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THE DISTRIBUTION AND MINERAL HOSTS OF SILVER IN EASTERN AUSTRALIAN VOLCANOGENIC MASSIVE SULFIDE DEPOSITS

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ABSTRACT

Silver, an important by-product in volcanogenic massive sulfide (VMS) deposits of eastern Australia, is enriched mainly in Zn-rich zones; in a few deposits it is enriched in Cu-rich zones. Minerals that contain significant amounts of Ag include galena, tetrahedrite and chalcopyrite. The contribution of Ag sulfosalts, native silver and Ag tellurides to the total Ag budget is generally small. The hosts of Ag in VMS deposits vary spatially as follows: (1) in Cu-rich zones, Ag occurs mainly in chalcopyrite or Bi-rich galena; (2) in overlying Zn-rich zones, Ag occurs mainly in galena and, to a lesser extent, tetrahedrite; (3) in barite-bearing zones, Ag occurs mainly in Ag-rich tetrahedrite. The geochemical factors that seem to influence the mineralogical distribution of Ag in VMS deposits include: (1) temperature, (2) the relative abundances of semi-metals in the mineralizing fluids, (3) fractional crystallization of tetrahedrite–tennantite minerals, and (4) redox conditions during ore deposition. Higher temperatures and more reduced conditions favor partitioning of Ag into chalcopyrite, and then galena. Silver partitions into tetrahedrite under lower temperature, oxidized conditions, assisted by fractional crystallization, hence enriching later-precipitated tetrahedrite in Ag and Sb.

Keywords: silver, mineral hosts, volcanogenic massive sulfide deposits, eastern Australia.

SOMMAIRE

L'argent, important produit secondaire dans l'exploitation de gisements volcanogéniques de sulfures massifs, est surtout concentré dans les zones enrichies en Zn. Dans quelques gisements, il est plutôt associé aux zones cuprifères. Parmi les minéraux qui renferment de quantités importantes d'argent figurent galène, tétraédrite et chalcopyrite. Les contributions des sulfosels argentifères, l'argent natif et les tellurures de Ag au bilan global de l'argent sont mineures, en général. Les minéraux hôtes varient dans l'espace dans ce type de gisement comme suit: (1) dans les zones enrichies en Cu, on trouve l'argent surtout dans la chalcopyrite ou la galène bismuthifère; (2) dans les zones supérieures enrichies en Zn, l'argent se trouve surtout dans la galène et, à un degré moindre, dans la tétraédrite; (3) dans les zones à barite, l'argent se trouve surtout dans la tétraédrite argentifère. Parmi les facteurs géochimiques qui régissent une telle distribution seraient: (1) température, (2) abondance relative des semi-métaux dans la phase fluide, (3) cristallisation fractionnée des minéraux du groupe de la tétraédrite–tennantite, et (4) conditions d'oxydation au cours de la formation du minerai. Aux températures plus élevées et dans les milieux plus fortement réducteurs, l'argent favorise la chalcopyrite, et ensuite la galène. Aux températures plus faibles et dans les milieux plus oxydants, l'argent est davantage réparti dans la tétraédrite; un facteur secondaire, la cristallisation fractionnée, mène à un enrichissement de l'argent et de l'antimoine dans la tétraédrite tardive.

(Traduit par la Rédaction)

Mots-clés: argent, minéraux hôtes, gisements volcanogéniques de sulfures massifs, Australie orientale.

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INTRODUCTION

Of the major metals recovered from volcanogenic massive sulfide (VMS) deposits, Ag is unique in that it occurs mainly as a trace or minor element in ore minerals. As Ag is recovered as a by-product in Pb or Cu concentrates, extensive research has been undertaken on bulk samples and metallurgical concentrates to determine its mineralogical hosts (*e.g.*, Henley & Steveson 1978, Jambor & Laflamme 1978, Chen & Petruk 1980, Harris *et al.* 1984, Laflamme & Cabri 1986a, b). Less attention has been paid to spatial variations in the occurrence of Ag in VMS deposits, which typically have well-developed zonation in the distribution of minerals and metals. The objectives of this study are to present new data on the mineralogical distribution of Ag in spatially constrained samples from eastern Australian VMS deposits, to establish patterns of zoning in this distribution, and to propose geological and geochemical controls on the distribution of Ag in VMS deposits.

GEOLOGY OF THE DEPOSITS STUDIED

Mineralogical observations and electron-microprobe analyses were undertaken on samples from the Mt. Chalmers, Waterloo, Agincourt, Balcooma, Dry River South and Rosebery deposits in order to determine the mineralogical distribution of Ag. The mineralogical hosts of Ag in these and other VMS deposits are summarized in Table 1.

TABLE 1. MINERALOGICAL DISTRIBUTION OF SILVER IN VOLCANOGENIC MASSIVE SULFIDE DEPOSITS

Deposit	Mineral hosts to silver	Source
Mobrun, Quebec	Pyrite: 0.6-1400 ppm (x = 42 ppm). Chalcopyrite: 1-200 ppm (x = 29 ppm).	1
Izok Lake, NWT	Chalcopyrite: ~500 ppm (76% of total silver). Galena: 0.07-0.29% (9% of total silver).	2
Kidd Creek, Ontario		3
Zn-rich massive sulfide	Chalcopyrite: 224-2580 (x = 1047 ppm; n = 6). Pyrite: <7-20 ppm (n = 14; 10 below detection). Galena: 87-1167 ppm (x = 638 ppm; n = 8). Sphalerite: <12-308 (n = 15; 7 below detection). Other minerals: native silver, acanthite, tetrahedrite, stephanite, pyrargyrite, pearcite, miargyrite and dyscrasite.	
Cu-rich massive sulfide	Chalcopyrite: x = 183 ppm; 59.6% of Ag. Pyrite: <7 ppm (n = 6). Galena: x = 300 ppm; 0.25% of Ag. Sphalerite: <12 ppm (n = 2). Other minerals: native silver and acanthite (40.15% of Ag).	
Bornite zone	Chalcopyrite: <10-57 ppm (n = 4; 1 below detection). Pyrite: <7 ppm (n = 1). Sphalerite: 36 ppm (n = 1). Other minerals: naumannite.	
Pyhasalmi, Finland	Chalcopyrite and Ag sulfosalts.	4
Garpenberg, Sweden	Tetrahedrite, acanthite and native silver.	5
Saxberget, Sweden	Mainly galena and chalcopyrite with rare pyrargyrite, acanthite, stephanite and native silver.	6
Hellyer, Tasmania	Tetrahedrite: 1.9-28.3%; 60% of Ag. Most important at the top of the ore lens. Ag-rich tetrahedrite occurs in remobilized veins. Galena: 0.01-0.42% (40% of Ag). More important and Ag-rich towards the base of the ore lens. Pyrite: 200-350 ppm in the hanging wall precious metal zone.	7
Heath-Steele, New Brunswick	Tetrahedrite: 1.5-34.0% (x = 12.4%); 35% of Ag. Galena: 0.0-0.9% (x = 0.15%); 27% of Ag. Ag correlates with Bi. Other minerals: kobellite (0.6%), cosalite (1.0-1.4%), Pb-Bi-Sb(Ag) sulfosalts, acanthite, stephanite, pyrargyrite and miargyrite; 39% of Ag.	8
Caribou, New Brunswick	Tetrahedrite: 0.6-19.2%; 68% of Ag. In the East ore lens Ag levels increase from 0.6-2.1% at the base to 7.9% at the top. Galena: <0.04-0.20% (x = 0.10%); 28% of total Ag. Other minerals: electrum, polybasite, chalcopyrite, acanthite and stephanite; 4% of Ag.	9
Brunswick No. 12, New Brunswick	Tetrahedrite: 0.1-36.5%; 60% of Ag. Galena: to 0.29% (x = 0.07%); 30% of Ag. Ag correlates with Bi (r = 0.80). Other minerals: sphalerite, chalcopyrite and pyrrhotite; 7.5% of Ag.	10
Cofer, Virginia	Mainly tetrahedrite.	11
Hokuroku district, Japan	Mainly tetrahedrite and galena, with minor contributions from acanthite, jalpaite, stromeryerite, mckinstryite, sternbergite, polybasite, pearcite, pyrargyrite, proustite and native silver.	12

Data sources: (1) Larocque et al. (1995); (2) Harris et al. (1984); (3) Cabri et al., (1985); Cabri (1988), and Walker & Mannard (1974); (4) Helovouri (1979); (5) Vivallo (1985); (6) Amcoff et al. (1985); (7) Ramsden et al. (1990); (8) Chen & Petruk (1980); (9) Jambor & Laflamme (1978); (10) Laflamme & Cabri (1986a,b), Chryssoulis & Surges (1988), and Cabri (1992); (11) Miller & Craig (1983); and (12) Shimazaki (1974) and Sato (1974).

