TRACE-ELEMENT CONTENTS AND PARTITIONING OF ELEMENTS IN ORE MINERALS FROM THE CSA Cu-Pb-Zn DEPOSIT, AUSTRALIA

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ABSTRACT

The Se, Cd, Mn, Sn, Ag, Co and Ni contents of ore minerals from the CSA Cu-Pb-Zn deposit at Cobar, New South Wales, Australia have been determined. The temperature of ore formation and the partitioning of Se, Mn and Cd between sphalerite and galena do not show a correlation; the trace elements in these mineral phases do not seem to indicate equilibrium. Partitioning of Fe and Zn between coexisting sphalerite and stannite give an ore-formation temperature of approximately 260°C. This value is lower than temperatures interpreted from fluid inclusions and compositions of chlorite, which average 350°C; this lowering is due to postdepositional, late metamorphic changes. FeS contents of sphalerite range from 14.7 to 11.8 mole % and indicate a pressure range from 4.8 to 7.9 kbar. The pressures are too high for metamorphic conditions at Cobar. The sphalerite likely re-equilibrated at temperatures below the metamorphic peak. The Co/Ni values of pyrite from Cobar ore are lower than those of most Cu-rich exhalative deposits, but are similar to those from remobilized vein deposits, and hence support the proposed metamorphic origin of the deposit.

Keywords: trace elements, Co/Ni values, partitioning, geothermometer, geobarometer, CSA deposit, Cobar, Australia.

SOMMAIRE

La concentration de Se, Cd, Mn, Sn, Ag, Co et Ni dans les minéraux du minerai du gisement de Cu-Pb-Zn CSA, à Cobar (au New South Wales, en Australie), a fait l'objet de cette étude. La température de formation du minerai et la répartition de Se, Mn et Cd entre sphalérite et galène n'ont aucun rapport; d'après la concentration de ces éléments, ces deux minéraux ne semblent pas équilibrés. La répartition de Fe et du Zn entre sphalérite et stannite indique une température de formation d'environ 260°C, inférieure à celle qu'indiquent les inclusions fluides et la composition de la chlorite, en moyenne 350°C. Ce décalage serait dû à des ajustements métamorphiques tardifs. La teneur en FeS de la sphalérite, entre 14.7 et 11.8% (base

molaire), indique une pression entre 4.8 et 7.9 kbar. Ces valeurs sont trop élevées pour décrire les conditions métamorphiques à Cobar. La sphalérite aurait ré-équilibré à une température inférieure à celle du paroxysme métamorphique. Les valeurs du rapport Co/Ni dans la pyrite de Cobar sont inférieures à celles de la plupart des gisements exhalatifs cuprifères; elles ressemblent toutefois à celles qui caractérisent les gisements formés par remobilisation de minerai en fissures, ce qui étaye l'hypothèse d'une origine métamorphique du gisement.

(Traduit par la Rédaction)

Mots-clés: éléments traces, rapport Co/Ni, répartition, géothermomètre, géobaromètre, gisement CSA, Cobar, Australie.

INTRODUCTION

Numerous trace-element studies have been carried out on sulfides in order to deduce the temperature and environment of ore formation. Even though some of the earlier studies have been unsuccessful in this regard (Hegemann 1943, Rost 1939, Fryklund & Harner 1955), many have been useful in indicating genetic indicators of ore deposition (Carstens 1941, Edwards & Carlos 1954, Hawley & Nichol 1961, McIntire 1963, Loftus-Hills & Solomon 1967, Bralia *et al.* 1979, Mookherjee & Philip 1979, Campbell & Ethier 1984). A detailed summary of mainly reconnaissance work before 1955 can be found in Fleischer (1955). The concentration of certain trace elements and the ratio of specific trace elements, such as Co/Ni, have been recognized as being useful to discriminate between magmatic, hydrothermal and sedimentary deposits (Hawley & Nichol 1961, Loftus-Hills & Solomon 1967, Price 1972, Bralia *et al.* 1979). Partitioning of certain trace elements, especially Cd, Mn and Se between coexisting mineral phases such as sphalerite and galena has been studied experimentally in the temperature range 300–800°C, and the distribution coefficients for these systems have been found to be dependent on the temperature of formation (Bethke & Barton 1971, Halbig & Wright 1969).

