrusion-related replacement (porphyry) to sub-sea-floor replacement and sea-floor exhalative systems. Although we do not favor use of the term "high-sulfidation" VHMS for these hybrid-style massive sulfide and disseminated deposits, as proposed by Sillitoe et al. (1996), we do agree that their formation probably involved subsea-floor replacement, in relatively shallow water, with involvement of a magmatic fluid component.

This spectrum of submarine volcanic-hosted deposits is not considered to be unique to the Mount Read Volcanics and the

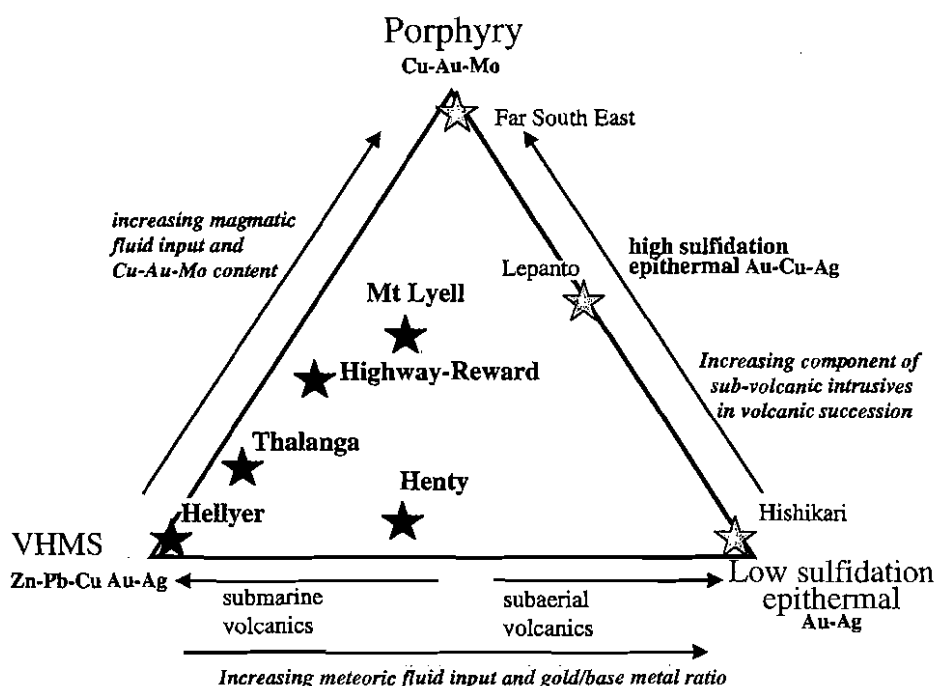


FIG. 7. Triangular representation showing the spectrum of ore deposits in volcanic successions, using selected deposits from the Mount Read Volcanics and Mount Windsor subprovince as examples.

Mount Windsor subprovince, but other cases probably occur in the major VHMS districts worldwide. Based on metal ratios, alteration assemblages, morphology, and volcanic environment, additional examples of hybrid Cu-Au-bearing massive sulfides that would plot within the triangle in Figure 7 are possibly the Horne and Bousquet deposits in the Abitibi district, Canada, the Gai and Kul-Yurt-Tau deposits in the Southern Urals, Russia, the Mount Morgan deposit in Eastern Australia, and the Boliden deposit in the Skellefte district, Sweden.

### Spectrum of Ore Deposit Alteration Halos

The studies in this special issue on the character, extent, and composition of hydrothermal alteration and volcanic facies related to the Australian VHMS deposits discussed above enables a comparison of hydrothermal alteration across the spectrum of deposits.

#### *Morphology, zonation, and extent of halos*

The morphology and zonation of the hydrothermal alteration halos associated with the polymetallic zinc-rich deposits (Rosebery, Hellyer, and Thallanga) and the pyritic Cu-Au deposits

(Western Tharsis-Mt. Lyell and Highway-Reward) are shown in Figure 8, based on data from Doyle (2001), Gemmell and Fulton (2001), Herrmann and Hill (2001), Huston and Kamprad (2001), Large et al. (2001), and Pauhick et al. (2001). The polymetallic zinc-rich deposits each have an alteration envelope, which is typically elongate parallel to volcanic stratigraphy, with the footwall alteration more intense and more extensive than the hanging-wall alteration (Fig. 8a, b, c). In the copper-gold-bearing deposits, the alteration halo extends a greater distance into the hanging wall and appears to cut across volcanic facies boundaries (Fig. 8d, e). In all cases, there is a simple zonation from chlorite  $\pm$  quartz-rich alteration close to the ore lenses, to sericite-rich alteration farther away. In the polymetallic zinc-rich ores, the chlorite  $\pm$  quartz-rich zone is commonly present immediately below the ore lenses (Fig. 8a, b, c) and is thickest and most intense below copper-rich parts of the orebody. At Hellyer (Fig. 8b), the chlorite and sericite alteration forms a zoned pipe, similar to those described for many Archean deposits in Canada (e.g., Sangster, 1972; Franklin et al., 1981); however, at Rosebery (Fig. 8a) the alteration zones are strata bound, and at Thallanga (Fig. 8c) there is evidence for a combination of pipes

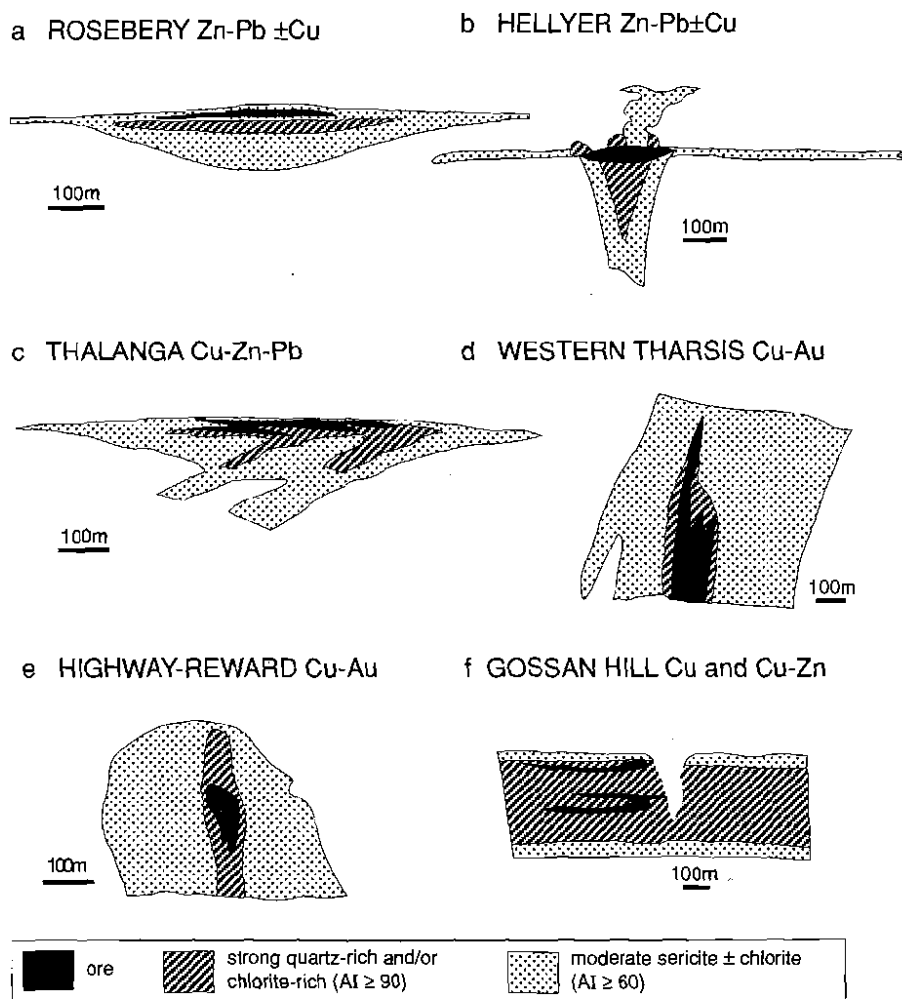


FIG. 8. Comparative sketches of alteration halos surrounding some Zn-rich (a), (b), (c) and Cu-rich (d), (e), (f) orebodies in the Mount Read Volcanics, Mount Windsor subprovince, and Murchison province (WA). Abbreviation AI = Alteration Index.

and strata-bound zones. Previous workers (e.g., Morton and Franklin, 1987; Large, 1992) have discussed the importance of permeability and faults in the footwall as controls on ore fluid discharge and the formation of alteration pipes or strata-bound zones.