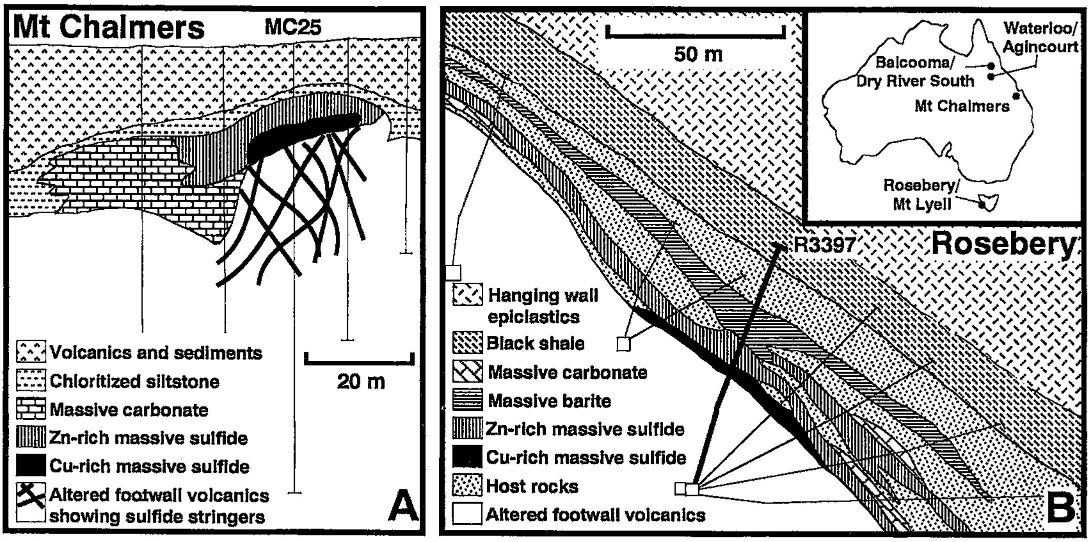

FIG. 1. Cross sections showing the geology of the (A) Mt. Chalmers West Lode (modified from Large & Both 1980), and (B) Rosebery north-end orebody (modified after Huston & Large 1988).

Mt. Chalmers

The Mt. Chalmers deposit contains of two Cu-gold-rich massive sulfide lenses that occur above well-developed pyrite – chalcopyrite stringer zones within the Permian Beserker Beds in central Queensland (Large & Both 1980, Taube & van der Helder 1983; Fig. 1A). As Mt. Chalmers is one of the least deformed VMS deposits in Australia, primary textures are commonly preserved in the ores. Massive sulfide and stringer ore are dominated by pyrite and chalcopyrite. Sphalerite, galena and barite occur in the upper portions of the massive sulfide lenses, along with minor tennantite. Electrum is a trace Ag-bearing mineral.

Silver grades are highest (50–100 g/t) in the Zn-rich upper portion of the massive sulfide lens. In the Cu-rich lower part of the massive sulfide lens and in the stringer zone, Ag grades are 5–20 ppm. The distribution of Ag correlates best with those of Zn and Pb (Large & Both 1980).

Rosebery

The Zn–Pb-rich Rosebery deposit consists of a series of sheet-like massive sulfide and barite-bearing lenses within a lens of fine-grained tuffaceous sandstone and siltstone above an extensive zone of pyrite-bearing quartz – sericite ± chlorite-bearing altered felsic volcaniclastic rocks in the Cambrian Mt.

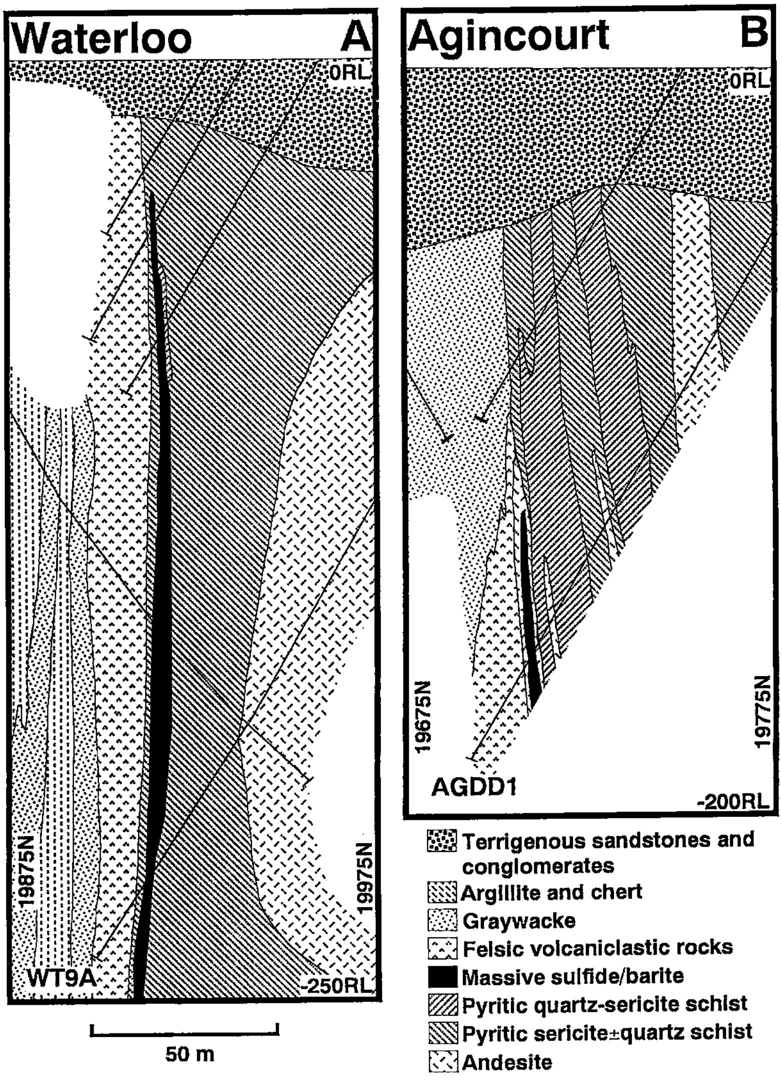

FIG. 2. Cross sections showing the geology of the (A) Waterloo and (B) Agincourt deposits (modified after Berry *et al.* 1992).

Read Volcanic Suite of western Tasmania (Brathwaite 1974, Green *et al.* 1981). Samples analyzed in this study were collected from the north end of the mine, which contains a lower lens of Zn–Pb-rich massive sulfide and an upper barite-bearing lens. The base of the Zn–Pb-rich lenses contains local zones of Cu-rich massive sulfide (Fig. 1B). Common ore minerals include pyrite, sphalerite, galena and chalcopyrite. Other Ag-bearing minerals include tetrahedrite, electrum, pyrargyrite, miargyrite and acanthite.

The distribution of Ag strongly correlates with that of Pb, with the highest grades (>500 g/t) occurring most commonly in barite-bearing zones (Brathwaite 1969, Huston & Large 1988). On the basis of production assays from the 15-level fan-drilling program (conducted in the early 1980s), the barite-bearing zone and Zn-rich massive sulfide have similar average grades at 160 g/t, whereas Cu-rich massive sulfide has a much lower average grade, 70 g/t Ag.

Waterloo and Agincourt

Waterloo (Fig. 2A) and Agincourt (Fig. 2B) are two small barite-bearing VMS deposits in the Cambro-Ordovician Seventy Mile Range Group of northern Queensland (Berry *et al.* 1992). The Waterloo deposit is relatively Zn- and Cu-rich, but Pb-poor, and the Agincourt deposit is Zn- and Pb-rich, but Cu-poor (Huston *et al.* 1995a). Major ore and Ag-bearing minerals include sphalerite, pyrite, chalcopyrite, galena, tennantite and electrum at both deposits, and hessite and petzite at Waterloo. Waterloo has higher Ag grades (20–300 g/t) than Agincourt (5–60 g/t). The distribution of Ag correlates with that of Pb, Cu and gold at both deposits.

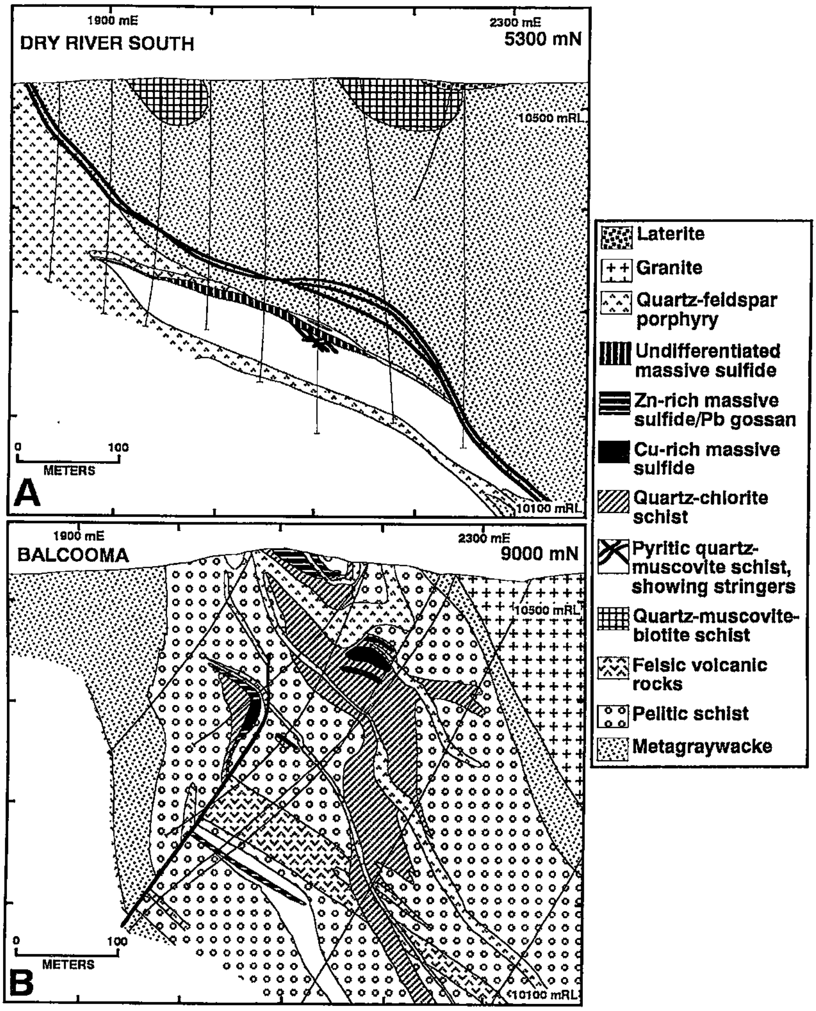

FIG. 3. Cross sections showing the geology of the (A) Dry River South and (B) Balcooma deposits (modified after Huston *et al.* 1992a).