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Previous reports of trace element studies of CSA (Cornish–Scottish–Australian) ore minerals, mainly used for reconnaissance purposes, were not concerned with element partitioning between ore minerals (Rayner 1969, Harris 1965, Robertson 1974, Ramsden et al. 1979). In this study, the trace elements Se, Co, Ni and Ag have been determined in single grains of pyrite, pyrrhotite and chalcopyrite using the electron microprobe; also, Se, Cd, Mn and Ag have been determined in galena and Se, Cd, Mn and Sn in sphalerite. The analyses of galena and sphalerite represent a combination of electron microprobe determinations of single grains and atomic absorption and emission spectroscopy analyses of separates. Special attention was paid to the partitioning of Cd and Mn between sphalerite and galena, and to that of Zn and Fe between sphalerite and stannite, because of their potential in geothermometry (Halbig & Wright 1969, Bethke & Barton 1971, Nekrasov et al. 1979, Nakamura &
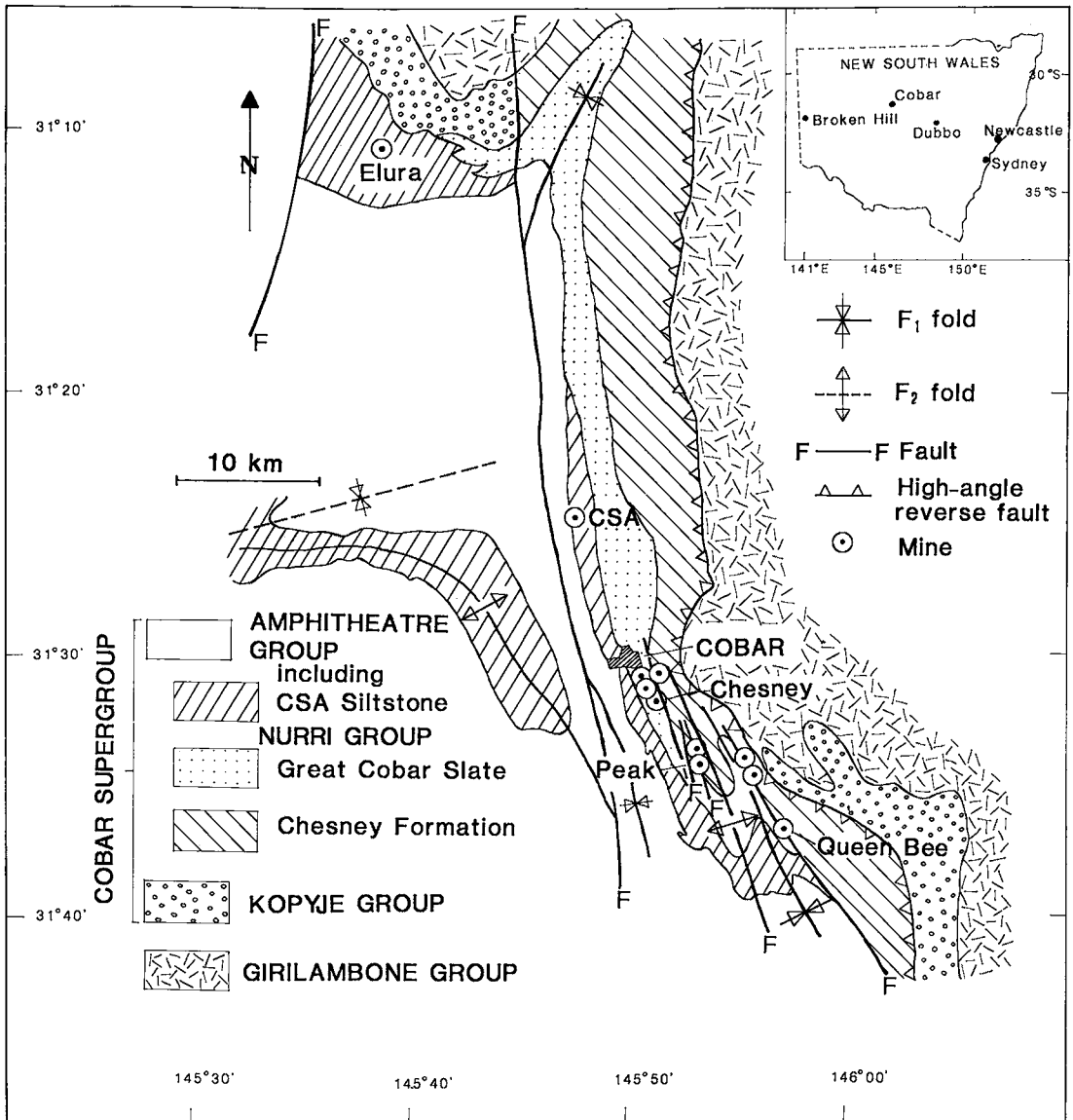

FIG. 1. Simplified geology of the Cobar area. Modified from Glen (1985, 1987).

Shima 1982). Fe and Zn were determined by electron-microprobe analysis. In addition, reference will be made to the FeS contents of sphalerite, although these seem to be unreliable as pressure indicators at the CSA mine. Values of Co/Ni in the pyrite are compared with those from other ore deposits. Co and Ni contents and their ratios are found to support a metamorphic origin for the CSA deposit, in agreement with data obtained from fluid inclusion and stable-isotope studies (Brill, in prep.).

GEOLOGY OF THE CSA ORE DEPOSIT

The CSA Cu–Pb–Zn orebody is one of several Cu–Au and Cu–Pb–Zn deposits in the Cobar district to be hosted by Early Devonian distal turbidites of the Cobar Supergroup (Fig. 1). Deposition of the host sediments took place within the Cobar basin, one of several fault-controlled basins developed at this time through rifting in Eastern Australia (Scheibner 1973, 1974). The whole sequence was affected by deformation and metamorphism, which reached lower greenschist grade and pressures of approximately 3 kbar during Early Carboniferous time (Brill 1988).

