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# PARTIAL MELTING OF SULFIDE ORE DEPOSITS DURING MEDIUM- AND HIGH-GRADE METAMORPHISM

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## Abstract

Minor elements, such as Ag, As, Au and Sb, have commonly been remobilized and concentrated into discrete pockets in massive sulfide deposits that have undergone metamorphism at or above the middle amphibolite facies. On the basis of our observations at the Broken Hill orebody in Australia and experimental results in the literature, we contend that some remobilization could be the result of partial melting. Theoretically, a polymetallic melt may form at temperatures as low as 300°C, where orpiment and realgar melt. However, for many ore deposits, the first melting reaction would be at 500°C, where arsenopyrite and pyrite react to form pyrrhotite and an As-S melt. The melt forming between 500° and 600°C, depending on pressure, will be enriched in Ag, As, Au, Bi, Hg, Sb, Se, Sn, Tl, and Te, which we term low-melting point chalcophile metals. Progressive melting to higher T (ca. 600°-700°C) will enrich the polymetallic melt progressively in Cu and Pb. The highest-T melt (in the upper amphibolite and granulite facies) may also contain substantial Fe, Mn, Zn, as well as Si, H<sub>2</sub>O, and F. In our model, we suggest that the presence of polymetallic melts in a metamorphosed massive sulfide orebody is recorded by: (1) localized concentrations of Au and Ag, particularly in the presence of low-melting-point metals, (2) multiphase sulfide inclusions in high-T gangue minerals, (3) low interfacial angles between sulfides or sulfosalts suspected of crystallizing from the melt and those that are likely to have been restitic, (4) sulfide and sulfosalt fillings of fractures, and (5) Ca- and Mn-rich selvages around massive sulfide deposits. Using these criteria, we identify 26 ore deposits worldwide that may have melted. We categorize them into three chemical types: Pb- and Zn-rich deposits, either of SEDEX or MVT origin, Pb-poor Cu-Fe-Zn deposits, and disseminated Au deposits in highgrade terranes.

Keywords: ore deposits, low-melting-point chalcophile elements, sulfide melts, polymetallic melts, remobilization, metamorphism of sulfides.

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#### THE CANADIAN MINERALOGIST

#### SOMMAIRE

Dans plusieurs cas, les éléments mineurs, par exemple Ag, As, Au et Sb, ont été remobilisés et concentrés dans des zones distinctes de gisements de sulfures massifs qui ont subi un épisode de métamorphisme jusqu'au faciès amphibolite supérieur, ou au delà. Nos observations au gisement de Broken Hill, en Australie, et les résultats d'études expérimentales prélevées de la littérature, nous font penser que cette remobilisation pourrait bien avoir impliqué une fusion du gisement. En théorie, un bain fondu polymétallique pourrait se former à une température aussi faible que 300°C, domaine de fusion de l'orpiment et du réalgar. Toutefois, pour plusieurs gisements, la première réaction entraînant la fusion serait à 500°C, où arsénopyrite + pyrite réagissent pour former pyrrhotite et un liquide As-S. Entre 500° et 600°C, dépendant de la pression, le liquide sera enrichi en Ag, As, Au, Bi, Hg, Sb, Se, Sn, Tl, et Te, tous des métaux chalcophiles à faible point de fusion. Une progression vers une température plus élevée (entre 600° et 700°C) enrichira progressivement le bain fondu polymétallique en Cu et Pb. Le liquide caractéristique des températures les plus élevées (au faciès amphibolite supérieur et granulite) pourrait bien aussi contenir des quantités substantielles de Fe, Mn, Zn, ainsi que de Si, H<sub>2</sub>O, et F. Dans notre modèle, nous préconisons les caractéristiques suivantes pour signaler la présence d'un bain fondu polymétallique dans un gisement de sulfures massifs métamorphisé: (1) concentrations locales d'or et d'argent, en particulier en présence de métaux à faible point de fusion, (2) inclusions de sulfures multiphasées dans un hôte faisant partie de la gangue, (3) faible angle interfacial entre sulfures et sulfosels soupconnés d'avoir cristallisé à partir du bain fondu et ceux faisant partie de l'assemblage résiduel, (4) remplissage de fractures par des venues de sulfures et de sulfosels, et (5) enveloppe enrichie en Ca et Mn autour des gisements de sulfures massifs. En utilisant ces critères, nous identifions 26 gîtes minéraux à l'échelle mondiale qui auraient pu avoir fondu. Nous les regroupons en trois catégories: gisements de Pb et de Zn, soit d'origine SEDEX ou MVT, gisements Cu-Fe-Zn à faible teneur en Pb, et gisements d'or disséminé dans des socles à degré de métamorphisme élevé.

(Traduit par la Rédaction)

*Mots-clés*: gîtes minéraux, éléments chalcophiles à faible point de fusion, bain fondu sulfuré, bain fondu polymétallique, remobilisation, métamorphisme de sulfures.

#### INTRODUCTION

The concept that sulfide orebodies may crystallize from sulfide melts is not new. It is well known that orthomagmatic ore deposits crystallize from Fe-(Ni)-(Cu)-S melts, but these melts are associated with mafic intrusions and form at temperatures above 1100°C (Naldrett 1997). Some ore petrologists have also contended that volcanogenic massive sulfide (VMS) deposits may have formed from sulfide melts (Spurr 1923, Hutchinson 1965). This theory died away in the 1980s with the discovery of black smokers, which clearly demonstrated the hydrothermal origin of VMS deposits (Francheteau et al. 1979). But it is also possible that sulfide ore deposits are modified by partial melting during high-grade metamorphism. This possibility was raised on the basis of experiments (Brett & Kullerud 1967, Craig & Kullerud 1967, 1968a) and has been used to explain mineralogical relations observed at Broken Hill, Australia (Lawrence 1967) and Bleikvassli, Norway (Vokes 1971). In addition, S-poor polymetallic melts have also been postulated as the cause for inclusions of native Sb in rhodonite from Broken Hill, Australia (Ramdohr 1950) and for the Au-Te-Bi accumulations in the Lucky Draw deposit in Australia (Sheppard et al. 1995).