Dry River South and Balcooma

Dry River South and Balcooma occur in the lower- to middle-amphibolite-facies Cambro-Ordovician Balcooma metamorphic suite of northern Queensland (Huston *et al.* 1992a). The Dry River South deposit (Fig. 3A) consists of a sheet-like polymetallic massive sulfide lens along the contact between an extensive zone of pyrite-bearing quartz–muscovite schist (altered volcanic rocks) and hanging-wall turbiditic metasedimentary rocks. Major ore minerals at Dry River South include pyrite, sphalerite, chalcopyrite and galena. Silver-bearing minerals include tetrahedrite, Sb sulfosalts and electrum (Huston *et al.* 1992a). Both Dry River South and Balcooma lack barite.

At Dry River South, silver is enriched in Zn–Pb-rich zones that typically grade 70–140 g/t Ag. In Cu-rich zones, Ag grades are typically 20–50 g/t. The distribution of Ag correlates with that of Pb and gold throughout the deposit, but with that of Cu in Cu-rich zones.

Balcooma consists of five massive sulfide bodies in a pelitic lens within a metaturbiditic sequence (Fig. 3B). Sulfide lenses occur at three stratigraphic positions, with Cu-rich lenses occupying the intermediate position. Copper-rich zones contain pyrite, chalcopyrite, magnetite and pyrrhotite as major ore minerals; Ag-bearing minerals include sphalerite, galena, tetrahedrite and electrum (Huston *et al.* 1992a). Silver grades at Balcooma are highest in Zn–Pb-rich massive sulfide lenses (50–150 g/t). Within these lenses, the distribution of Ag correlates only with Pb. Silver grades in Cu-rich zones are 5–50 g/t. In Cu-rich lenses, the distribution of Ag has a strong correlation with that of Cu, and a weaker correlation with that of gold and Pb.

HOSTS OF SILVER

Minerals in which Ag is an essential component are not major hosts of silver in most VMS deposits. As tetrahedrite-group minerals, galena and chalcopyrite are the most common major hosts of Ag (Table 1), this study emphasized Ag contents in these three phases.

Analytical techniques

The CSIRO proton microprobe was used to determine levels of Ag in pyrite, sphalerite and chalcopyrite. Relative to the electron microprobe, the proton microprobe has the advantage of lower limits of detection, but the disadvantage of a larger sampling volume. In the minerals analyzed, the effective depth of analysis is 30–40 µm, and the spot size is typically 20 µm. For Ag, typical detection-limits (3σ) are 5–15 ppm for all three minerals. Detailed descriptions of analytical methods are summarized by Sie & Ryan (1986) and Huston *et al.* (1995b). The results of proton-microprobe analyses are summarized in Huston *et al.* (1995b).

TABLE 2. ABUNDANCE OF SILVER IN IMPORTANT SILVER-BEARING MINERALS

Deposit	Tetrahedrite			Galena			Chalcopyrite[1]			Sphalerite[1]		
	n	Range (%)	Mean (%)	n	Range (%)	Mean (%)	n	Range (ppm)	Mean (ppm)	n	Range (ppm)	Mean (ppm)
Mt Chalmers	18	<0.01 - 2.49	0.22	44	0.03 - 0.69	0.25	22	<10 - 80	17	10	<10 - 30	13
Agincourt	16	2.01 - 16.13	4.11	16	0.03 - 0.08	0.05	—	—	—	5	30 - 110	60
Waterloo	28	<0.01 - 0.25	0.07	23	0.04 - 0.24	0.08	5	<8 - 30	10	4	<15 - 30	20
Rosebery												
Cu-rich stringers	—	—	—	5	0.85 - 1.07	0.96	5	150 - 200	170	—	—	—
Zn-rich massive sulfide[2]	61	1.00 - 33.56	8.56	59	0.09 - 0.67	0.24	5	200 - 470	220	9	<15 - 50	11
Zn-rich massive sulfide[3]	48	1.00 - 20.10	3.67	33	0.09 - 0.67	0.27	5	200 - 470	220	9	<15 - 50	11
Zn-rich massive sulfide[4]	—	—	—	23	0.09 - 0.16	0.11	—	—	—	—	—	—
Zn-rich massive sulfide[5]	13	19.81 - 33.56	26.35	23	0.16 - 0.24	0.20	—	—	—	—	—	—
Barite-bearing massive sulfide	60	0.41 - 13.70	5.33	29	0.04 - 0.08	0.06	3	<14 - 17	12	4	<30 - 30	11
Remobilized	29	13.04 - 26.32	18.71	5	0.09 - 0.12	0.10	—	—	—	—	—	—
Dry River South												
Cu-rich	—	—	—	28	0.24 - 0.82	0.43	10	57 - 120	92	—	—	—
Zn-rich	—	—	—	27	0.07 - 0.82	0.35	5	<5 - 15	9	11	<15 - 65	25
Balcooma												
Cu-rich	—	—	—	22	0.14 - 0.70	0.40	36	<8 - 120	46	—	—	—
Zn-rich	—	—	—	78	0.04 - 0.37	0.13	—	—	—	10	<15 - 20	10

[1] To estimate mean Ag concentrations, analyses below the detection limit were assigned a value of 5 ppm.

[2] All data.

[3] Less Ag-rich (> 300 g/t) samples.

[4] As above, less Bi-rich galena.

[5] Ag-rich samples.

Electron-microprobe analysis was used to determine the concentration of Ag and related elements in electrum, tetrahedrite and galena. Electron-microprobe analysis of galena was used in preference to proton-microprobe analysis because it offers better detection limits for Bi. Bismuth *M* lines are difficult to resolve from Pb *M* lines on energy-dispersion spectra, hence the detection limit of the proton microprobe is of the order of several thousand ppm. Conversely, the use of wavelength-dispersion spectrometers on the electron microprobe allowed detection limits of several hundred ppm.

Electron-microprobe analyses were done using the University of Tasmania's Cameca SX50 microprobe. Software supplied by Cameca (Pouchou & Pichoir 1984) was used for analysis and data reduction. Prior to analysis, potential interferences involving the lines of interest were determined, and potential problems with interferences were avoided by adjusting background offsets or using background-slope corrections.

Tetrahedrite

Minerals of the tetrahedrite–tennantite series occur in all deposits except Balcooma. Table 2 summarizes the abundance of Ag in tetrahedrite–tennantite from Rosebery, Mt. Chalmers, Agincourt and Waterloo. Tetrahedrite from Cu-poor (*i.e.*, <1%) deposits at Rosebery and Agincourt tends to be richer in Ag than tetrahedrite–tennantite from the Cu-rich Mt. Chalmers West Lode and Waterloo. Dry River South, which averages about 1% Cu, has Ag-rich (16.9–24.2%) and Sb-rich (24.5–28.2%) tetrahedrite associated with galena [D. Patterson in Huston *et al.* (1992a)].

As in other VMS (*e.g.*, Jambor & Laflamme 1978, Ramsden *et al.* 1990) and epithermal deposits (Hackbarth & Petersen 1984, Petersen *et al.* 1990), Ag-rich tetrahedrite is enriched in Sb. This trend is present at Rosebery and Agincourt (Fig. 4). No Ag–Sb correlation was noted at Mt. Chalmers and Waterloo, possibly because of the Sb-poor character of the tennantite.

The relationship between Ag and Sb in tetrahedrite from Rosebery varies with ore type. End-member tetrahedrite in veins that were remobilized during Devonian deformation is Ag-rich (mainly 16–20%). Tetrahedrite from barite-bearing zones has moderate Ag contents (mainly 1–10%) and Sb/(Sb + As + Bi) values that range from 0.45 to 0.95. By contrast, with the exception of a small group of Ag- and Sb-rich samples, tetrahedrite–tennantite grains within massive sulfide zones have the lowest Ag contents (mainly 1–6%), but the largest spread in Sb/(Sb + As + Bi) values (0.1–0.9). In both barite-bearing and massive sulfide zones, Ag/(Ag + Cu) increases linearly with Sb/(Sb + As + Bi), but the rate of increase is greater in barite-bearing zones. The small group of Ag-rich tetrahedrite compositions in the massive sulfide zone come from three very Ag-rich samples (350–1860 ppm). The most Ag-rich tetrahedrite (32.1–33.6%) is associated with pyrargyrite in the highest-grade sample.