The CSA orebody consists of several ore shoots, shown in Figure 2. Each ore shoot contains mineralized vein systems that are commonly nearly parallel to the principal north-trending, steeply east-dipping schistosity in the surrounding metasediments. Overprint of the mineralization by deformation has resulted in a complex paragenesis (Fig. 3). Some of the mineralized veins formed prior to, or early, in the deformation history, but most of the mineralization is syntectonic. A broad predeformation alteration halo surrounds the ore zones and consists mainly of chloritized and silicified host-rocks. The main ore minerals in the CSA mine are chalcopyrite, pyrite, pyrrhotite, sphalerite and galena, with minor amounts of bismuthinite, galenobismutite, boulangerite, stromeyerite, arsenopyrite, clausthalite, tetrahedrite, bismuth, stannite and retrograde orthorhombic cubanite and mackinawite. Two different styles of ore exist: Cu-rich ore, comprising mainly chalcopyrite – pyrrhotite – pyrite, and Pb–Zn-rich ore, composed principally of galena – sphalerite – pyrrhotite – pyrite. The Pb–Zn ore occurs in two main phases (Fig. 3), the latter of which is associated with chlorite-filled shears that dissect earlier mineralization.

The genesis of the deposit has been the cause of dispute; epigenetic (Rayner 1969) through syngenetic (Sangster 1979) to remobilized syngenetic (Brooke 1964, 1975, Robertson 1974, Gilligan & Suppel 1978, Marshall & Sangameshwar 1982) modes of formation have been proposed. Recent research has shown that the mineralization is likely to be of metamorphic
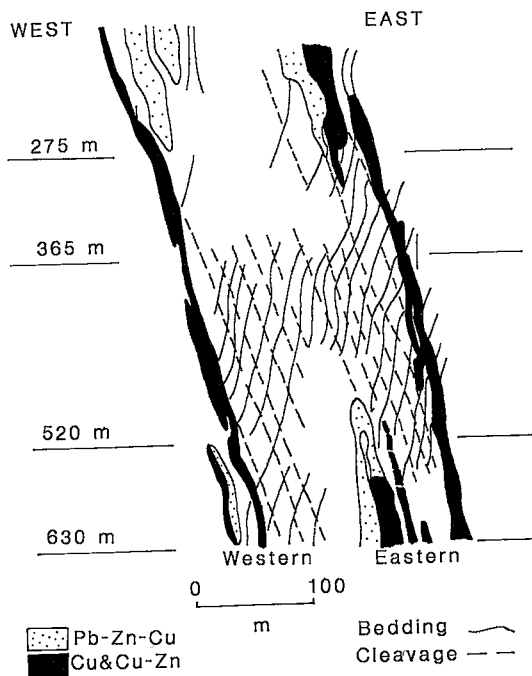

FIG. 2. Cross-section through the CSA orebody (after O'Connor 1980).

origin, as mineralized veins are clearly related to deformation, and an igneous source is absent in the Cobar region (Glen 1985, 1987, Brill, in prep).

ANALYTICAL METHODS

All analyzed samples were taken from underground workings in the Eastern and Western vein systems on the 6 and 7 levels (520 and 630 m) of the CSA mine (see Fig. 2). In this study the analyses were done on polished blocks using a CAMECA electron microprobe at 20 kV. In that way a more detailed control on the paragenesis of the ore minerals was possible than with bulk analyses by atomic absorption and atomic emission spectroscopy. Pure elements were used as calibration standards, except that ZnSe was used for Se determinations. Electron-microprobe analyses of Se and Mn commonly indicate less than the detection limits of 100 ppm; as the partitioning of these elements between sphalerite and galena is of concern in applying the geothermometer, additional analyses were done by atomic absorption (AA) and atomic emission (AE) spectroscopy on mineral separates prepared from ore samples containing these two minerals as coexisting phases. Detection limits for AA are 1 ppm for Se and 20 ppm for Mn; detection limits for AE are 50 ppm for Se and Mn.
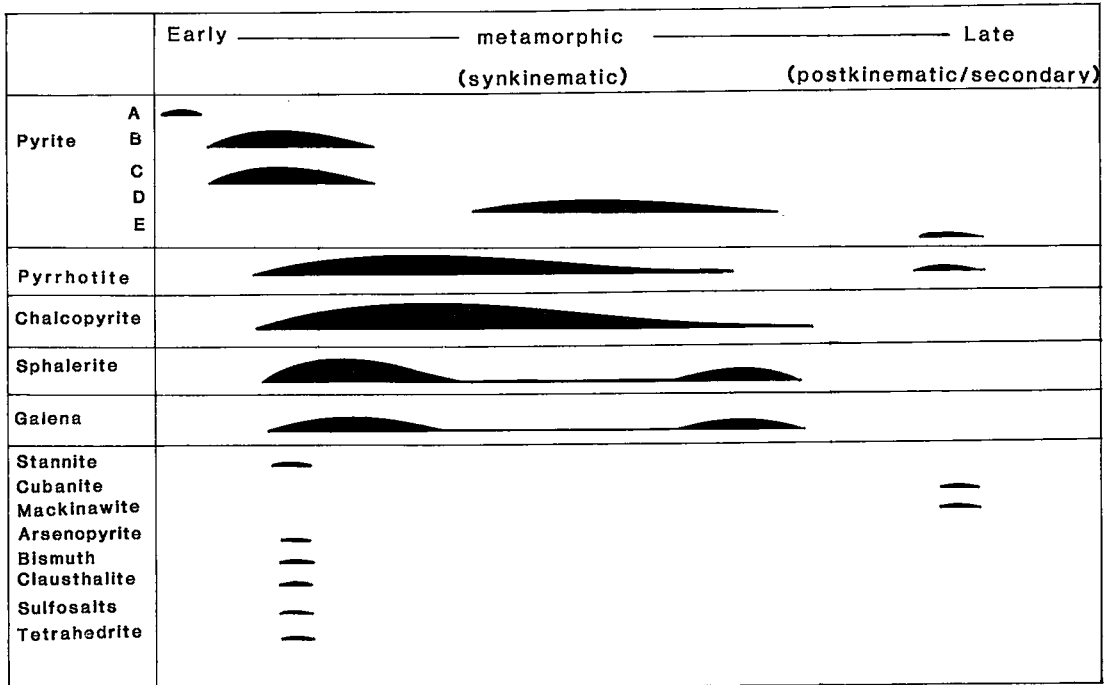
FIG. 3. Paragenesis of CSA ore minerals.