The copper-gold pyritic ores commonly show intense chlorite  $\pm$  quartz alteration within and immediately surrounding the ore, both on the hanging-wall and footwall sides. The sericite  $\pm$  chlorite halo can be very extensive and commonly shows a symmetric pattern surrounding the chlorite  $\pm$  quartz-rich zone (Fig. 8d, e). At Western Tharsis in the Mount Lyell field, Huston and Kamprad (2001, fig. 3) have recognized a pyrophyllite-rich alteration zone, which forms an overprinting zone surrounding the Cu-bearing chlorite  $\pm$  quartz-rich core. The zone contains other minerals (topaz, fluorite, zunyite, and alunite types), which together with pyrophyllite indicate advanced argillic alteration, similar to that found in high-sulfidation epithermal systems (White and Hedenquist, 1995). Although Highway-Reward is a similar Cu-Au-bearing system to Mount Lyell, no advanced argillic assemblages have been reported.

Alteration zonation related to the Henty strata-bound disseminated gold deposit is very different from that in the zinc- and copper-rich VHMS deposit discussed above. In the gold orebodies the alteration is concentrically zoned, with a core of massive microcrystalline silica showing marked aluminum depletion, surrounded by an intermediate silica-sericite zone, followed by an outer zone of silica-sericite-pyrite-chlorite (Callaghan, 2001). Footwall alteration consists of intense sericite  $\pm$  pyrite  $\pm$  carbonate, whereas hanging-wall alteration consists of albite-silica  $\pm$  chlorite in strata-bound zones intercalated with carbonate-altered volcanoclastics and bedded carbonate (Halley and Roberts, 1997; Callaghan, 2001). Thus, compared to the zinc- and copper-bearing VHMS systems, the Henty gold system shows more intense silica rich and aluminum depleted alteration close to ore and extensive albite alteration within the hanging wall, consistent with a subseafloor replacement origin. Callaghan (2001) interprets the intense silica enriched, aluminum depleted, alteration core to form from a highly acidic, possibly magmatic, fluid.

#### *Hanging-wall alteration*

As described above, the pyritic Cu-Au deposits (Fig. 8d, e) are associated with extensive hanging-wall alteration (up to 200 m thick) of similar mineralogy but generally less intensity than the footwall alteration. This distribution reflects formation by subseafloor replacement rather than exhalation (Large, 1992). The stratiform sheetlike zinc-rich deposits at Rosebery and Thalanga (Fig. 8a, c) show little obvious visual hanging-wall alteration in drill core; however, lithogeochemical studies at Rosebery (Large et al., 2001) have revealed a weak chemical halo, indicated by the whole-rock Ba/Sr ratio and Mn content of carbonate, extending up to 100 m into the hanging-wall volcanoclastics. No similar hanging-wall halo has been defined at the Thalanga deposit (Paulick et al., 2001).

Hellyer is unusual as it is the only Paleozoic polymetallic VHMS deposit to exhibit a well-developed hanging-wall alteration zone. Studies by Gemmell and Fulton (2001) have defined a distinctive and zoned alteration plume overlying the central part of the deposit within the hanging-wall basalts.

Five alteration zones have been identified: fuchsite, chlorite, carbonate (calcite), quartz-albite, and sericite. Fuchsite-dominated alteration occupies the central portion of the hanging-wall alteration plume. Chlorite and carbonate alteration surrounds the fuchsite zone with carbonate zones forming near to the ore deposit, and chlorite zones extending above and lateral to the carbonate. Outward is quartz-albite alteration, which extends laterally into distal sericite alteration. After rapid burial of the deposit by basalt, continuation of upward hydrothermal fluid flow created the zoned hanging-wall alteration. Distribution of hanging-wall alteration assemblages suggests a temperature gradient from a higher temperature core (fuchsite) to a lower temperature rim (quartz-albite and sericite; Gemmell and Fulton, 2001).

In contrast to the crosscutting carbonate-bearing and quartz-albite zones at Hellyer, similar, but strata-bound, carbonate and quartz-albite  $\pm$  chlorite alteration lenses are present in the hanging wall of the Henty gold-rich volcanogenic ores (Large, C.P., 1995; Callaghan, 2001). It is significant from an exploration perspective, that whereas albite destruction is a ubiquitous feature of footwall alteration in the VHMS system, albite addition may be present in the hanging wall of some Zn- and Au-rich VHMS deposits.

#### *Carbonate alteration*

The distribution of carbonate alteration in the five deposits studied is shown in Figure 9. In the stratiform zinc-rich deposits, carbonate is commonly developed in either the chlorite- or sericite-bearing zones close to ore (Fig. 9a, b, c). In contrast the copper-gold ores show less or no significant carbonate alteration, and if present it is developed within an outer propylitic-type alteration halo surrounding the sericite zone (Fig. 9d). Hydrothermal carbonate is generally present as disseminated spots comprising 2 to 20 wt percent of the altered rock, although massive carbonate zones occur above, below, or lateral to zinc-lead ore at Rosebery and Thalanga. Textural evidence (e.g., Khin Zaw and Large, 1992; Sharp and Gemmell, 2001) and chemical evidence (e.g., Herrmann and Hill, 2001; Large et al., 2001) indicate that the carbonate zones form by infill of porosity and selective replacement of various components of the volcanic rocks, rather than by direct precipitation on the sea floor. Studies by Allen et al. (1998) of carbonate alteration in the Rosebery-Hercules area of the Mount Read Volcanics indicate that carbonate alteration distal to ore is generally low intensity and not texturally destructive, occurring as disseminations, filling primary porosity such as vesicles and replacing or rimming glass shards and feldspar phenocrysts, in advanced stages. However, close to ore, more intense carbonate alteration masks primary volcanic textures, resulting in fine-grained massive homogeneous pale-colored rock. The alteration carbonate minerals are commonly complex mixtures of Fe-Mn-Mg-Ca carbonates, as summarized in Figure 9. At Rosebery the carbonates are commonly Mn rich (Large et al., 2001), whereas at Hellyer, Western Tharsis, and Gossan Hill ferroan dolomite, ankerite, and siderite are the common species.

Chlorite-tremolite-dolomite-calcite assemblages are prominent in thin strata-bound zones in, and laterally adjacent to, the western ore leuses at Thalanga. Their major element, immobile trace element, and isotopic compositions indicate they

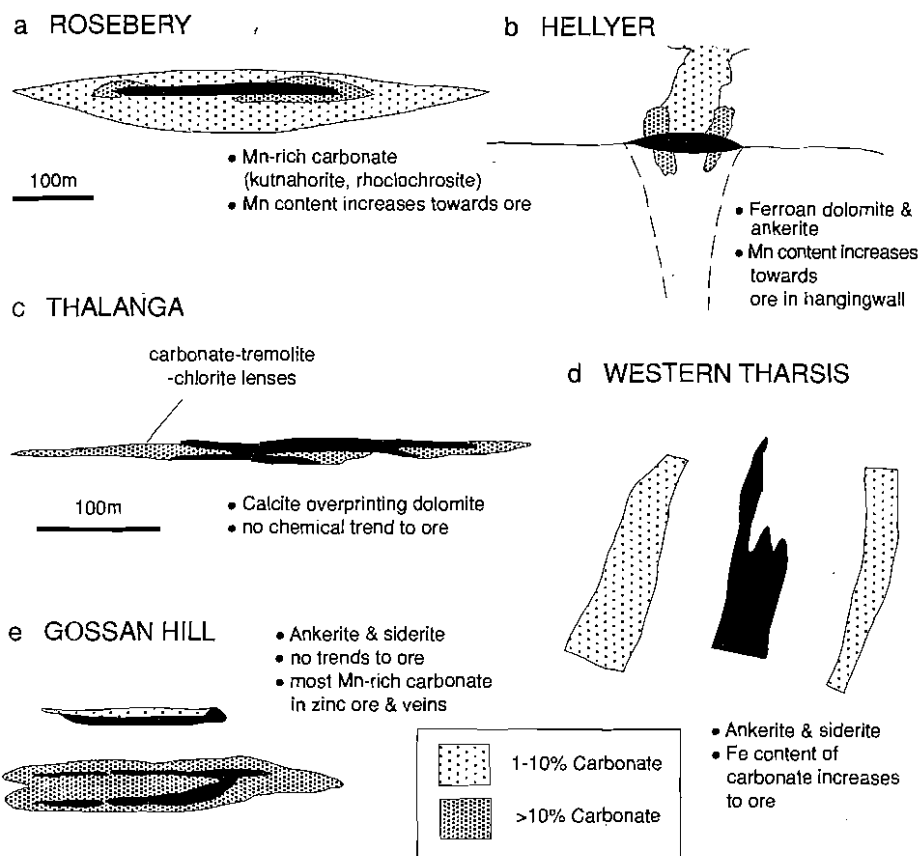


FIG. 9. Comparative sketches showing extent of carbonate alteration at Rosebery, Hellyer, Thalanga, Western Tharsis, and Gossan Hill.

are the metamorphic products of chlorite-dolomite assemblages that originated by hydrothermal alteration of rhyolitic volcanics, close to the paleosea floor (Herrmann and Hill, 2001). The chlorite and tremolite have magnesian compositions that do not show systematic lateral variations in relationship to ore. Dolomite and calcite have nearly ideal compositions. Dolomite contains up to 0.02 and 0.06 cations per formula unit of iron and manganese. Iron content of dolomite increases slightly toward the central ore lens (<0.005–0.02 cations) but there is no systematic spatial variation in manganese.