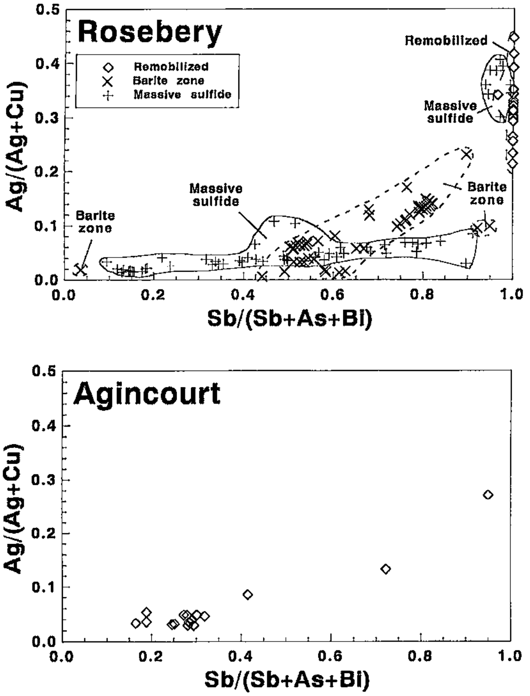

FIG. 4. Scattergrams showing the relationship between Sb/(Sb + As) and Ag/(Ag + Cu) (atomic proportions) in tetrahedrite from the Rosebery and Agincourt deposits. Data are from this study, Smith (1975), and Huston & Large (1988).

Galena

Diaphorite ($Pb_2Ag_3Sb_3S_8$) inclusions may account for much of the Ag in argentiferous galena (Laflamme & Cabri 1986a, Sharp & Buseck 1993). To avoid these inclusions, analytical spots were examined using back-scattered electron images at a magnification of 20,000×.

Table 2 summarizes Ag contents of galena from the deposits studied. Although the maximum concentrations exceed 1.0%, most galena grains contain less than 0.5% Ag. Galena from deposits with an overall Cu grade of 1.0% or more (Mt. Chalmers, Dry River South, Balcooma and Waterloo) commonly contain greater amounts of Ag than galena from Cu-poor deposits. This gross relationship is also present within deposits. At Rosebery, galena from Cu-rich stringer-like zones has more Ag than does galena from massive

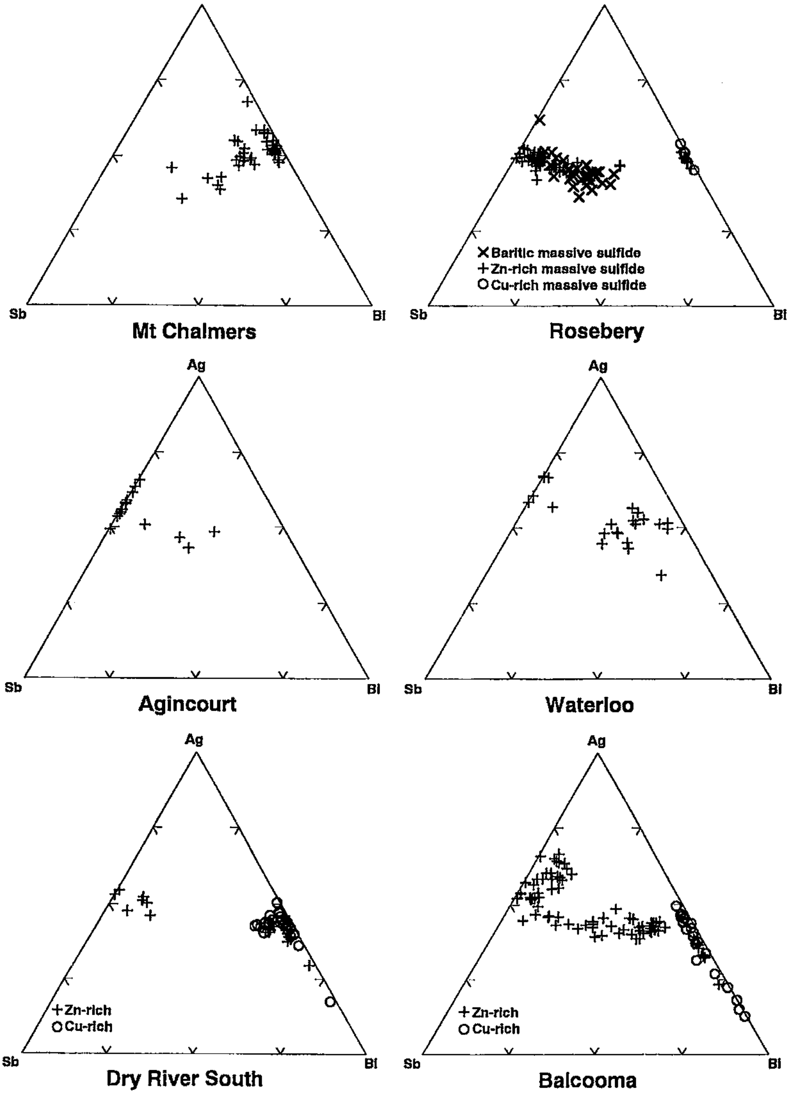

FIG. 5. Triangular diagrams showing the relationships among silver, antimony and bismuth (in relative atomic proportions) in galena from the Rosebery, Mt. Chalmers, Dry River South, Balcooma, Agincourt and Waterloo deposits. All data are from this study.

sphalerite – galena – pyrite and barite-bearing zones. At Balcooma, galena from Cu-rich massive sulfide lenses and stringer zones contains higher levels of Ag than galena from Zn-rich massive sulfide zones. Although less well defined, a similar relationship holds at Dry River South.

Figure 5 shows triangular diagrams relating the atomic abundances of Ag, Sb and Bi in galena. In all six deposits, most data plot such that Ag approximates the proportion of Sb + Bi. Deviations from this generalization occur at Agincourt, where some compositions plot closer to the Ag apex along the Ag–Sb join, and at Dry River South and Balcooma, where many of the data points (mainly from Cu-rich zones) plot closer to the Bi apex along the Ag–Bi join. Galena from Cu-poor deposits (Agincourt and Rosebery) generally is Sb-rich, relative to Bi, whereas galena from Cu-rich deposits tends to be Bi-rich. A similar relationship is present in other deposits. At Rosebery, Dry River South and Balcooma, galena from Cu-rich zones is Bi-rich. Conversely, galena from Zn-rich zones is more Sb-rich, although Bi-rich galena

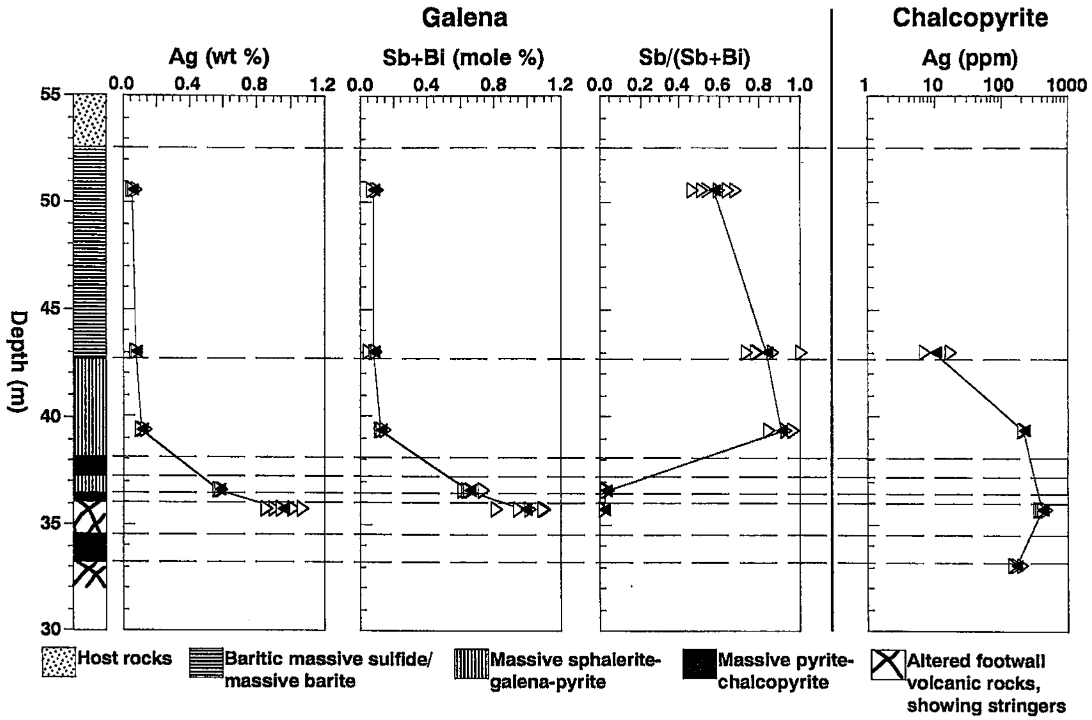

FIG. 6. Variations in silver, total Sb + Bi and Sb/(Sb + Bi) in galena and silver in chalcopyrite in drill hole R3397, which passes through the Rosebery north-end massive sulfide lens and barite zone.

also is present, especially at Dry River South. At Rosebery, galena from barite-bearing zones is generally more Bi-rich than galena from massive sphalerite – galena – pyrite zones.

In core from drill hole R3397 at the Rosebery deposit (Fig. 6), galena from stringer zones and the basal part of the massive sphalerite – galena – pyrite zone is extremely Bi-rich relative to Sb; the relative Sb content increases into the massive sphalerite – galena – pyrite zone, and then decreases significantly in the barite-bearing zone. The differences in Sb/(Sb + Bi) occur within an overall trend of decreasing Sb + Bi, which closely mimics a trend of decreasing Ag contents.