TRACE-ELEMENT CONCENTRATIONS

Chalcopyrite

Se contents of chalcopyrite average 294 ppm (Table 1) and are higher than most reported Se values from Australian deposits (Great Cobar, Captains Flat and Broken Hill: Edwards & Carlos 1954; Rosebery: Loftus-Hills & Solomon 1967; West Lyell: Loftus-Hills *et al.* 1969; Big Cadia: Bajwah *et al.* 1987). Chalcopyrite from CSA averages 245 ppm Ag, also high when compared to that of other Australian deposits (Big Cadia: Bajwah *et al.* 1987; Golden Grove: Frater 1978) and to many Canadian volcanogenic deposits. Chalcopyrite is enriched in Ag compared to pyrite, an observation made by many previous workers (Hawley & Nichol 1961, Nishiyama 1974, Seccombe 1977, Frater 1978, Thole 1976). Both Co and Ni were found to be below their respective detection-limits.

Pyrrhotite

The Se content of pyrrhotite from the CSA mine (av. 153 ppm) is relatively high compared to that of

other Australian deposits (see Edwards & Carlos 1954) but is similar to some of the Canadian volcanogenic deposits. Edwards & Carlos (1954) suggested using the Se content as a genetic indicator for an ore deposit. However, as pointed out by Loftus-Hills *et al.* (1969), the Se content is unsatisfactory as a genetic indicator of Tasmanian ore deposits because fluid-inclusion studies show that no relationship exists between the temperature of formation and the Se content of the sulfides. The same problem has been found in sulfides from the CSA mine, especially when considering element partitioning (see discussion below). The unusually high Se content of CSA pyrrhotite and other sulfides from CSA makes the Se content an unsuccessful genetic or province indicator for the CSA mine. However, Ramsden *et al.* (1979) investigated the use of Se in pyrrhotite (average 106 ppm) and pyrite for exploration and suggested that the sudden increase in the Se content toward the ore zones may be a useful guide in exploration.

Ag values in pyrrhotite from CSA (av. 353 ppm) are higher than those from a wide variety of ore deposits. The amount of Co (av. 646 ppm) is lower than in some volcanogenic deposits (Flin Flon and Chibougamau: Hawley & Nichol 1961; Golden Grove: Frater 1978), but higher than in sedimentary ores, skarn deposits (Hawley & Nichol 1961) and

TABLE 1. MAJOR- AND MINOR-ELEMENT CONCENTRATIONS[*] IN ORE SAMPLES FROM THE CSA MINE

1A. Pyrite, pyrrhotite, chalcopyrite

Mineral	Se	Ag	Co	Ni	Co/Ni	Analyses	
							* in ppm
Pyrite							
r	112-644	126-308	251-3011	106-289	1.1-4.2	40	
x	316	198	1027	197	2.4		
Pyrrhotite							
r	122-180	117-1685	183-415	591-719	3.9-5.1	15	
x	153	353	291	646	4.3		
Chalcopyrite							
r	141-426	119-474				27	
x	294	245					

1B. Sphalerite, galena, stannite

Mineral	Se	Cd	Mn	Ag	Sn	Fe	Zn	Zn/Cd	Analyses
Sphalerite									
r	122-530	518-1125	113-1046		111-286	7.0-8.3	57.4-58.1	520-1127	22
x	277	851	633		172	8.1	57.9	689	
AA/AE r	70-396		474-1024						4
AA/AE x	256		831						
Galena									
r	115-1295	137-899		156-903					37
x	576	453		491					
AA/AE r	46-3681		25-158						4
AA/AE x	1970		86						
Stannite									
r						12.8-16.7	0.9-4.6		7
x						13.6	2.1		

Key: r = range; x = average. All analyses by electron microprobe unless indicated AA/AE (Atomic Absorption/Atomic Emission) Spectroscopy). Detection limits - microprobe analyses: 100 ppm for all elements; Se 1ppm (AA) and 50 ppm (AE), Mn 20 ppm (AA) and 50 ppm (AE)

remobilized vein deposits (Tuscany: Bralia *et al.* 1979). Ni values (av. 153 ppm) are lower than in most comparable deposits and are higher than in remobilized vein deposits (Tuscany: Bralia *et al.* 1979). The Co/Ni ratio, obtained from only 4 pyrrhotite samples, averages 4.3.