Bedded carbonates and carbonate-altered volcanoclastic facies are features of the Henty deposit (Halley and Roberts, 1997; Callaghan, 2001). The carbonate minerals (dominantly calcite) occur both in the footwall alteration zone (sericite-pyrite-carbonate) and as massive lenses in both the footwall and hanging wall.

Early studies of the carbonate lenses at Rosebery, Thalanga, and Henty (Braithwaite, 1974; Gregory et al., 1990; Halley and Roberts, 1997) concluded that they were of exhalative origin forming distal to the sea-floor sulfide lenses. However, in each case, more recent work has demonstrated their infill and replacement origin, involving mixing of hydrothermal fluid and seawater below the paleosea floor, in permeable volcanic units (e.g., Herrmann and Hill, 2001). Khin Zaw and Large (1992) used the isotopic composition of the ore-related carbonate minerals to interpret a seawater source for both carbon and oxygen. Callaghan (2001) used

isotopic data on the carbonates at Henty to suggest that they resulted from a district-wide magmatic  $\text{CO}_2$  devolatilization event, which commenced during early hydrothermal activity and continued for a period beyond ore formation. Carbonate deposition resulted from mixing of small amounts of a magmatic  $\text{CO}_2$ -rich fluid with seawater at, or below, the paleosea floor (Callaghan, 2001).

#### *Volcanic influences on alteration styles in VHMS successions*

The facies architecture of submarine volcanic successions that host VHMS deposits is inherently complicated, and additional stratigraphic and structural complexities may be introduced by the synvolcanic intrusions and synvolcanic faults. Sites of ore deposition are highly variable and may comprise thick lava and breccia successions (e.g., Hellyer, Thalanga), synvolcanic intrusions (e.g., Highway-Reward), and volcanoclastic mass-flow units (e.g., Rosebery and Hercules). Orebodies may have formed in shallow subsea-floor settings as replacements of volcanoclastic (e.g., Rosebery and Hercules) or synvolcanic intrusions (e.g., Highway-Reward), or else at the sea floor (e.g., Hellyer).

Even though submarine volcanic successions are potentially immensely complex, their initial response to alteration is at least in part predictable. Factors that appear to influence responses to alteration include the presence of volcanic glass, the porosity and permeability (including fracture density and faulting), the rock composition, and external conditions such

as pressure, temperature, fluid composition, and fluid/rock ratio. Of particular importance is the presence of volcanic glass and the porosity and permeability characteristics.

**Proportion and distribution of glassy versus crystalline domains:** Submarine lavas, high-level intrusions, and some volcanoclastic facies are commonly initially glassy or at least partly glassy (Fig. 10). Once formed, both the texture and composition of volcanic glass may be partially or completely modified by a variety of processes, such as hydration, devitrification (crystallization below the glass transition temperature), diagenetic alteration, and compaction. The rate at which these modifications proceed is in general accelerated by the presence of water and by elevated temperature. In contrast, crystalline components of volcanic facies are generally unaffected by hydration and compaction and may remain largely stable during diagenetic alteration. Thus, glassy domains will undergo longer and more complex textural evolution and exhibit greater compositional changes than crystalline

domains in the same facies. This generalization holds scales ranging from millimeters, such as in the case of versus crystalline flow laminae in lavas, to meters, such as the case of glassy margins versus the crystalline interiors of lavas and synvolcanic intrusions.

**Porosity and permeability characteristics:** The extent of physical and chemical interaction of various volcanic facies with seawater, diagenetic fluids, and/or hydrothermal fluids depends on the porosity and permeability. These properties vary enormously among different volcanic facies types, both spatially within some volcanic facies, and also temporally, during the time of emplacement through compaction and diagenetic alteration. However, in simplest terms, coherent and coherent volcanic facies show fundamentally different styles of porosity and permeability (Fig. 10).

Coherent domains of lavas and intrusions are dominated by fracture-controlled porosity and permeability. This style varies in scale from very large (meters) quench fractures or cooling joints to very small (millimeters) perlitic fractures. The former generally prevail in the interior of lavas and synvolcanic intrusions, whereas the latter may occur in any glassy domain within glassy clasts. In volcanoclastic facies, the interparticle and intraparticle pores control porosity and permeability, so that grain type (pumice or scoria versus nonvesicular clasts), grain size, and sorting are all important. Well-sorted pumice breccias, such as that forming the footwall to the Rosebery and other massive sulfide deposits, at least initially has uniform high porosity and permeability. Poorly sorted mixtures of scoria, crystals, and dense volcanic clasts (for example, resedimented autoclastic facies) have lower and more heterogeneous porosity and permeability. The matrix character and abundance are particularly important in poorly sorted aggregates.

Thus, there is a wide spectrum in the textural and compositional responses of different volcanic facies to diagenetic and other alteration even within one succession. Glass-rich, more porous and permeable facies in submarine volcanic successions are the most easily affected. The textural and compositional contrasts that initially exist between glassy and crystalline domains will persist during, and influence, any alteration, including alteration related to VHMS ore-forming hydrothermal activity.

#### Chemical mass changes

The intense hydrothermal alteration of the footwall of VHMS deposits may be associated with significant changes in the mass of mobile chemical components (e.g., Barrett and MacLean, 1991, 1994; Barrett et al., 1993). Estimates of mass changes in variably altered and spatially related samples have been used in lithogeochemical exploration (MacLean and Barrett, 1993; Galley, 1995). This technique has not been widely applied in Australian VHMS deposits. However, the available data for Australian deposits indicate that large net mass gains associated with silicification of footwall zones are typical. This pattern contrasts with net mass losses in the chloritic zones that exist beneath some Canadian VHMS deposits (e.g., Noranda; Barrett and MacLean, 1993).

Gemmell and Large (1992) applied a modified method to estimate mass changes in the zoned alteration beneath the Hellyer deposit. They found that alteration includes a stringer envelope, sericitic, chloritic, and siliceous core

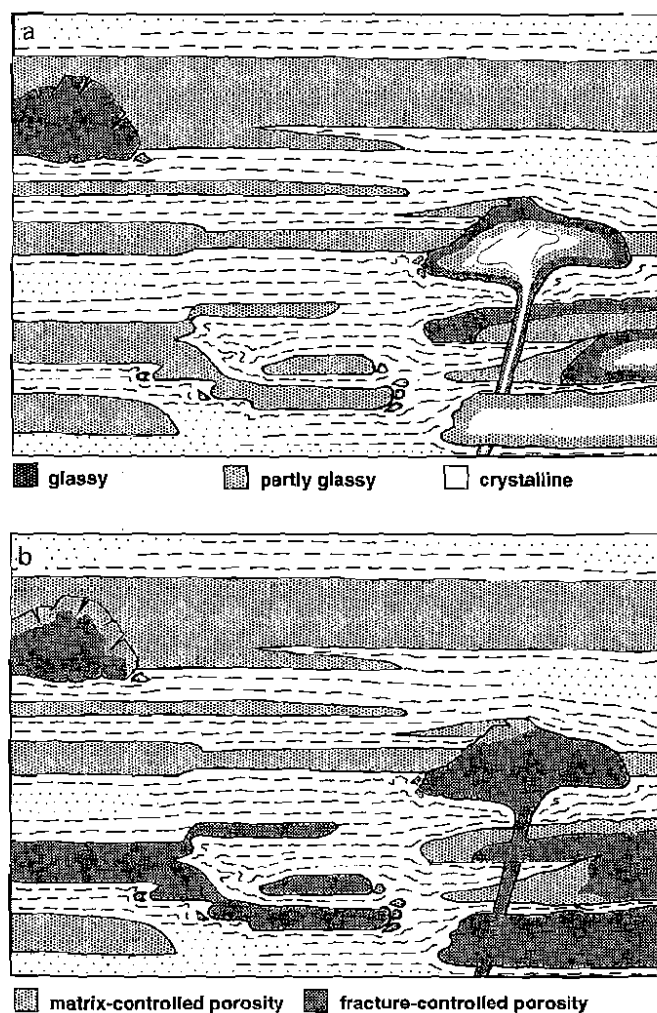


FIG. 10. a. Abundance and distribution of glassy, partly glassy, and crystalline domains within the principal volcanic facies types found in submarine volcanic successions. b. Distribution of fracture- vs. matrix-controlled porosity in the principal volcanic facies types found in submarine volcanic successions. The coherent parts of lavas and intrusions have fracture-controlled porosity, whereas the porosity of volcanoclastic facies is matrix controlled (after Mc Phie et al., 1993).

involved net mass gains of 4/100 g, 2/100 g, 18/100 g, and 108/100g, respectively. These zones reflect increasing alteration intensity from the outer shell to the inner core of the subvertical feeder system. All the zones lost substantial  $\text{Na}_2\text{O}$  and minor  $\text{CaO}$ . The major gains were in  $\text{Fe}_2\text{O}_3$ , S, and  $\text{SiO}_2$ , with additional slight gains in  $\text{K}_2\text{O}$  in most zones, and  $\text{MgO}$  in the sericitic and chloritic zones (Table 2). Paradoxically, the chlorite zone appears to have lost  $\text{SiO}_2$  (-13/100g). That contrasts with the  $\text{SiO}_2$  gains in the adjacent sericitic and siliceous core zones (13 and 95/100 g, respectively).