Figure 7 illustrates the relationship between Ag and Sb/(Sb + Bi) in more detail. In all deposits except Agincourt (which lacks Bi-rich galena; not shown), all data points plot along a curvilinear trend in which the Ag content is low (<0.2 mol.%) and relatively constant for Sb/(Sb + Bi) above 0.2. Below 0.2, the Ag content increases rapidly to values that commonly exceed 0.5 mol.% where Sb/(Sb + Bi) is less than 0.05. Although Ag is generally not correlated with Sb/(Sb + Bi) where Sb/(Sb + Bi) exceeds 0.2, a significant positive correlation (r = 0.66; n = 32) is present in barite-bearing samples from Rosebery.

Previous analytical data on Ag contents of galena exist only for Rosebery. Henley & Steveson (1978) reported that galena from Rosebery averages 0.10% Ag, which differs from the average of 0.21% for all galena compositions determined in this study. However, our samples were not collected in a representative manner; hence the results are biased, particularly by the collection of extremely high-grade samples. Samples of massive sphalerite – galena – pyrite in which Ag grades exceed 350 g/t contain Ag-rich galena (0.16–0.23%). If these samples, and samples from Cu-rich zones, which are not mined, are excluded, the average Ag concentration of galena is 0.16%, closer to the value determined by Henley & Steveson (1978).

Huston *et al.* (1992a) estimated that galena in Zn-rich zones at Balcooma would contain 0.12% Ag if galena hosted all Ag. This value is close to the average 0.15% content for galena from Zn-rich massive sulfide zones at Balcooma.

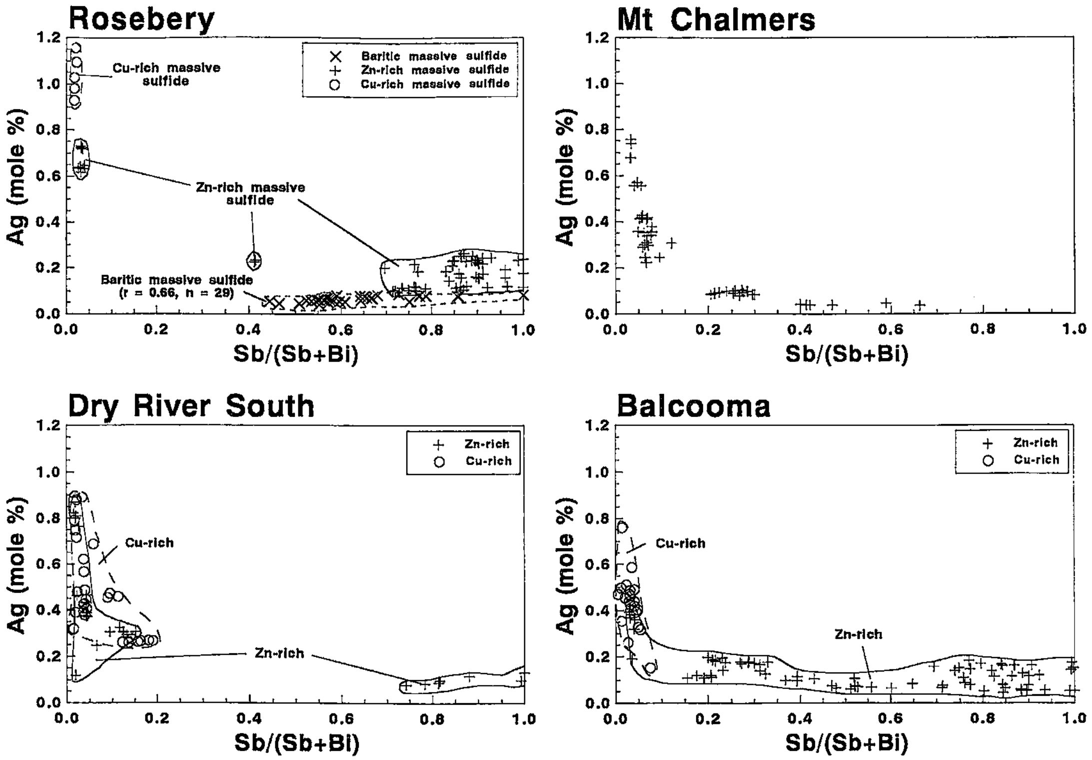

FIG. 7. Scattergrams showing the relationships between silver and Sb/(Sb + Bi) (atomic proportions) in galena from the Rosebery, Mt. Chalmers, Dry River South and Balcooma deposits. All data are from this study.

Chalcopyrite

Table 2 summarizes the results of proton-microprobe analyses of chalcopyrite from all deposits except Agincourt. The maximum concentration of Ag in chalcopyrite grains was found to be 470 ppm, although most analyses indicated less than 100 ppm. These levels are similar to values reported at Mobrun (Larocque *et al.* 1995) and Kidd Creek (183 ppm; Cabri 1988), but lower than values reported at Izok Lake (500 ppm; Harris *et al.* 1984), and much lower than values reported for the Hilton sediment-hosted massive sulfide deposit (2000 ppm, Harris *et al.* 1984).

The most Ag-rich chalcopyrite occurs at Rosebery, where chalcopyrite from pyrite – chalcopyrite stringer and massive sphalerite – galena – pyrite ores contains 150–470 ppm Ag. In contrast, chalcopyrite from one barite-bearing sample contains less than 20 ppm Ag (Fig. 6). The average of all determinations at Rosebery, 220 ppm, compares well with an average estimated for Rosebery mill feed by Henley & Steveson (1978), 180 ppm.

Balcooma shows the next highest levels of Ag in chalcopyrite (<10–120 ppm). A small number of determinations in material from Dry River South suggests that chalcopyrite from Cu-rich zones is more Ag-rich (55–120 ppm) than that from Zn-rich zones (<15 ppm). Chalcopyrite from the Cu-rich Mt. Chalmers and Waterloo deposits has relatively low levels of Ag (mainly <30 ppm). Chalcopyrite from the stringer zone at Mt. Chalmers has a higher average Ag content (20 ppm; "not detected" values taken as 5 ppm; MDL = 10–15 ppm) than chalcopyrite in the massive sulfide lens (13 ppm).

Sphalerite

Owing to the great abundance of sphalerite in many VMS deposits, even low levels of Ag in sphalerite could account for a large portion of the silver budgets. However, half of all determinations of Ag in sphalerite were below the detection limit of 15–10 ppm, and a significantly higher proportion of the determinations in material from Balcooma, Mt. Chalmers and Rosebery were below this limit. Most determinations from Dry River South, Agincourt and Waterloo exceeded the detection limit. Even in deposits with detectable Ag in sphalerite, the values are mainly below 30 ppm. Agincourt has the highest levels of Ag in sphalerite; the maximum concentration was found to be 110 ppm, and the average is 60 ppm. These results suggest that sphalerite is not a major host of Ag, except possibly at Agincourt.

Other major ore minerals

As pyrite is the most abundant ore mineral in most VMS deposits, it also could host a significant portion of Ag. Huston *et al.* (1995a) analyzed pyrite grains from all six deposits. They recorded Ag contents to 460 ppm, but suggested that this results from inclusions of tetrahedrite or galena, as the level of Ag commonly is correlated with concentrations of Sb and Pb. The concentration of Ag in the pyrite structure was inferred to be less than 5 ppm, the detection limit of the proton microprobe.

Silver minerals

In addition to electrum, which was observed in all deposits, two of the deposits contain small amounts of Ag minerals. At Waterloo, hessite occurs as a moderately widespread trace mineral, and petzite was observed in one instance. At Rosebery, trace quantities of pyrargyrite occur in Ag-rich samples in association with Ag-rich tetrahedrite and miargyrite, and acanthite occurs as a rare trace mineral in massive sphalerite – galena – pyrite ore at Rosebery.

QUALITATIVE MINERALOGICAL BALANCE OF SILVER

To illustrate the importance of various hosts of Ag among and within deposits, Table 3 shows the results of qualitative mineral-balance calculations. The calculations used compositional data derived from this study (Table 2), and grade data either from the literature, or calculated for different ore-types (*cf.* Rosebery and Balcooma) using diamond drill-core assay data. The results are inherently qualitative owing to the nature of data collection. If "unusual" samples are excluded, the calculations suggest several interesting differences both among and within deposits.

Of the deposits and ore types considered, in only one (Rosebery barite-bearing samples) does the total Ag accounted for by significant Ag-bearing minerals amount to the estimated Ag grade (±10%). Two others (Mt. Chalmers and Balcooma Zn-rich) are within 25% of the Ag grade. The calculated mineral-balances for Ag of these three deposits or ore types probably approximate the true mineral-balances, given the large

TABLE 3. QUALITATIVE ESTIMATES OF THE MINERALOGICAL BALANCE OF SILVER IN SOME EASTERN AUSTRALIAN VMS DEPOSITS

Deposit			Tetrahedrite[2]		Galena[3]		Chalcopyrite[4]		Sphalerite[5]		Electrum[6]			
	Ag in ore (g/t)	Sb[1] in ore (ppm)	Mineral abundance (%)	Ag budget (g/t)	Mineral abundance (%)	Ag budget (g/t)	Mineral abundance (%)	Ag budget (g/t)	Mineral abundance (%)	Ag budget (g/t)	Mineral abundance (ppm)	Ag level (%)	Ag budget (g/t)	Ag budget (%)[7]
Mt Chalmers	44	<50	<0.086	<1.9	1.2	29	4.9	0.8	5.2	0.7	2.7	14	0.4	74-79
Waterloo	94	—	0.1-0.2	0.7-1.4	3.3	26	11.0	1.1	29.4	5.9	2.4	17	0.4	36-37
Rosebery[8]														
Zn-rich massive sulfide	162	282	0.13	47	9.7	247	1.2	2.6	34.8	3.8	4.3	33	1.4	186
	162	282	0.11	42	9.7	109	1.2	2.6	34.8	3.8	4.3	33	1.4	98
Barite-bearing massive sulfide	160	550	0.28	150	3.0	18	0.35	<0.1	8.0	0.9	3.4	29	1.0	106
Dry River South	97	36	0.008	15	3.9	152	3.2	2.0	14.0	3.5	1.3	40	0.5	161-176
Balcooma[9]														
Zn-rich	55	—	—	—	4.7	61	2.7	1.3	12.8	1.3	0.79	27	0.2	124
Cu-rich	21	—	—	—	0.092	3.7	10.6	4.9	0.39	<0.1	0.59	27	0.2	43

[1] The Mt. Chalmers estimate is a composite analysis of all ore types (Huston et al., 1992b). The Rosebery estimates are calculated from average Ag assays using the strong correlation between Sb and Ag (cf. Smith and Huston, 1992). The Dry River South estimate is a weighted average of Sb analyses of drill core massive sulfide samples (Huston, 1988).