Pyrite

Se values in pyrite (av. 316 ppm) also are unusually high when compared to other deposits recorded in the literature. Pyrite is enriched in Se relative to chalcopyrite, as was observed in pyrite from remobilized veins at West Lyell (Loftus-Hills *et al.* 1969). Partitioning of Se or differential mobility of Cu, Fe and Se during hydrothermal remobilization was regarded by those authors as the cause for the enrichment in pyrite; similar interpretations could apply for the CSA mine. Se could have been leached from the marine sediments that host the mineralization and concentrated in the veins by the metamorphic fluids that were responsible for the mineralization at the CSA mine. An alternative explanation for the anomalously high Se content in an otherwise Se-poor province (Edwards & Carlos 1954, Schmidt 1980) could be a localized Se-enriched source (magmatic?); however, geochemical (fluid inclusions, isotopes) and geophysical (Agostini 1985) data do not indicate a magmatic source in the Cobar area. Therefore, it remains unclear why the mineralization at the CSA mine, which is similar to that in most other deposits in the Cobar area, is characterized by a higher Se content. The conclusion that the Cobar area is a

Se-depleted region was based on a few analyses by Edwards & Carlos (1954); further data from other deposits in the area are needed to substantiate the Se-poor character of the province. Limited data for the Elura mine, 50 km north of Cobar, show Se concentrations of less than 5 ppm for mixed ore samples (Schmidt 1980); however, a genetic link between the Elura and CSA deposits is not obvious, and the values are possibly not representative for the entire Cobar area. Ag values in pyrite (average 198 ppm) are also higher than in other deposits.

The Co/Ni ratio in pyrite

Many studies of trace elements have related the ratio Co/Ni to the genetic type of an ore deposit (Carstens 1941, Hegemann 1943, Gavelin & Gabrielson 1947, Hawley & Nichol 1961, Loftus-Hills & Solomon 1967, Bralia *et al.* 1979, Mookherjee & Philip 1979, Green *et al.* 1981). It has been found that pyrite of volcanic association commonly shows Co/Ni values greater than 1 (Loftus-Hills & Solomon 1967), greater than 5 to 10 (Bralia *et al.* 1979), or typically between 5 and 50 (Price 1972). Pyrite of sedimentary origin yields a value of less than 1 (Loftus-Hills & Solomon 1967), 0.63 being typical (Price 1972); the ratio in hydrothermal (vein) pyrite averages close to 1.7, and is invariably less than 5 (Price 1972).

The Co and Ni values in pyrite from the CSA mine range from 251 to 3011, and from 106 to 289 ppm, respectively. Co/Ni values range from 1.07 to 4.22 and yield an average of 2.4. A relationship between
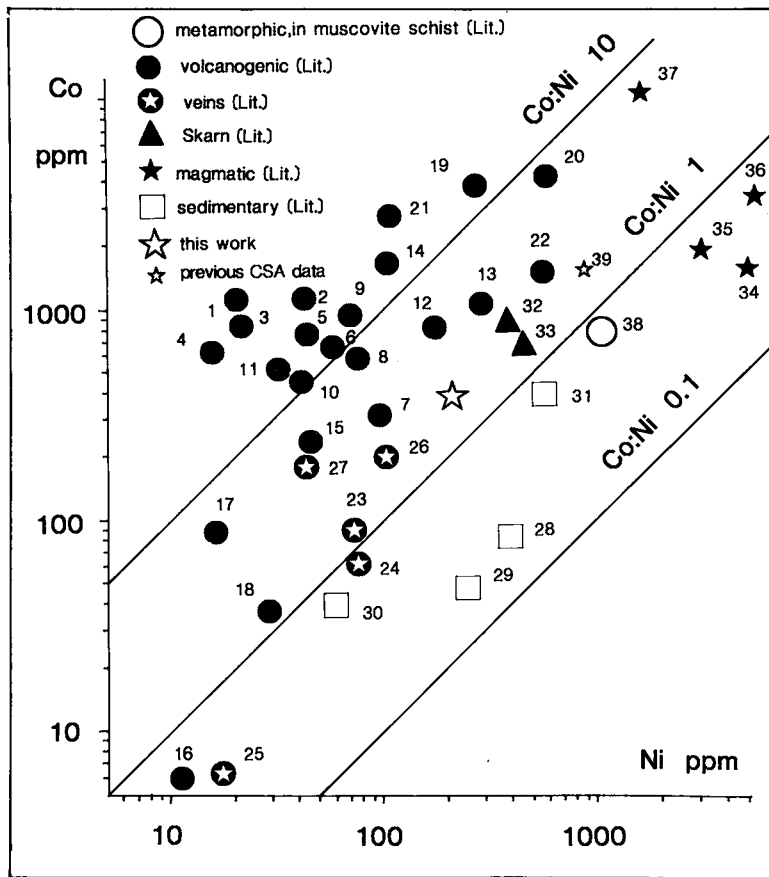
FIG. 4. Co-Ni plot of CSA pyrite. Shown for comparison are values for pyrite
from orebodies of different origins (Table 2).