At Thalanga, most footwall alteration zones were associated with net mass gains up to about 50/100g; mainly attributable to large gains in  $\text{SiO}_2$  (Herrmann and Hill, 2001). The pyritic stringer zones also gained substantial  $\text{Fe}_2\text{O}_3$  and S, and the peripheral siliceous white rhyolite zones gained minor  $\text{K}_2\text{O}$ . In contrast, some volumetrically small footwall sericite-chlorite and chlorite-tremolite zones are characterized by net mass losses due to significant losses of  $\text{SiO}_2$ . All Thalanga footwall alteration zones exhibit major or total loss of  $\text{Na}_2\text{O}$ .

Consideration of limited geochemical data from Rosebery (Large et al., 2001) suggests that the footwall alteration was also mainly associated with net mass gains, dominated by significant gains in  $\text{SiO}_2$ . Estimates of absolute mass changes for variably altered samples from beneath the K lens reveal losses of  $\text{Na}_2\text{O}$  in all the footwall hydrothermal alteration assemblages (Table 2). With the exception of a slight loss of  $\text{SiO}_2$  in the chloritic zone immediately below the ore, all other footwall-altered samples exhibit minor to large gains of  $\text{SiO}_2$  (Table 2).

#### *Conditions of formation of hydrothermal alteration in VHMS systems*

Previous workers (e.g., Large, 1977; Riverin and Hodgson, 1980; Lydon and Galley, 1986) have suggested that alteration zonation in the footwall of VHMS deposits probably reflects fluid/rock interaction controlled by decreasing temperature with distance from the center of the hydrothermal upflow zones. However, the Mg-free nature of modern sea-floor hydrothermal fluids suggests that Mg-bearing chlorite development in footwall alteration zones most likely relates to the

entrainment of seawater into the hydrothermal system (Roberts and Reardon, 1978; Lydon, 1988).

The idea of alteration zonation due to a decreasing thermal and fluid/rock ratio has been tested and refined by Schardt et al. (2001) in a thermodynamic model designed to reproduce the zonation present in the footwall alteration pipe at Hellyer, passing from the silica-rich core, through a chlorite-rich shell, to the sericite-rich envelope. Schardt et al. (2001) have shown that alteration mineral zonation depends principally on variations in temperature, pH, redox state, and reaction progress (or fluid/rock ratio), as hydrothermal fluids move outward from the center to edges of the alteration system. The classic footwall zonation of quartz  $\rightarrow$  chlorite  $\rightarrow$  sericite at Hellyer was reproduced by reacting a fluid at 250° to 350°C (starting temperatures) and pH of 4.5 to 5.0 with andesite over a decreasing fluid/rock ratio from 50,000 down to 20. Reactions during cooling over the temperature range 350° to 100°C reproduced the full range of footwall alteration assemblages. The pH of the reacting fluid showed little variation (4.5–4.0) during reaction progress (Schardt et al., 2001). Mg-rich chlorite formed in the inner chlorite-rich zone and Fe-rich chlorite developed in the outermost part of the sericite zone, similar to the pattern observed in many massive sulfide deposits (Urabe et al., 1983). This modeling was carried out employing an Mg-bearing ore fluid, with the assumption that a component of seawater Mg was entrained into the ore fluid at depth. Further coupled fluid flow-fluid chemical modeling is planned to study footwall chlorite formation related to the interaction of an upwelling Mg-free hydrothermal fluid with advected Mg-bearing seawater, as proposed by several workers (e.g., Roberts and Reardon, 1978; Franklin et al., 1983).

The modeling by Schardt et al. (2001) demonstrated that, for the case of Mg-bearing hydrothermal fluids, extensive chlorite alteration zones are favored by higher temperatures (>250°C) and less acidic pH (4.5–5.5) fluids. Sericite-dominated alteration, on the other hand, forms at lower temperatures (<250°C) and more acidic conditions (pH = 4.0–4.5). At lower pH, kaolinite and pyrophyllite are stabilized, and at higher pH and lower temperatures (<200°C), K feldspar becomes an important component of the outermost alteration

TABLE 2. Summary of Major (absolute) Mass Changes in Alteration Zones Associated with Hellyer, Rosebery, and Thalanga Massive Sulfide Deposits

Deposit	Alteration zone	Net mass change (g/100g)	Major mass gains	Major mass losses
Hellyer	Siliceous core	108	Si, Fe, S, (K)	Na, (Ca)
	Chlorite	18	Fe, Mg, S	Si, Na, (Ca)
	Sericite	2	Si, Fe, S, (K)	Na, (Ca)
	Stringer envelope	4	Si, S, Fe, (K)	Na, (Ca)
Rosebery	Quartz-sericite	~10–60	Si, Fe, $\pm$ (S, K, $\text{CO}_2$ )	Na
	Sericite	~10–30	Si, (K, $\text{CO}_2$ )	Na
	Chlorite	~0	Mg	Si, Na
Thalanga	Chlorite-tremolite-carbonate (CTC 2 and 3)	147	Ca, Mg, $\text{CO}_2$ (Fe, S, Zn)	Na, K
	Chlorite-tremolite (CTC 1)	-28	Mg, (Fe, S)	Si, Na
	Qtz-Py stringer zones	52	Si, Fe, S	Na
	Qtz-Ks white rhyolite	47	Si, K	Na
	Qtz-Ser-Chl moderately altered rhyolite	19	Si, (Fe, S)	Na
	Ser-Chl foliated rhyolite	-27	(Mg)	Si, Na

Abbreviations: chl = chlorite, Ks = K feldspar, Py = pyrite, qtz = quartz



zone (Schardt et al., 2001). The modeling supports previous interpretations (e.g., Walshe and Solomon, 1981) that intense chlorite and quartz rich alteration associated with copper-gold VHMS deposits results from high-temperature hydrothermal systems ( $>300^{\circ}\text{C}$ ), whereas sericite-dominated alteration associated with zinc-lead-silver ores results from lower temperature hydrothermal systems ( $<200^{\circ}\text{C}$ ). At intermediate temperatures ( $200^{\circ}$ – $300^{\circ}\text{C}$ ), mixed chlorite-sericite assemblages are typically developed. Carbonate alteration was not considered by Schardt et al. (2001); however, it is likely that significant carbonate alteration, particularly chlorite-carbonate assemblages, indicates more alkaline conditions that may develop where hot, near-neutral hydrothermal fluids have mixed with, and heated, entrained seawater, leading to saturation of carbonate at the periphery of the hydrothermal upflow zones.

#### Alteration Vectors Useful for Exploration

A summary of the alteration vectors discussed in the papers of this special issue is given below. The reader is also referred to an excellent review on this topic by Galley (1995), which is based principally on case studies of Canadian VHMS deposits.

##### *Mineral zonation vectors*

Zonation from sericite-rich alteration assemblages to more chlorite- or quartz-rich alteration has been recognized for some time as an empirical vector toward the center of hydrothermal systems associated with VHMS deposits (e.g., Sangster, 1972; Lydon, 1984). Chlorite-rich alteration is more common close to copper-rich ores, especially those containing magnetite or pyrrhotite, such as the Archean Noranda-type Cu-Zn deposits (e.g., Franklin, 1995), and quartz-rich alteration may be present close to gold-rich ores (e.g., Henty). Carbonate alteration may occur in both the chlorite and sericite zones but is more commonly associated with the zinc- (e.g., Rosebery, Thalanga) and gold-rich deposits (e.g., Henty) than the copper-rich deposits.

The most intense carbonate alteration is commonly laterally adjacent to inferred fluid upflow zones and probably developed in porous volcanic units where the hydrothermal fluids mixed with seawater (e.g., Thalanga; Herrmann and Hill, 2001).