[2] Tetrahedrite mineral abundances were estimated from residual Sb levels (i.e. total Sb less Sb in galena) and average analyses of tetrahedrite. For the Waterloo deposit, the tennantite abundance was estimated from thin section.

[3] Galena abundances were determined from average lead assays. Two budgets fpr galena were estimated for Rosebery massive sphalerite-galena-pyrite ore. In both estimates analyses from highly Ag-rich samples were excluded. The first estimate used all other data, whereas the second estimate also excluded Bi-rich galena.

[4] Chalcopyrite abundances were determined from average Cu assays.

[5] Sphalerite abundances were determined from average Zn assays.

[6] Electrum abundances and Ag concentrations in electrum were determined from average Au assays, electrum fineness data and cyanide leaching data (Huston et al., 1992b).

[7] Total Ag budget expressed as a percentage of the average Ag assay.

[8] Assay values used to estimate mineral abundances for Rosebery ore types are average values of assays from drill holes collared on 15 level in the north-end orebodies. The assays were assigned to these ore type based on company drill logs and core logging by the senior author.

[9] Assay values used to estimate mineral abundances for Balcooma ore types are average values of assays fromdrill holes drilled between 1978 and 1986. The assays were assigned ore types based on company drill logs and core logging by the senior author.

uncertainty of the calculations.

For massive sphalerite – galena – pyrite ore at Rosebery and at Dry River South, the Ag budget calculated for major Ag-bearing minerals exceeds the true grade by more than 50%. This results mainly from the inclusion of anomalously Ag-rich galena in the calculations. As discussed above and summarized in Table 1, the Ag content of galena from these two deposits is highly variable. A few "atypically" high Ag concentrations significantly bias the final average value. When analytical results for Ag–Bi-rich galena, which is restricted to the lower portion of the massive sulfide lens, are excluded from the data set for Rosebery massive sphalerite – galena – pyrite ore, the average Ag content decreases from 0.27% to 0.11%, and the total Ag budget decreases from 186% to 98% (Table 3).

In the Waterloo deposit and Balcooma Cu-rich lenses, major Ag-bearing minerals account for less than 50% of the total Ag, suggesting the presence of other major hosts of the Ag. At Waterloo, hessite and petzite could account for the 65% Ag deficit. The siting of the unaccounted Ag at Balcooma is problematic. Huston *et al.* (1992a) suggested that chalcopyrite hosts Ag at a level of 140 ppm owing to an excellent correlation between concentrations of Ag and Cu, but this study suggests that chalcopyrite contains, on average, only 46 ppm Ag. Hence, either the chalcopyrite analyzed in this study is unusually Ag-poor, or some other mineral accounts for the Ag. A possible candidate is pyrrhotite, which can contain up to 100 ppm Ag (Fleischer 1955, Cabri *et al.* 1985), and is common in Cu-rich zones. Alternatively, Ag could occur in Bi sulfosalts in Cu-rich zones.

Comparisons among and within deposits

Mineral-balance calculations suggest that the mineralogical distribution of Ag differs among and within deposits. Except for the Waterloo deposit, Rosebery barite-bearing ores, and Balcooma Cu-rich massive sulfide ores, galena is the main host of Ag. In Balcooma Cu-rich zones, chalcopyrite is the dominant host, whereas in Rosebery barite-bearing ore, tetrahedrite is the main host. Tetrahedrite is a significant host of Ag only in Cu-poor deposits. In contrast, tetrahedrite–tennantite accounts for at most 4% of the total Ag in Cu-rich deposits at Balcooma, Mt. Chalmers and Waterloo. Except for Balcooma Cu-rich lenses, chalcopyrite, sphalerite and electrum account for small fractions (mainly <5%) of the Ag. The Waterloo deposit is unique in that hessite is the probable major host of Ag.

Mineral-balance calculations at Rosebery and Balcooma also suggest intradeposit variations in the distribution of Ag. At Rosebery, tetrahedrite accounts for more than 90% of Ag in barite-bearing massive sulfide ore, but for only 25% in barite-free massive sphalerite – galena – pyrite. The proportion estimated by Henley & Steveson (1978; 65%) lies between the proportions estimated for the two ore types in this study.

At Balcooma, chalcopyrite is the predominant Ag host in Cu-rich massive sulfide, but it is insignificant in Zn-rich massive sulfide ore. In contrast, galena is a significant Ag host in both types of massive sulfide ore, but even more important in Zn-rich massive sulfide.

Other deposits

Silver is enriched in the upper and lateral portions of most deposits, mainly in association with Zn and Pb [*e.g.*, Mobrun: Larocque *et al.* (1993), Hellyer: McArthur & Dronseika (1990), Hokuroku district: Shimazaki (1974)]. An important exception is the Millenbach deposit (Knuckey *et al.* 1982), in which Ag occurs mainly with Cu in the pyrrhotite-rich core of the massive sulfide lens. Perhaps the most complicated distribution occurs at Kidd Creek, where Ag-rich zones occur in both the Zn-rich tops and Cu-rich bases of massive sulfide lenses, and also in the stringer zones (M. Hannington and E. Koopman, pers. comm. 1994). The highest Ag grades occur in a bornite-rich zone that has locally replaced chalcopyrite-rich ore.

In most VMS deposits, galena and tetrahedrite are the main hosts of Ag (Table 1), although chalcopyrite is a significant, if not dominant, host of Ag in Cu-rich zones within the Izok Lake (Harris *et al.* 1984), Kidd Creek (Cabri 1988), and Pyhasalmi (Helovouri 1979) deposits. Deposits in which tetrahedrite is the predominant host of Ag outnumber those in which galena is the predominant host. In particular, tetrahedrite dominates in the Mt. Read and Bathurst districts, in which the deposits are rather Cu-poor. Conversely, galena is the dominant host in the more Cu-rich deposits. Deposits in which Ag minerals host a significant portion of the total Ag are not that common. Native Ag accommodates a significant portion of the Ag at Kidd Creek (Cabri 1988); Ag sulfosalts are significant hosts at Heath-Steele (Chen & Petruk 1980).

GEOLOGICAL AND GEOCHEMICAL CONTROLS ON THE DISTRIBUTION OF SILVER IN VOLCANOGENIC MASSIVE SULFIDE DEPOSITS

Although in most VMS deposits, Ag undergoes zone refinement like Pb and Zn, the detailed mechanisms of Ag enrichment are complicated, owing to the large variability in the mineralogical hosts of Ag. Factors that may affect its spatial and mineralogical distribution include: (1) the temperature, pH and redox state of the hydrothermal fluid, (2) the speciation of Ag, Sb and Bi in the hydrothermal fluid, and (3) the solubility of Ag in sulfide minerals and the effect of Sb and Bi on that solubility.

Physicochemical parameters of volcanogenic fluids

Owing to detailed paragenetic, isotopic and fluid-inclusion studies of ancient VMS deposits over the past twenty years, the physicochemical parameters of ore-forming fluids have been well constrained (*e.g.*, Large 1977, Green *et al.* 1981, Pisutha-Arnond & Ohmoto 1983, Ohmoto *et al.* 1983). The most important parameters that affect Ag contents, distribution and mineralogy include temperature, pH, salinity, H_2S concentrations and redox state.

Speciation of Ag, Sb and Bi in volcanogenic fluids

In volcanogenic fluids above 200°C, Ag is transported as chloride complexes (mainly $AgCl_2$; Seward 1976). Antimony is transported by a neutral hydroxyantimonite complex [$Sb_2S_2(OH)_2$] below 275°C (Krupp 1989) and a neutral hydroxide complex [$Sb(OH)_3$] above 275°C (Wood *et al.* 1987). Bismuth is probably transported as a neutral hydroxide complex [$Bi(OH)_3$; Wood *et al.* 1987]. In all cases, a decrease in temperature or an increase in H_2S concentration causes precipitation of metals. Changing pH has no effect on Sb and Bi solubility, but increasing pH causes precipitation of Ag.

For a 350°C volcanogenic fluid, the solubilities of Ag (relative to Ag_2S) and Sb (Sb_2S_3) are 23–40 ppm and 340–1900 ppm, respectively (calculated from compositional and thermodynamic data mentioned in the above two paragraphs). Hence, it is unlikely that Ag or Sb were saturated in higher-temperature fluids that formed Cu-rich ores. As a consequence, both Ag and Sb were probably dissolved from the Cu-rich cores of the deposits and moved outward to the upper and lateral portions, where they precipitated as the fluid quenched when it mixed with seawater. This process, termed "zone refining" (Eldridge *et al.* 1983), also applies to Pb and Zn, hence the common association of Ag with Pb in the lateral and upper portions of VMS deposits.