the Co and Ni content, or Co/Ni values, and the paragenetic position of the analyzed CSA pyrite is not evident. The average Co and Ni concentrations have been plotted in Figure 4 and are compared with pyrite of different genetic types that have been recorded in the literature. All Co/Ni values from the CSA mine are greater than 1 and less than 5 and belong to the hydrothermal (vein) pyrite group, as defined by Price (1972). The values are far removed from that for average sedimentary pyrite and also do not show any magmatic signature. Pyrite from most volcanogenic Cu-rich deposits shows higher Co, lower Ni and higher Co/Ni values than the CSA data. Figure 4 shows also that Pb–Zn-rich volcanogenic deposits have lower Co/Ni values (close to 1) than the Cu-rich deposits, a trend that has been observed by Loftus-Hills & Solomon (1967) and confirmed by Price (1972). However, some sediment-hosted Pb–Zn deposits do not follow this trend and show rather high Co and Ni contents and Co/Ni

values (i.e., Sullivan and Faro orebodies). The CSA Co/Ni values do not indicate an affinity to any of the Pb–Zn deposits or to the majority of the Cu-rich volcanogenic deposits. Instead, the Co and Ni data for pyrite in the sediment-hosted CSA Cu–Pb–Zn orebody fall close to the values for the sediment-hosted and metamorphosed Cu mineralization of Shamrocke and some of the remobilized vein deposits from Tuscany. Even though not indisputable, similarity to the remobilized vein deposits of Tuscany is favored; the evidence from tectonic (Glen 1985, 1987), fluid-inclusion, and isotope studies (Brill, in prep.) indicates that the CSA deposit is of metamorphic origin.

Galena

Se values in galena average 576 ppm and are lower than the only available data from the carbonate-

TABLE 2. SOURCES OF GEOCHEMICAL DATA USED TO CONSTRUCT THE Co/Ni PLOT (FIGURE 4)

Pyrite from volcanogenic, massive sulfide deposits: 1 Sulitjelma, 2 Noranda, 3 Quemont, 4 Normetal (Hawley & Nichol 1961), 5 New Brunswick (Sutherland 1967), 6 Flin Flon, 7 Manitouwadge, 8 Matagami (Hawley & Nichol 1961), 9 Horne (Roscoe 1965), 10 Golden Grove (Frater 1978), 11 Tuscany (Bralia et al. 1979), 12 Faro, 13 Sullivan (Campbell & Ethier 1984), 14 Flin Flon (Sangameshwar 1972), 15 Rosebery (Green et al 1981), 16 Rosebery (Loftus-Hill & Solomon 1967), 17 Czechoslovakia (Cambel & Jarkovsky 1968), 18 Shakanai (Nishiyama 1974), 19 Big Cadia (Bajwah 1985), 20 Ingladahl (Mookheerjee & Philip 1979), 21 Chibougamau (Hawley & Nichol 1961), 22 Mt. Lyell (Walshe & Solomon 1981)

Pyrite from remobilized veins: 23 Tuscany (Bralia et al. 1979), 24 West Lyell (Loftus-Hills & Solomon 1967), 25 Sulitjelma (Gehrisch et al. 1975, in Bralia et al. 1979), 26 Nigadoo, New Brunswick (Sutherland 1967), 27 Agnese, Italy (Dill 1979, in Bralia et al. 1979)

Sedimentary pyrite: 28 Tasmania, shales (Loftus-Hills & Solomon 1967), 29 Czechoslovakia (Cambel & Jarkovsky 1968), 30 av. sedimentary pyrite (Price 1972, in Bralia et al. 1979), 31 black shales, Rosebery (Loftus-Hills & Solomon 1967)

Pyrite from skarn deposits: 32, 33 Czechoslovakia (Cambel & Jarkovsky 1968)

Pyrite from magmatic deposits: 34, 35, 36 Czechoslovakia , 37 Sudbury (Cambel & Jarkovsky 1968)

Pyrite from metamorphic rocks: 38 metamorphic porphyroblasts in muscovite schists (Sieh & Chen 1983)

Previous Cobar data: 39 CSA mine (Robertson 1974)

hosted deposit of Darwin (Hall *et al.* 1971). Galena from the CSA mine is enriched in Cd (av. 453 ppm) compared to volcanogenic (Kuroko: Takanashi 1963, 1966), hydrothermal (Yugoslavia: Dangic 1985), carbonate-hosted (Wood River: Hall & Czamanske 1972; Fankou: Xuexin 1984) and Japanese epithermal deposits (Urabe 1977). The Mn contents (av. 86 ppm) are higher than those from hydrothermal vein deposits (Yugoslavia: Dangić 1985), the massive sulfide deposits of Kuroko (Takanashi 1963, 1966) and some Japanese epithermal vein deposits (Urabe 1977). The level of Ag (av. 491 ppm) is lower in CSA galena than in that from Broken Hill (Both 1973) and the carbonate-hosted deposits of Darwin (Hall *et al.* 1971) and Fankou (Xuexin 1984).