##### *Major element lithogeochemical vectors*

All deposits studied in this investigation show zones of plagioclase destruction and sodium depletion in the footwall. Similar zones of sodium depletion have been known about, and applied in, mineral exploration for the Kuroko deposits of Japan and the Archean massive sulfide deposits of Canada for over 30 yr (Franklin et al., 1981). These zones are commonly associated with iron and magnesium enrichment, depending on the degree of pyrite and chlorite alteration, the Fe/Mg ratio of the chlorite, and the original composition of the volcanic rock. Potassium may be enriched or depleted within the alteration zone, depending on the ratio of sericite to chlorite. The following three lithogeochemical approaches based on variations in whole-rock composition may serve to define vectors to ore: (1) ratios such as the Ishikawa alteration index (AI) and the chlorite-carbonate-pyrite index (CCPI), which track the chemical and mineralogical changes associated with

hydrothermal alteration (Ishikawa et al., 1976; Large et al., 2001); (2) Pearce element ratios (Stanley and Madeisky, 1994), which involve mathematic treatment of the whole-rock data to distinguish igneous fractionation and volcanic component mixing trends from hydrothermal alteration associated with mineralization; and (3) determination of elemental mass changes associated with hydrothermal alteration, using the procedure of Gresens (1967), modified by Grant (1986), in conjunction with immobile element chemostratigraphy (Barrett and MacLean 1994; Barrett et al., 2001).

The first of these methods combines two alteration indices, AI and CCPI, to produce the alteration box plot and is simple and easily applied in the exploration context. It has the added advantage of relating chemical to mineralogical changes in a graphic method, highlighting any trends that may be spatially related to VHMS ores (Fig. 11; Large et al., 2001).

Figure 11 depicts the most common alteration trends generated by hydrothermal systems associated with VHMS deposits. Least altered volcanic samples plot within a central box with an AI = 20 to 65 and a CCPI = 15 to 85, depending on primary composition (Large et al., 2001, fig. 7). Hydrothermally altered samples define a trend to the right, depending on the relative significance of sericite, chlorite, pyrite, K feldspar, and carbonate alteration. Diagenetic alteration, which includes albite, epidote, paragonite, and calcite, and some types of weak hanging-wall alteration, produces trends to the left on the box plot.

##### *Mineral composition vectors*

Previous studies have emphasized the composition of chlorite, in particular the variation in Fe/Mg ratio, as a vector to mineralization (e.g., Urabe and Scott, 1983; McLeod and Stanton, 1984; Lydon, 1988). However, research in the Mount Windsor and Mount Read volcanic successions suggests that subtle changes in the composition of white mica may be just as useful (Herrmann et al., 2001; Huston and Kamprad, 2001; Large et al., 2001).

Herrmann et al. (2001) have shown that spectral analysis of rock samples by short wavelength infrared analysis (SWIR) using the PIMA can reveal changes in the Fe and Mg content ("phengicity"), Si/Al ratios, and the Na/(Na + K) ratios of white mica. White mica in the symmetrical hydrothermal alteration zones surrounding the pyritic Cu-Au deposits at Western Tharsis (Mt. Lyell, Tasmania) and Highway Reward (Mt. Windsor subprovince, Queensland) vary systematically in composition from phengite at the outer edge of the alteration to sodic muscovite close to ore. At Rosebery, a zone of phengitic white mica surrounds the ore zone, and a zone of sodic white mica occurs in a volcanoclastic unit above the highest grade ore. The most barium rich mica (between 5 and 10% Ba ion substituting for K) occurs close to ore in the immediate hanging-wall and footwall positions.

Although our research shows that there are significant variations in chlorite composition surrounding VHMS deposits, there is no common and systematic pattern related to the distance from the ore. This is at variance with studies elsewhere which have shown that the Mg content of Fe-Mg chlorite commonly increases passing from the margin to the core of the footwall alteration system (e.g., Seneca, Southbay, and Corbet deposits; Urabe et al., 1983). In contrast, in the

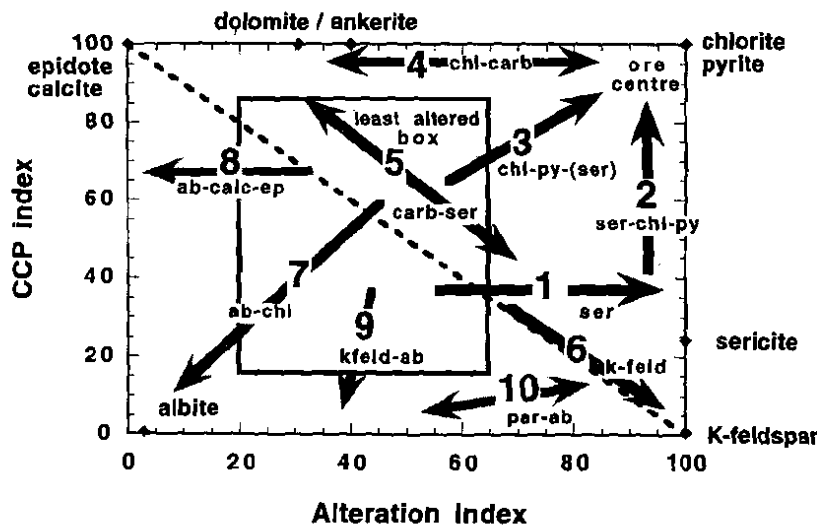


FIG. 11. Alteration index (AI)-chlorite-carbonate-pyrite index (CCPI) box plot showing principal hydrothermal and diagenetic alteration trends in submarine volcanics associated with VHMS deposits (from Large et al., 2001).  $AI = 100(MgO + K_2O)/(MgO + K_2O + Na_2O + CaO)$ ,  $CCPI = 100(FeO + MgO)/(FeO + MgO + Na_2O + K_2O)$ .

Bathurst district also in Canada, the reverse pattern has been recorded, with the Fe content of chlorite increasing toward the alteration core (e.g., Heath Steele, Lentz et al., 1997; Brunswick 2, Luff et al., 1992). Thalanga is the only deposit in this program of study where a consistent trend of chlorite composition has been recorded. Paulick et al. (2001) have identified an increase in the  $Mg/(Mg + Fe)$  ratio of hydrothermal chlorite toward the ore from values of 40 to 50 in the least altered footwall rhyolites to 85 to 95 in the footwall rhyolites close to ore. Although no trends were defined at Rosebery and Hellyer, our research indicates that chlorite close to ore, or within the ore host stratigraphy, tends to be Mg rich, whereas chlorite outside the alteration zones tends to be Fe rich (Gemmell and Fulton, 2001; Large et al., 2001). Studies in the Mount Read Volcanics (Herrmann et al., 2001) have shown that in most regional and weakly altered zones distal to massive sulfides where fluid/rock ratios are low, the chlorite composition is controlled by the bulk-rock composition, rather than a position relative to mineralization.

Of all minerals studied here, carbonates seem to have the most potential as vectors to ore, both in hanging-wall and footwall alteration. Distal carbonate, in small amounts (2–10 wt %), within least altered volcanic samples commonly has a relatively pure dolomite or calcite composition. Alteration dolomite commonly shows an increase in iron and/or manganese content as it approaches the ore. For example, at Rosebery the  $MnCO_3$  content of dolomite increases systematically from values of 1 to 10 mole percent in the outer alteration envelope to values of 50 to 95 mole percent close to the ore (Large et al., 2001). At Hellyer, the Mn content of dolomite and ankerite in the hanging wall increases toward the ore (Gemmell and Fulton, 2001), whereas at Western Tharsis, the Fe content of ankerite and siderite in the outer envelope of the alteration system increases toward the ore (Huston and Kamprad, 2001). Similar trends in carbonate composition (dolomite to Mn-bearing siderite) have been

recorded in the footwall alteration zone of the Matabi VHMS deposit, Canada (Franklin et al., 1975).

#### Thallium and antimony halos

Certain volatile elements such as thallium, mercury, and antimony are known to form extensive halos surrounding particular types of vein- and massive sulfide-style deposits (e.g., Shaw, 1952; Ikrauddin et al., 1983; Smith and Huston, 1992). Smith (1973) was the first to record Tl dispersion around a VHMS deposit, later described in detail by Smith and Huston (1992) for the Rosebery deposit, and considered further by Large et al. (2001). Our recent research on several VHMS deposits in Australia has shown that the stratiform Zn-rich deposits, such as Rosebery, Hellyer, and Thalanga, have significant thallium and antimony halos, whereas the Cu-Au deposits (Western Tharsis, Highway-Reward, and Gossan Hill) show no halos (Figs. 12 and 13).

Both Rosebery and Hellyer exhibit halos extending several hundred meters into the hanging wall in which Tl and Sb are greater than 1 ppm. Within and close to the ores, values greater than 10 ppm are common, with a systematic decrease outward and stratigraphically upward from the ore lenses (Figs. 12 and 13). The halo at Thalanga is less well developed, extending less than 50 m into the hanging wall and footwall.