Crystal-chemical controls on Ag solubility in major ore-forming minerals

Silver occurs as a trace or minor element in ore-forming minerals in VMS deposits; thus the crystal chemistry of these minerals plays an important role in determining the abundance of Ag in host minerals, but that role is not uniform.

Although the solubility of Ag_2S in *galena* is insignificant below 500°C (Van Hook 1960), significant amounts of Ag can dissolve in galena by coupled substitution with Sb or Bi. Above 200°C, $AgBiS_2$ forms a complete solid-solution with galena (Van Hook 1960), and above 390°C, $AgSbS_2$ forms a complete solid-solution with it (Amcoff 1976). At temperatures below 390°C, $AgBiS_2$ is more soluble than $AgSbS_2$. These solubility relationships led Amcoff (1984) to propose that coupled substitution of Ag with (mainly) Sb or Bi in galena controls the distribution of Ag in VMS deposits. The overall relationship in galena of Ag ≈ Sb + Bi (in atoms per formula unit) observed in this study is consistent with the model of Amcoff (1984), but the overall control on Ag is more complicated, as tetrahedrite is also a major Ag host in many VMS deposits.

Studies of the composition of *tetrahedrite–tennantite* in Ag-rich epithermal vein (*e.g.*, Hackbarth & Petersen 1984) and VMS deposits (*e.g.*, Jambor & Laflamme 1978, Miller & Craig 1983, Ramsden *et al.* 1990) demonstrated a strong positive correlation between Ag and Sb contents of tetrahedrite–tennantite. Hackbarth & Petersen (1984) proposed a "fractional crystallization" model for the covariations of Ag with Sb. By assuming that Cu and As fractionate preferentially into tennantite relative to the fluid, they duplicated variations observed at grain and ore-deposit scales: early or proximally precipitated tennantite is enriched in Cu and As, whereas later or more distally precipitated tetrahedrite is enriched in Ag and Sb. Experimental results at 500°C were interpreted by Sack & Loucks (1985) to be consistent with the fractional crystallization model of Hackbarth & Petersen (1984). The effect of fractional crystallization may be enhanced by a (crystal-chemistry controlled?) correlation of Ag/(Ag + Cu) with Sb/(Sb + As), noted in the electrum-buffered experiments of Ebel & Sack (1989). Fractional crystallization seems to be an important control on the composition of the tetrahedrite–tennantite-group phase.

Of the three major hosts of Ag in VMS deposits, the crystal chemistry of Ag in *chalcopyrite* is least known. Experiments by Prouvost (1966) showed that chalcopyrite can contain up to 5–8 wt% Ag in solid solution, probably substituting for Cu. However, in nature, levels of Ag in chalcopyrite are much lower. Sandecki (1983) recorded up to 1.8% Ag in chalcopyrite from the Grapenburg Norra deposit in Sweden, but in most deposits the amount of Ag is below 2000 ppm (*e.g.*, J.F. Riley in Knights 1983, Harris *et al.* 1984, Cabri *et al.* 1985, Larocque *et al.* 1995; this study). Cabri & Harris (1984) suggested that the high concentrations reported by Sandecki (1983) probably result from Ag diffusion that forms a thin film of Ag_2S at the surface of chalcopyrite rather than the true Ag content of the chalcopyrite (*cf.* Chen *et al.* 1980).

A model for the concentration of Ag in VMS deposits

Amcoff (1984) presented a model for the distribution of Ag in VMS deposits in which he emphasized the importance of coupled substitution of Ag with Sb or Bi in galena. According to his model, a small fraction of Ag precipitates in chalcopyrite at high temperature (>300°C), but most Ag precipitates in galena; higher temperatures favor coupled substitution with Bi rather than with Sb. Although Amcoff's (1984) model is consistent with observations in deposits in which galena is the dominant host to Ag, it does not account for the distribution in deposits where tetrahedrite is an important host.

On the basis of data from this and previous studies, we have developed a geochemical model for the spatial and mineralogical distributions of Ag in VMS deposits. This model extends the original model of Amcoff (1984) to include deposits in which galena is not the major host.

Chemical factors that affect partitioning of Ag among major hosts

Although not precisely describing the partitioning of Ag, these reactions illustrate the most important controls:

$$8AgSbS_2\ (ss) + 12CuFeS_2 + 4ZnS + 6H_2S\ (aq) + 3O_2 = 2Cu_6Ag_4Zn_2Sb_4S_{13} + 12FeS_2 + 6H_2O \quad (1),$$

$$AgSbS_2\ (ss) + Bi(OH)_3\ (aq) = AgBiS_2\ (ss) + Sb(OH)_3\ (aq) \quad (2),$$

and

$$8AgFeS_2\ (ss) + 8Bi(OH)_3\ (aq) + 16H_2S\ (aq) + 2O_2 = 8AgBiS_2\ (ss) + 8FeS_2 + 28H_2O \quad (3).$$

In all reactions, $AgSbS_2$ (ss) and $AgBiS_2$ (ss) occur as solid solution in galena, and in reaction (3), $AgFeS_2$ (ss) occurs as solid solution in chalcopyrite. Important controls on Ag partitioning include temperature, $m\text{H}_2\text{S}$, $m\text{Sb(OH)}_3/m\text{Bi(OH)}_3$, and the redox condition of the fluid.

Reaction (1) suggests that $m\text{H}_2\text{S}$, redox and temperature of the fluid control partitioning of Ag between Sb-rich galena and tetrahedrite. As $m\text{H}_2\text{S}$ is fairly constant in VMS systems (*cf.* Large 1977), the main controls appear to be redox and temperature. At constant temperature, Ag is partitioned into tetrahedrite under more oxidized conditions. In addition, empirical evidence suggests that Ag is partitioned into tetrahedrite at lower temperature.

Reaction (2) suggests that the $m\Sigma\text{Bi}/m\Sigma\text{Sb}$ ratio of the fluid determines the dominant semi-metal with which Ag enters into linked substitution in the structure of galena. At temperatures below 275°C, where hydroxyantimonite complexes predominate over Sb hydroxide complexes, increasing $m\text{H}_2\text{S}$ favors coupled substitution with Bi:

$$Sb_2S_2(OH)_2\ (aq) + 2AgBiS_2\ (ss) + 4H_2O = 2Bi(OH)_3\ (aq) + 2AgSbS_2\ (ss) + 2H_2S\ (aq) \quad (4).$$

Reaction (3) indicates that Ag fractionates more into chalcopyrite relative to galena from reduced, Bi-poor or H_2S-poor fluids. A limiting factor in the above reactions is the abundance and stability of galena. Most Archean VMS deposits are Pb-poor, and galena is only a minor to trace mineral in parts of Cu-rich zones in many Phanerozoic and Proterozoic deposits.

Conditions of ore formation

In addition to the well-documented differences in temperatures of deposition among VMS ore types, there may also be differences in redox conditions. The best evidence for redox variations within deposits is the common presence of barite in the upper portions of Proterozoic and Phanerozoic VMS lenses, but its absence in the lower portions of the same deposits. Additional mineralogical evidence for redox variations include changes in iron – sulfur – oxygen minerals and in the FeS content of sphalerite. Pyrrhotite occurs mainly at the base of the Millenbach deposit (Knuckey *et al.* 1982), and trace quantities of pyrrhotite occur in Cu-rich zones, but not in overlying zones at Rosebery (Huston & Large 1988). At Rosebery, the FeS content of sphalerite is commonly higher (2–14 mol.%) in barite-free massive sulfide zones, and lower (<2 mol.%) in barite-bearing zones (Green *et al.* 1981, Khin Zaw & Large 1996). Green *et al.* (1981; Rosebery) and Ramsden *et al.* (1990; Hellyer) observed that the FeS content of sphalerite decreases from the Cu-rich base to the Zn-rich top. These data suggest that in well-zoned deposits, Cu-rich ores tend to be most reduced, whereas barite-bearing zones are most oxidized.

The model

On the basis of the above differences in the conditions of ore formation, likely reactions governing the partitioning of Ag, and observations of the mineralogical occurrence of Ag, Figure 8 illustrates a model for the concentration of Ag in VMS deposits.

At the thermal peak of ore formation, higher temperature (300–350°C), relatively reduced Cu-rich fluids interact with the base of a pre-existing massive sulfide lens. The fluids dissolve and replace Zn-rich ores to form Cu-rich ores (Eldridge *et al.* 1983). During this process, there is a net gain of Ag in the fluid phase, as the Ag grades of Cu-rich zones are generally lower than those of Zn-rich zones. This results mainly from the dissolution of tetrahedrite and galena. However, some Ag is retained in chalcopyrite and relict galena.