Sphalerite

Se concentrations of sphalerite from CSA exceed those found in other ore deposits (Fankou: Xuexin 1984; Golden Grove: Frater 1978; Flin Flon: Hawley & Nichol 1961; Darwin: Hall *et al.* 1971). Sphalerite is low in Cd (av. 851 ppm) compared to that from volcanogenic deposits (Flin Flon: Hawley & Nichol 1961; Arrow and South Bay: Seccombe 1977; Rosebery and Mt. Lyell: Green *et al.* 1981; Broken Hill: Both 1973) and Japanese vein deposits (Shimizu & Shikazono 1985). Zn/Cd values of sphalerite have been proposed as genetic indicators for ore deposits by Jonasson & Sangster (1978), who observed typical mean values of 377 for sphalerite from Cu–Zn-rich deposits of volcanosedimentary association, and 117 for Canadian vein-type

deposits. The highest Zn/Cd values are found in sphalerite of the volcanosedimentary type [range 417–531, calculated in Xuexin (1984) from Vokes (1976)], average values, in metamorphosed sedimentary deposits [252–330, calculated in Xuexin (1984) from Both (1973)], and the lowest values, in hydrothermal (skarn) deposits [range 104–214, in Xuexin (1984)]. Sphalerite from the CSA mine, with average Zn/Cd values of 698, is unusual and does not fit any of the categories outlined above. Mn contents also are low (av. 633 ppm); a slightly higher Mn content is present in an earlier sphalerite, which occurs as inclusions within galena. Sn has been detected in only two samples; their average of 172 ppm is lower than in sphalerite from massive sulfide deposits (Arrow and South Bay: Seccombe 1977; Japanese vein deposits: Shimizu & Shikazono 1985) and in sphalerite from the Wood River deposit (Hall & Czamanske 1972).

PARTITIONING OF Se, Co AND Mn BETWEEN SPHALERITE AND GALENA

The partitioning of Se between sphalerite and galena has been studied experimentally between 300 and 650°C by Halbig & Wright (1969). Bethke & Barton (1971) studied the distribution of Se, Cd and Mn between coexisting sphalerite and galena experimentally in the temperature range 600–800°C. The distribution coefficients are dependent on temperature. In these studies, Se tends to be enriched in galena relative to sphalerite, and this trend is enhanced at lower temperature. Subsequently, Yamamoto *et al.* (1984) studied the distribution of

Se between sphalerite and galena at 450 and 500°C and substantiated the temperature dependence of the partitioning between the two mineral phases.

Using the data of Bethke & Barton (1971), the partition coefficients of Se, Mn and Cd have been calculated. The deduced temperatures are in the range 990–2234°C for the partitioning of the three trace elements. These temperatures are unreasonably high for conditions of ore formation at the CSA mine; data from other sources (fluid-inclusion analyses, chlorite compositions) indicate temperatures in the range 300–350°C.

The unreasonable results are most likely due to disequilibrium involving the trace elements in the two mineral phases. Rose (1967) suggested that such disequilibrium may exist because the minerals were not deposited simultaneously or, if they were, the trace elements may have been incorporated in non-equilibrium amounts. As pointed out in the geological discussion, complex relationships exist among the ore minerals at the CSA mine, and two major stages of ore formation are evident. Because the analyses for Mn and Se were done on concentrates using AA and AE techniques, the detailed paragenetic control was lost. Nevertheless, because the later Pb–Zn phase is mainly restricted to the shear zones, it has been possible to distinguish between the two major Pb–Zn stages. No difference was found in their trace-element contents. Concentrations of Cd were determined by electron microprobe, and thus paragenetic control was possible; in most samples there is no reason to assume that the analyzed sphalerite and galena were not deposited simultaneously. It seems, therefore, that even though sphalerite and galena apparently are in textural equilibrium, they have not attained equilibrium in their distribution of trace elements. Alternatively, a possible low-temperature overprint (see below) may have influenced the partitioning of Cd, Se and Mn between sphalerite and galena.

PARTITIONING OF Fe AND Zn BETWEEN STANNITE AND SPHALERITE

Minor stannite commonly coexists with sphalerite in the CSA deposit. Stannite forms wide regions of solid solutions; the zinc and iron contents of stannite were proposed to be related to temperature (cf. Springer 1972). Experimental studies of the partitioning of Fe and Zn between stannite and sphalerite at 300, 400 and 500°C and pressures up to 5 kbar (Nekrasov et al. 1979) and 250, 350 and 450°C and pressures between 400 to 800 kg/cm² (Nakamura & Shima 1982) indicate a temperature dependence. Successful application of the geothermometer has been recorded by Shimizu & Shikazono (1985) for ore deposits associated with tin

mineralization in Japan. However, as pointed out by these authors, there has been no extensive application of the geothermometer to natural sphalerite-stannite pairs, and no comparison with results from other geothermometers.

Coexisting stannite–sphalerite pairs from the CSA mine in association with iron sulfides (pyrite, pyrrhotite) and galena have been analyzed for Fe and Zn. Assuming equilibrium between the two mineral phases, temperatures have been calculated using the data of Nekrasov et al. (1979) and Nakamura & Shima (1982): 1) $\log K_D = -1274/T + 1.174$ (Nekrasov et al. 1979), and 2) $\log K_D = -2800/T + 3.5$ (Nakamura & Shima 1982), where K_D is equal to $(Fe/Zn)_{sph}/(Fe/Zn)_{st.}$.

The calculated temperatures from 13 analyses vary between 128 and 194°C using the geothermometer of Nekrasov et al. (1979), and between 236 and 306°C based on the geothermometer of Nakamura & Shima (1982).