There is a variation in Tl/Sb ratio for the three Zn-rich deposits with significant halos (Fig. 13): Rosebery has a Tl/Sb ~1, compared to Hellyer, which has a Tl/Sb ~0.1, and Thalanga, which has a Tl/Sb ~5. Overall the halo data for all six deposits (Figs. 12 and 13) suggest a relationship between the mean Zn/Cu ratio of the orebodies and the extent and magnitude of the Tl halo. Western Tharsis, Highway-Reward, and Gossan Hill have Zn/Cu ratios <1 and no significant Tl halo, Thalanga with a Zn/Cu ~6 has a weakly developed halo, and Hellyer and Rosebery have Zn/Cu ratios >30 and well-developed halos. This trend may also be extended to include the HYC SEDEX deposit, northern Australia, with a Zn/Cu >50, and a

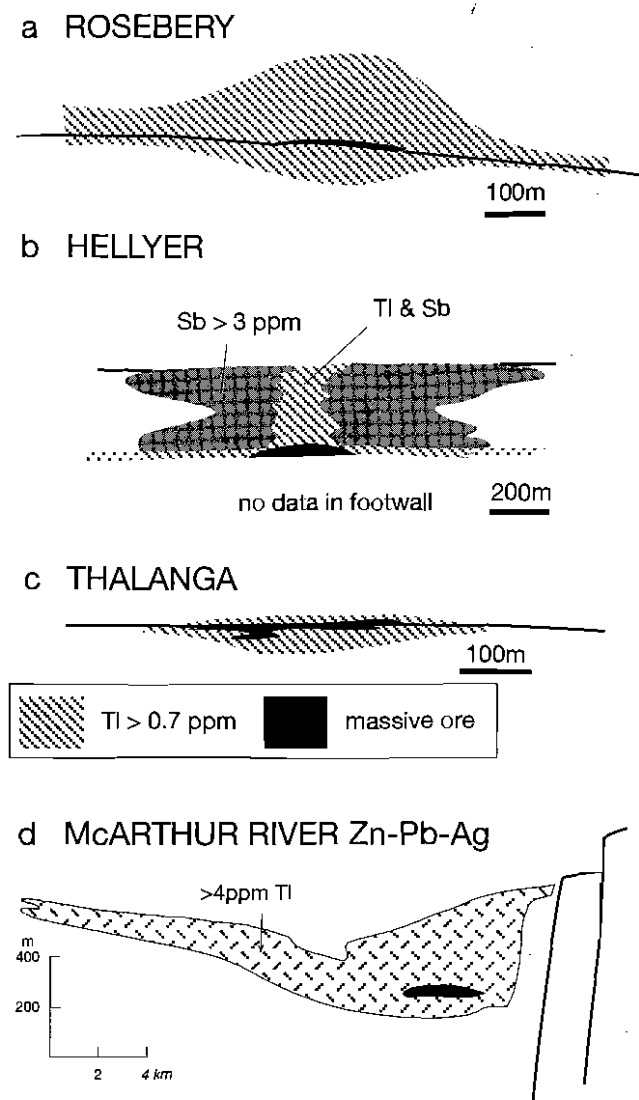


FIG. 12. Extent of thallium halos associated with three zinc-rich VHMS deposits: Rosebery, Hellyer, and Thalanga compared to the McArthur River SEDEX Zn-Pb-Ag deposit (Large et al., 2000). Note the scale change for McArthur River, where the halo extends for over 20 km compared to the VHMS deposits, where the halos extend for less than 1 km beyond the ore zones.

Tl halo which extends hundreds of meters into the hanging wall and tens of kilometers along strike (Fig. 12d; Large et al., 2000). The lack of Tl in the Cu-rich ores and their associated alteration halos may relate to their higher temperature of formation. Tl and Sb tend to concentrate in the lower temperature Zn-rich systems but are probably too soluble for precipitation in the higher temperature copper-rich systems.

#### Isotope discrimination and vectors

Previous studies (e.g., Green et al., 1983; Cathles, 1993; Taylor et al., 2000) have demonstrated the use of whole-rock oxygen isotopes to define hydrothermal fluid/rock interaction and provide vectors to massive sulfide ores in volcanic successions. Research in the Mount Read Volcanics has confirmed the value of whole-rock oxygen isotopes in exploration

and also highlighted the potential use of carbon and sulfur isotopes (Solomon et al., 1988; Green and Taheri, 1992; Callaghan, 2001). Lead isotopes have been shown to be a discriminant for synvolcanic versus epigenetic mineralization styles in the belt (Gulson and Porritt, 1987). However, case studies, the foundation of ore vectors, are not well advanced for the isotopic systems in comparison to trace elements.

Altered volcanics beneath the stratiform Zn-rich deposits display low  $\delta^{18}\text{O}$  values (6.5–10‰; Green and Taheri, 1992), and these extend beyond the obvious Na depletion and Au-Cu-Pb-Zn enrichment of the visible alteration (e.g., Que River; Stolz and Large, 1992). This is typical of VHMS mineralization (e.g., Green et al., 1983; Cathles, 1993). Values higher than general footwall background occur within 500 m of the visible edge of alteration, forming a 900-m-wide zone at Hellyer with  $\delta^{18}\text{O}$  = 12.0 to 13.8 per mil and a 150-m-wide zone with  $\delta^{18}\text{O}$  = 14.0 to 15.6 per mil, 100 m beyond visible alteration at Hercules (Green and Taheri, 1992). Low-grade pyritic mineralization does not display values below background (Green and Taheri, 1992). Miller et al. (2001) outline and apply a method for the conversion of  $\delta^{18}\text{O}$  values in the Thalanga Range, Mount Windsor subprovince, to a pseudo-temperature profile, using XRD-determined mineral abundances and assumed values for the starting isotopic compositions of reacting water and rock. This provides a genetic basis for isotope vector interpretation but relies on (1) the accuracy of the assumed values, (2) a lack of isotopic resetting during later events, and (3) minimal influence of inherited oxygen during water-rock reaction.

Sulfur isotope vectors have only been studied at Rosebery, Hellyer, and, to a limited extent, Que River. By comparison, the sulfur isotope composition of the ores and stringer zone sulfides in most districts is very well known (e.g., Green et al., 1981; Solomon et al., 1988). The overall  $\delta^{34}\text{S}$  composition for mineral prospects has been proposed to be an economic discriminant for Cambrian deposits (Green and Taheri, 1992). For instance, economic stratiform mineralization in the Mount Read Volcanics has  $\delta^{34}\text{S}$  >6 per mil and commonly in the range of 8 to 12 per mil, probably reflecting the mixing of reduced Cambrian seawater sulfate ( $\delta^{34}\text{S}$  ~30‰; Claypool et al., 1980) with leached rock sulfur. Strata-bound pyrite with  $\delta^{34}\text{S}$  <5 per mil, such as the Boco prospect, is suggested to have formed at <200°C, which would prevent both sulfate reduction and base metal leaching (Solomon et al., 1998; Green and Taheri, 1992). However, some mineralization in the Mount Read Volcanics, with  $\delta^{34}\text{S}$  <5 per mil has recently been shown to relate to Au-Cu-bearing, high-sulfidation fluids, possibly derived from oxidized synvolcanic granites (e.g., Boda, 1991; Huston and Kamprad, 2001). This is an alternative explanation for the low  $\delta^{34}\text{S}$  values, and thus the  $\delta^{34}\text{S}$  discriminant requires modification to incorporate mineralogy.

The sulfur isotope composition of disseminated Fe sulfide in the footwall is emerging as a useful vector to the stratiform Zn-rich ores. Although the footwall stringer veins and disseminations have  $\delta^{34}\text{S}$  values similar to overlying ore, zones of high  $\delta^{34}\text{S}$  values occur lateral to the main footwall alteration at the three largest Zn-rich deposits in the Mount Read Volcanics. At Hellyer, Jack (1989) and Gemmell and Large (1993) found  $\delta^{34}\text{S}$  values of 11.9 to 40.7 per mil (avg of