The temperature and redox condition of the fluid probably govern the proportion and mineral siting of Ag retained in Cu-rich zones. Reaction (3) suggests that chalcopyrite will be the preferred host of Ag relative to galena under reducing conditions. In addition, reduced conditions are more favorable for

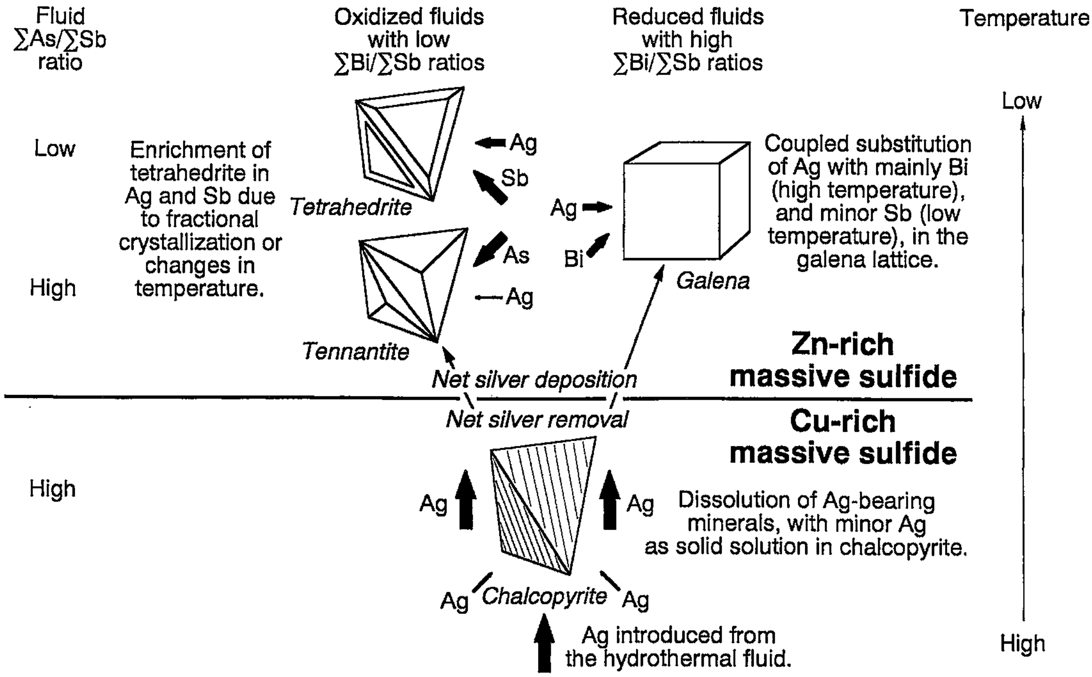

FIG. 8. Schematic diagram showing hypothesized controls on the distribution and mineralogy of silver in volcanogenic massive sulfide deposits.

precipitation of Ag into chalcopyrite from the fluid:

$$4AgFeS_2\,(ss) + 8Cl^- + 4H^+ + O_2 = 4AgCl^{2-} + 2H_2O + 4FeS_2 \qquad (5).$$

This may account for the higher Ag content of chalcopyrite in reduced deposits relative to oxidized deposits, and for the decrease in the contents of Ag in chalcopyrite from the relatively reduced Cu-rich to the relatively oxidized barite zones at Rosebery. Silver may be concentrated in the Cu-rich core of the Millenbach (Knuckey *et al.* 1982) and enriched in chalcopyrite at Izok Lake (Harris *et al.* 1984) because the reduced conditions of formation, as implied by the abundance of pyrrhotite, may have favored retention of Ag in chalcopyrite during zone refining.

In most other deposits, Ag has been leached from Cu-rich zones and deposited in galena or tetrahedrite in Zn-rich upper and outer zones. As the fluids cool and become more oxidized, Ag initially precipitates in galena, mainly by coupled substitution with Bi. Reaction (1) implies that galena is preferred as a host over tetrahedrite under reducing conditions, and empirical evidence suggests that galena, particularly Bi-rich galena, is favored over tennantite at higher temperature.

The relative importance of Sb or Bi in coupled substitution with Ag in galena depends on the ΣBi/ΣSb value of the hydrothermal fluid. High ΣBi/ΣSb values favor coupled substitution with Bi. Because Bi generally is concentrated in Cu-rich zones and Sb generally is concentrated in Zn-rich zones (Smith & Huston 1992), the ΣBi/ΣSb value in this fluid decreases as it passes through the massive sulfide lens. Coupled substitution of Ag with Sb is more important toward the top (Fig. 6), but as Sb-rich galena cannot dissolve as much Ag as Bi-rich galena, Ag concentrations in galena decrease toward the top of ore lenses. Silver- and Bi-rich galena is concentrated in Cu-rich zones and the lower parts of Zn-rich zones, whereas Sb-rich galena with lower Ag contents is concentrated in the upper parts of Zn-rich zones and in barite-bearing zones.

As the temperature continues to decrease and the fluids become more oxidized, argentian tetrahedrite becomes more important according to reaction (1). Incorporation of Ag into tetrahedrite rather than galena also may be favored by even lower ΣBi/ΣSb values in the fluid. Values of ΣCu/ΣAg and ΣSb/ΣAs in the fluid also influence the importance of tetrahedrite as a host to Ag (Hackbarth & Petersen 1989, Sack & Loucks 1985). Fractional crystallization of tetrahedrite–

tennantite, and chalcopyrite and arsenopyrite precipitation in the lower portions of ore lenses, increase both ratios such that the crystallization of Ag-rich tetrahedrite is favored in the upper portion of ore lenses.

Exceptions to the model

The above model for the distribution of Ag in VMS deposits accounts for most of the deposits summarized in Tables 1 and 2. The most important exceptions are Kidd Creek, Heath-Steele and Waterloo.

At Kidd Creek, native silver is a significant host in chalcopyrite-rich zones (*i.e.*, "A" ore), and perhaps in Zn-rich zones (Cabri 1988). In the bornite zone, naumannite is a significant host of Ag (Thorpe *et al.* 1976). Although pyrite and pyrrhotite are both present, pyrrhotite is more common in Cu-rich stringer zones than Zn-rich massive sulfide zones (Walker & Mannard 1974). The following reactions may govern stability of native silver in equilibrium with Ag-bearing chalcopyrite:

$$\mathrm{AgFeS_2\ (ss) = Ag + FeS_2} \quad (6),$$

and

$$\mathrm{2AgFeS_2\ (ss) + 2H_2O = 2Ag + 2FeS + 2H_2S + O_2} \quad (7).$$

For ores rich in pyrite relative to pyrrhotite, reaction (6) suggests that the stability of native silver depends on the solubility of Ag in chalcopyrite. In contrast, in ores richer in pyrrhotite, reaction (7) indicates that redox also is important: native silver is favored by more reduced conditions. Hence, one possible reason for a significant proportion of native silver, particularly in Cu-rich stringer zones, is the reduced character of the ores. As an alternative, the presence of native silver may result from metamorphic recrystallization.

At Heath-Steele, New Brunswick, a large portion of the total Ag resides in Ag–Sb sulfosalts and acanthite, and acanthite is commonly intergrown with native antimony (Chen & Petruk 1980). Chen & Petruk (1980) also found that galena contains little Sb (<500 ppm), and that Ag in galena was taken into solid solution by coupled substitution with Bi. In the absence of significant coupled substitution of Ag and Sb in galena, possibly as the result of low temperatures of deposition, reaction (1) suggests that Ag–Sb sulfosalts [*e.g.*, miargyrite ($\mathrm{AgSbS_2}$)] are stabilized relative to argentian tetrahedrite under reduced conditions. Heath-Steele and other VMS deposits in the Bathurst district are characterized by the very rare occurrence of barite (McCutcheon 1992); hence, a low temperature and relatively reduced conditions during the formation of the Heath-Steele deposit may have stabilized Ag–Sb sulfosalts. By analogy, the presence of Ag–Sb sulfosalts in Ag-rich, Zn-rich, barite-free massive sulfide samples at Rosebery may result from similar processes.

Lastly, Waterloo is an unusual VMS deposit because of the presence of significant quantities of telluride minerals. This implies that the Waterloo ore fluids were enriched in tellurium, which favored precipitation of hessite over other Ag-bearing minerals, particularly as the paucity of Bi minerals and the low Bi contents in galena suggest low levels of Bi in the mineralizing fluids.

CONCLUSIONS

Data from this and previous studies indicate the following generalized distribution of Ag in volcanogenic massive sulfide deposits:

(1) Ag is generally enriched in the Zn-rich, upper portion of the deposits. In a few deposits, Ag is enriched in the Cu-rich, basal portion.

(2) Galena and tetrahedrite are the most important hosts of Ag in most deposits. Tetrahedrite is commonly most important in the uppermost, barite-bearing portions, whereas galena, particularly Bi-rich varieties, is commonly more important deeper in the lenses. Chalcopyrite is a significant host to Ag at the base of a few deposits.

(3) In a small proportion of deposits, Ag sulfosalts, telluride minerals or native silver are important hosts of Ag.

The partitioning of Ag between the three major mineral hosts is probably controlled by temperature, fluid redox conditions, fractional crystallization of tetrahedrite–tennantite, and $\Sigma\mathrm{Bi}/\Sigma\mathrm{Sb}$ values in the fluid phase. High temperature and reduced conditions favor the partitioning of Ag into chalcopyrite, followed by galena. Silver is partitioned into tetrahedrite under lower temperature and relatively oxidized conditions.

In mature VMS deposits, upwelling hydrothermal fluids leach Ag from the base of the lens during zone refining, although a portion may be retained in chalcopyrite, particularly in more reduced deposits. As the fluid passes through the sulfide lens and cools, Ag precipitates into tetrahedrite or galena. Lower $\Sigma\mathrm{Bi}/\Sigma\mathrm{Sb}$ values in the fluid phase, lower temperatures and more oxidized conditions favor tetrahedrite over galena as a host for Ag. Consequently, galena is favored as a host in the lower part of Zn-rich zones, whereas tetrahedrite is favored in barite-bearing zones.

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