Shimizu & Shikazono (1985) pointed out that in their study, the results obtained using the formulation of Nakamura & Shima (1982) are in better agreement with the likely temperature of formation. Likewise, the higher range, of 236–306°C (av. 264°C), seems more realistic for the CSA mine, but the temperatures are still 50–100°C below those indicated by fluid-inclusion studies and chlorite compositions (i.e., range 300–350°C). The calculated temperatures for the CSA mine, however, are similar to temperatures from secondary inclusions and some chlorites that are thought to be of late metamorphic origin. The inference, therefore, is that some resetting of the trace-element distribution took place after the peak of metamorphism or that stannite and sphalerite were not formed simultaneously, as was initially assumed.

FeS CONTENT IN SPHALERITE AND GEOBAROMETRY

The FeS content of sphalerite coexisting with pyrite and hexagonal pyrrhotite has long been recognized as a potential geobarometer (Barton & Toulmin 1966, Scott & Barnes 1971). The sphalerite composition in this particular assemblage has been found to be independent of temperature (Barton & Toulmin 1966). The geobarometer has been calibrated by Scott (1973) for temperatures between 325 and 710°C, by Scott & Kissin (1973) for temperatures below 300°C, and has been further refined by Scott (1976) and Hutchison & Scott (1981); Lusk & Ford (1978) have extended the geobarometer to 10 kbars. The most successful application of the geobarometer has been found in rapidly cooled hydrothermal veins (Hutchison & Scott 1981), whereas many metamorphosed deposits indicate unrealistic pressures [Brown (1978) for the Balmat–Edwards district,

Ethier *et al.* (1976) for the Sullivan orebody, Bristol (1974) for the Flin Flon area, Moles (1983) for the Foss deposit]. The geobarometer also has been found to be less reliable for Cu-rich deposits (Hutchison & Scott 1981, Brown 1978), and as a consequence, "chalcopyrite-diseased" sphalerite (Barton 1978) should be avoided for analysis.

The samples from the CSA mine commonly contain "chalcopyrite-diseased" sphalerite, and such samples have been avoided in applying the geobarometer. Scott & Barnes (1971) pointed out that impurities in the solids may affect the geobarometer. However, only abnormally high concentrations of Co and Ni in the iron sulfides and up to several wt. % Cd and Mn in sphalerite would have a measurable effect (Scott & Barnes 1971). Neither the iron sulfides nor sphalerite from the CSA mine show such abnormal values. For successful application of the geobarometer, the assumption was initially made that sphalerite formed in equilibrium with pyrite and hexagonal pyrrhotite. The analyzed sphalerite grains coexist with pyrite or pyrrhotite (or both), pyrrhotite and galena, and with chalcopyrite. Pyrrhotite is mainly present as the hexagonal polymorph; however, grains that have undergone low-temperature conversion to monoclinic pyrrhotite can be observed along many fractures and grain boundaries. Regardless of the mineral association, the FeS contents of sphalerite were found to be moderately uniform, and to range from 14.7 to 11.8 mole % FeS (40 analyses), corresponding to pressures of 4.8 to 7.9 kbars ($\pm$ 0.3 kbar), using the data of Hutchison & Scott (1981).

These pressures are not in agreement with the silicate mineralogy and the pressure of 2.5 to 3 kbars that was indicated in a study of Si contents of white micas from regional metamorphic rocks of the Cobar area (Brill 1988). The reason for this disagreement is that sphalerite most likely re-equilibrated with monoclinic pyrrhotite at low temperatures late in the metamorphism. A postdepositional, low-temperature overprint of sphalerite has also been indicated by the trace element partitioning between sphalerite and galena and partitioning of Fe and Sn between stannite and sphalerite (see above). Similar conclusions were reached by Sangameshwar & Marshall (1980), who calculated a pressure range of 7.7 to 9 kbars in their study of sphalerite from the CSA mine.

CONCLUSIONS

The major ore minerals at the CSA mine show a strong variation in Se, Cd, Mn, Sn, Ag, Co and Ni concentrations. Se contents are unusually high in all ore minerals. The high Se contents from the CSA mine are possibly due to the leaching from marine sediments by a metamorphic fluid. An alternative explanation of a localized Se-enriched source seems unlikely, in the light of geochemical and geophysical studies. Ag has been preferentially taken up by galena. Co and Ni are enriched preferentially in pyrite with respect to pyrrhotite and chalcopyrite. Co/Ni values in pyrite average 2.4 and are typical of "hydrothermal pyrite", as defined by Price (1972). The Co and Ni data are consistent with evidence from other studies (tectonic: Glen 1985, 1987; isotope and fluid inclusions: Brill, in prep.) that the CSA orebody is of metamorphic origin. Partitioning of Se, Cd and Mn between sphalerite and galena indicate temperatures that are too high for conditions at the CSA mine. The geothermometer proposed by Bethke & Barton (1971) is, therefore, not applicable to the study area because sphalerite and galena did not attain trace-element equilibrium even though textural equilibrium appears to exist.

Postdepositional, low-temperature changes, seem to have influenced partitioning of Fe and Zn in coexisting sphalerite and stannite. Calculated temperatures of 236–306°C obtained from this geothermometer are likely to represent a late metamorphic signature. FeS contents in sphalerite also have been affected by late metamorphic re-equilibration; the sphalerite geobarometer thus yields unreliable results.

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