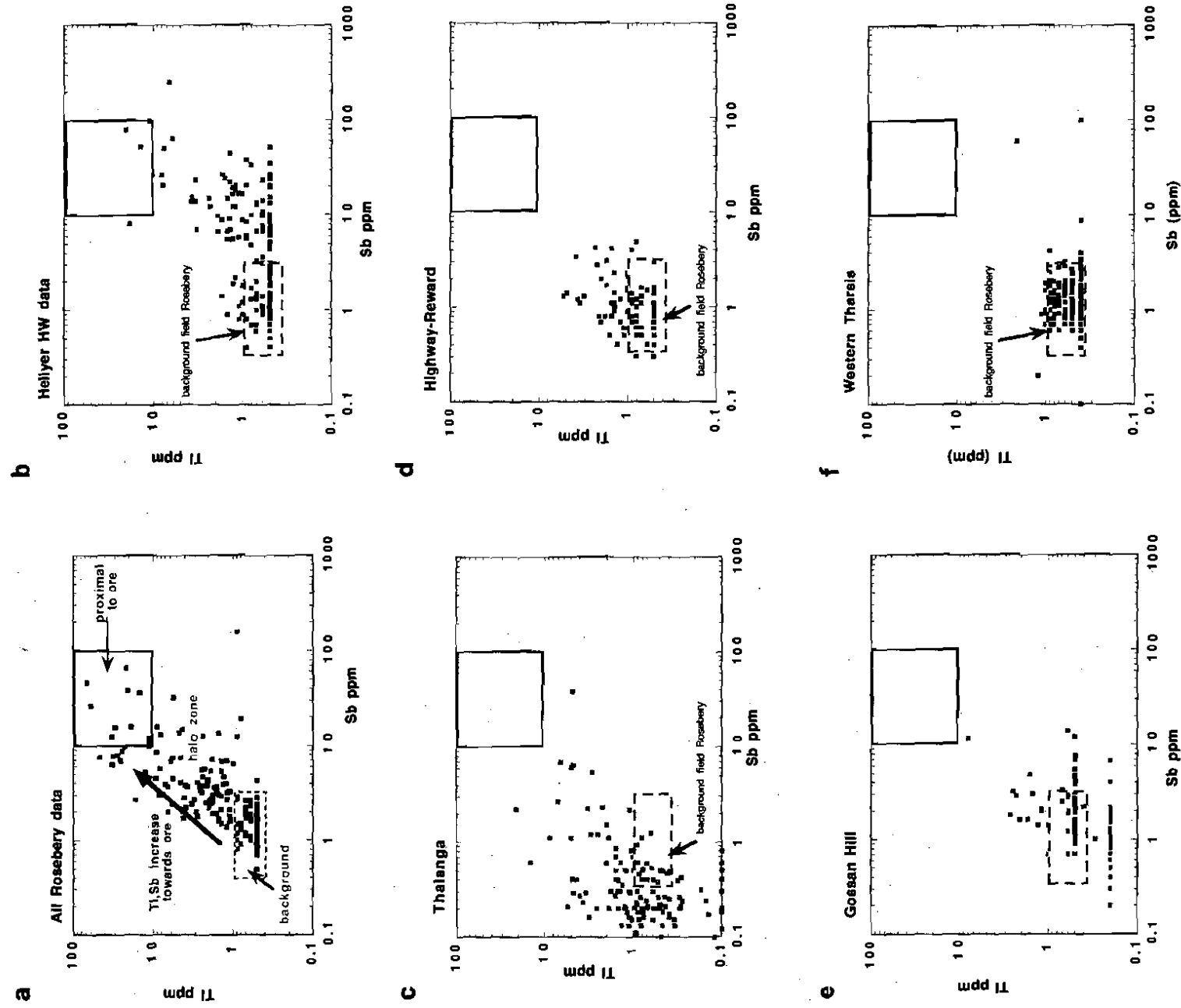


FIG. 13. Thallium-antimony relationships for ore and halo zones in three Zn-rich (Rosebery, Hellyer, Thalanga) and three Cu-rich (Highway-Reward, Gossan Hill Cu, and Western Tharsis) VHMS deposits.

25.0‰) in coarse pyrite up to 200 m from the central intense alteration. Similar enrichment has been discovered at Rosebery but is confined to a distinct, tabular 70-m-thick zone ~100 m from the ore that extends up to 500 m away from the hydrothermal vent (Davidson et al., 2000). These  $^{34}\text{S}$ -enriched zones approach and even exceed the isotopic composition of Cambrian seawater sulfate and probably formed by partial in situ seawater sulfate reduction. The values require that sulfate reduction occurred under closed or partly closed conditions that must have differed markedly from those of the main hydrothermal upflow stringer zones. Their precise relationship to associated whole-rock oxygen isotope values has not been established. They have the potential to significantly expand the isotopic halo of large systems and are predicted to be more tabular in porous volcanoclastic units (e.g., Rosebery) than in lavas (e.g., Hellyer, Que River). We speculate that similar zones may occur in other VHMS deposits but have not been detected because few studies have examined the isotopic composition of sulfides lateral to footwall vents, and such sulfides are fine grained requiring bulk sulfur dissolution or microanalytical techniques, both of which are not commonly applied.

#### *Rare earth element vectors*

The rare earth elements (REE) in Fe-Si-bearing ore-equivalent lateral marker beds and footwall alteration have been employed as vectors in massive sulfide districts (Lottermoser, 1989; Peter and Goodfellow, 1996; Spry et al., in press). To date, the ore-equivalent beds have proven most useful for this purpose, although Huston and Kamprad (2001) show there to be significant REE mobility in the very acid alteration zones of some Cu-Au systems, such as Western Tharsis.

The chemistry of Fe-Si lateral marker beds such as hematitic cherts can only be used in exploration where such units are common, as in the Mount Windsor subprovince. The REE composition of hematitic chert was successfully used as an exploration filtering tool by Miller et al. (2001) to discover satellite Zn-Pb ore in the Mount Windsor subprovince. Chert bodies above and along strike from the Thallanga Zn-Pb-Cu deposit exhibit strong positive Eu anomalies and LREE enrichment (Duhig et al., 1992). Davidson et al. (2001) show that positive Eu anomalies are not a feature of all hematitic chert bodies in the district, supporting the view that they are a valuable screening tool for exploration. Although some chert bodies developed from fluids that were sufficiently acid to destroy feldspar and mobilize  $\text{Eu}^{2+}$ , others have some features inherited from seawater, such as negative Ce anomalies, and probably originated from cooler recharge-dominated fluids (Davidson et al. 2001). Most examples formed in situ above diffuse alteration zones or within subsurface alteration zones (Doyle, 1997) and are very different from the extensive ore-equivalent marker beds that characterize other massive sulfide districts, such as the Bathurst district (Peter and Goodfellow, 1996). However, in all of these cases, high concentrations of host-rock REE, whether incorporated clastically or by replacement of wall rock, may mask the hydrothermal REE signature of the marker bed. Clastic REE are commonly held in resistate mineral phases that will survive reaction with most hydrothermal fluids (Davidson, 1998; Spry et al., in press). Consequently, if high concentrations of

clastic elements such as Zr, Ti, and Al are evident, the clastic REE signal must be quantified before the REE composition of the marker bed can be used as an exploration vector.

#### *Summary on exploration vectors*

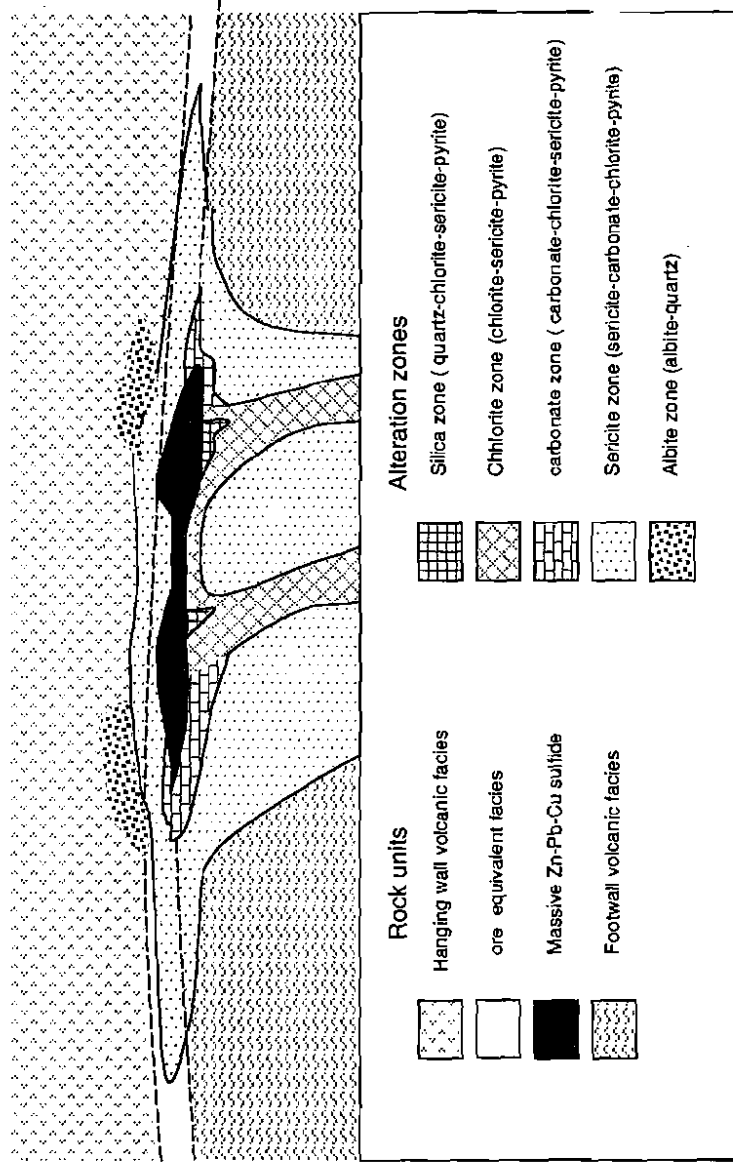
Schematic summaries of the mineralogical, lithogeochemical, and isotopic vectors useful for exploration are given for Zn-rich stratiform polymetallic ores in Figure 14 and for pyritic Cu-Au ores in Figure 15. Our recent research indicates that the most useful vectors for Zn-rich ores are Na depletion; the alteration index (AI); the chlorite-carbonate-pyrite index (CCPI); Mn content of carbonate; whole-rock Ti, Sb, and Ba/Sr ratio; and  $\delta^{34}\text{S}$  of pyrite and whole-rock  $\delta^{18}\text{O}$  (Fig. 14). The most useful vectors for pyritic Cu-Au ores are Na depletion, AI, CCPI, S/ $\text{Na}_2\text{O}$  ratio, Na content of white mica, and Fe content of carbonate (Fig. 15). Insufficient data is available to comment on the usefulness of whole-rock  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  pyrite as vectors in the pyritic Cu-Au hydrothermal systems.

#### *Conclusions*

The most significant conclusions to emerge from recent research on the nature and alteration of Australian VHMS deposits and their host volcanic rocks include the following:

1. There is a spectrum of sulfide deposits in submarine volcanic successions in Australia, including lens and sheet-style Zn-rich polymetallic deposits, massive and disseminated pyritic Cu-Au deposits, and disseminated strata-bound Au-only deposits.
2. The Zn-rich polymetallic deposits form either on, or just below, the sea floor, whereas the Cu-Au and Au-only deposits form subsea floor by replacement of particular volcanic units.
3. The pyrite Cu-Au deposits typically form in felsic volcanic centers dominated by synvolcanic intrusions, whereas the zinc-rich polymetallic deposits form in both felsic and mafic, moderate- to deep-water volcanic successions, dominated by lavas, volcanoclastic facies, and volcanogenic sedimentary facies. The gold-only deposits are confined to shallow-water volcanic sequences.
4. Alteration zoned outward from quartz  $\rightarrow$  Mg-Fe chlorite  $\rightarrow$  sericite  $\pm$  carbonate is typical of VHMS deposits across the spectrum. Quartz and carbonate alteration is dominant in the gold-only systems, whereas chlorite alteration is commonly developed close to copper-rich ores. Sericite and carbonate alteration zones are well developed in the stratiform zinc-rich ores.
5. Thermodynamic modeling indicates that chlorite-rich alteration is generated by higher temperature ( $>250^\circ\text{C}$ ) and/or less acidic ( $\text{pH} >5$ ) hydrothermal fluids, whereas sericite-rich alteration forms from lower temperature, slightly acidic fluids. Pyrophyllite associated with Cu-Au ores is indicative of strongly acidic fluids ( $\text{pH} <4$ ), possibly related to involvement of a magmatic fluid.
6. The variation in morphologies, metal ratios, volcanic environments, and alteration features in Australian volcanic-hosted ores indicates that a spectrum of deposits may exist—from those that fit the classic VHMS model to those that are hybrids between VHMS porphyry Cu and VHMS epithermal end members, developed in submarine volcanic successions.

a.



b.

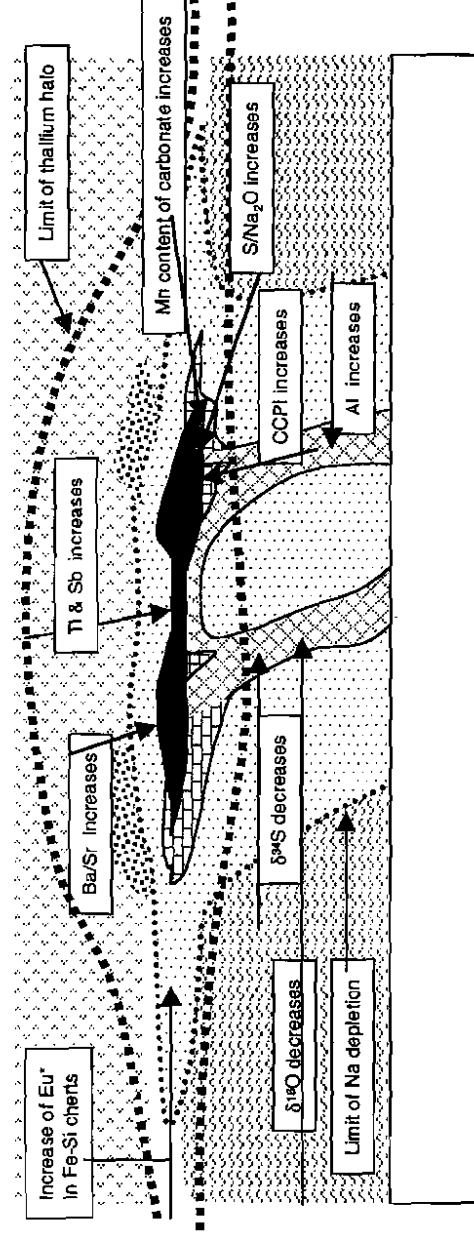


FIG. 14. a. Model of alteration zonation associated with Zn-rich polymetallic VHMS deposits. b. Alteration vectors useful for exploration of Zn-rich polymetallic VHMS deposits. Based on Large (1992), Gemmell and Large (1992), Gemmell and Fulton (2001), Herrmann et al. (2001), Large et al. (2001), Paulick et al. (2001).

7. Extensive, low-level thallium and antimony halos occur in the hanging wall surrounding the zinc-rich VHMS deposits and provide an important exploration guide. Similar halos do not occur around the Cu-Au deposits.

8. In addition to previously determined lithochemical and isotopic vectors (e.g., alteration indices, sodium depletion, whole-rock oxygen isotopes), the Mn and Fe content of hydrothermal carbonate, the composition of hydrothermal

white mica, the variation of sulfur isotopes of disseminated pyrite in footwall alteration zones, and the REE patterns of Fe-Si lateral marker units can be useful parameters to assist exploration.

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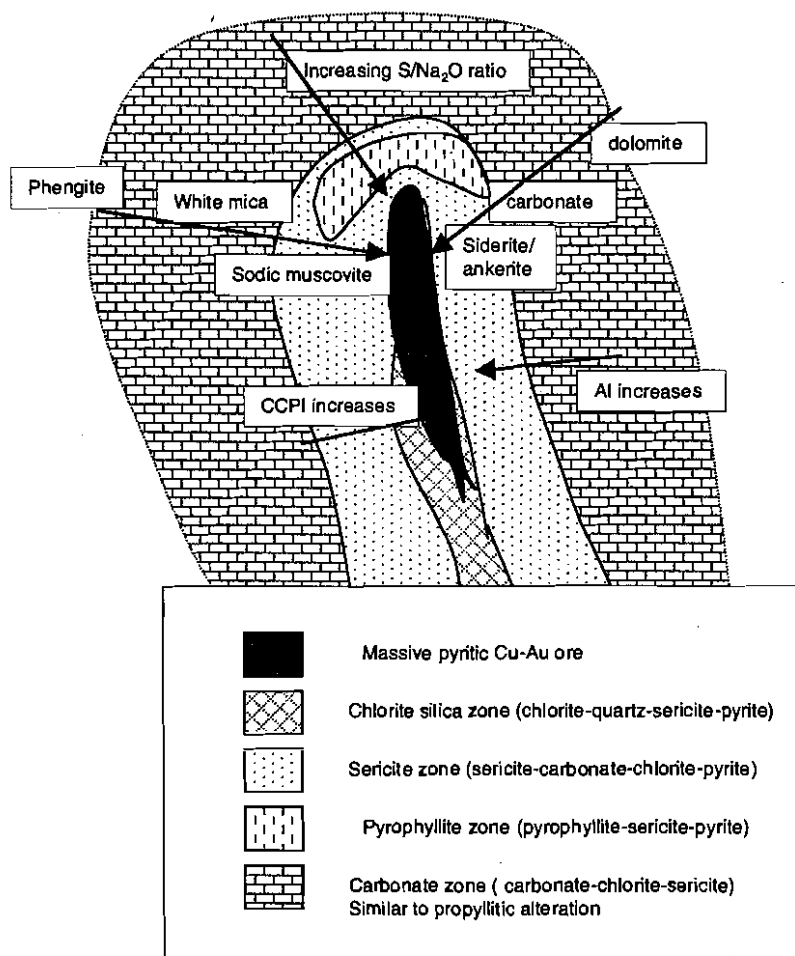


FIG. 15. Model of alteration zonation and key alteration vectors useful for exploration for pyritic Cu-Au VHMS deposits. Based on Doyle (2001), Herrmann et al. (2001), Huston and Kamprad (2001), and Large et al. (2001).

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