Despite these early papers, melting has not been considered an important process in the metamorphism of ore deposits (Skinner & Johnson 1987, Marshall *et al.* 2000). It is not surprising that the role of melting in metamorphosed sulfide ore deposits has been considered unimportant. First, unlike silicate melts, polymetallic sulfide melts never quench to a glass. Instead, they quench to a complex intergrowth of minerals that tend to re-equilibrate to very low temperatures. As a result of this fact, the textural evidence for the existence of a polymetallic melt is generally absent; if present, it is usually extremely subtle. Second, the requisite experimental work is available only for ternary and a few quaternary systems, such that it is impossible to tell at what temperature an assemblage involving elements such as Ag-Cu-Pb-Sb-As-S would melt. Finally, because it has naturally been assumed that massive sulfides do not melt at temperatures consistent with most metamorphic environments, few investigators in the field of metamorphosed ore deposits have been looking for features that might indicate the presence of a polymetallic melt.

During our recent examination of the Broken Hill orebody, New South Wales, Australia, we found many features that are consistent with melting (Mavrogenes *et al.* 2001). These features have led us to investigate the possibility that partial melting may also have affected other metamorphosed ore deposits. In this paper, we review the melt-induced features at Broken Hill, and show how they are similar to remobilization features observed in metamorphosed ore deposits. We then discuss the available experimental data for relevant sulfide systems to establish reasonable criteria to distinguish orebodies that have melted from those that have not. Finally, we will use these criteria to discuss a large number of ore deposits that may have melted. Because some melts in many sulfide systems may not be particularly



FIG. 1. Schematic diagram showing relations between ore at Broken Hill and the surrounding rocks. Width of the sketch is on the order of one to ten meters. Key relations are: 1. Contact between the country-rock gneiss and garnet quartzite is commonly gradational. Garnet quartzite may also occur as horizons within the gneiss, commonly cross-cutting the fabric of the gneisses. 2. In many places the garnet quartzite has a faint compositional banding that seems to parallel the layering in the gneiss. 3. The pyroxenoid horizon may be in contact with either the garnet quartzite or the garnetite. The contacts are commonly sharp. 4. Garnetite may occur as bands in the garnet quartzite that generally cut the fabric of the rock. 5. Garnetite may occur as islands within the pyroxenoid rock, commonly with irregular boundaries. 6. Massive ore is most abundantly found associated with the pyroxenoid or garnetite horizons, but stringers may also be found in the garnetite (7) and garnet quartzite (8). They are never found in the main gneiss. 9. The quartz-gahnite rock may cut the garnetite and garnet quartzite.

rich in sulfur, we will refer to them as *polymetallic* melts, rather than sulfide melts.

Melt-Induced Features at Broken Hill

The Broken Hill group of deposits consist of Agbearing galena-sphalerite orebodies that also contain minor amounts of pyrrhotite and chalcopyrite. The orebodies, hosted in granulite-grade metapelitic and metapsammitic gneisses, is surrounded by a halo of unusual rock-types (Fig. 1). In the Western A-lode, which we have studied in detail (Sloan 2000), the rock closest to the ore is a pyroxenoid-rich rock that, depending on the location in the orebody, may consist of wollastonite, bustamite, rhodonite, or hedenbergite. In places, the rock adjacent to the ore consists entirely of garnet. This garnetite may also occur adjacent to the pyroxenoids. Between the garnetite and the host gneisses lies a zone of garnet quartzite, a rock consisting almost entirely of quartz and garnet. We call these rocks associated with the orebody the ore package. Many investigators consider the silicate rocks in the ore package to be metamorphosed exhalative horizons and

to have formed at the same time as the deposition of the original orebody (Spry *et al.* 2000).

Recent experimental work (Mavrogenes et al. 2001) has shown that the quaternary eutectic temperature in the system PbS-Fe<sub>0.96</sub>S-ZnS-(1% Ag<sub>2</sub>S) at 5 kbar is 795°C, which is below the peak temperature of metamorphism at Broken Hill. Thus, the Broken Hill ores at least partially melted during peak metamorphism. As documented by Sloan (2000), garnet crystals surrounding the ore package contain multiphase sulfide inclusions, which we interpret as having been melt inclusions (Fig. 2A). In addition to Pb, Zn, Fe, and Cu, which are abundant in the main orebody, these inclusions also contain significant amounts of Ag and As. Some of these multiphase sulfide inclusions also contain needles of rhodonite, which raises the possibility that the pyroxenoid horizon, and perhaps the whole silicate envelope around the orebody, formed by reaction between the polymetallic melt and the surrounding pelitic gneisses.

A distinctive feature of the ores from the Broken Hill deposit, particularly those rich in sphalerite, is the development of low interfacial angles of galena, chalcopyrite, and pyrrhotite against sphalerite. Galena forms cuspate, low-angle interfaces against sphalerite-sphalerite boundaries (Fig. 2B), and locally occurs as isolated lozenges spread along sphalerite-sphalerite grain boundaries. The average interfacial angle between galena and sphalerite-sphalerite boundaries for rocks that have equilibrated in the solid state is 102° (Stanton 1965). Because in reflected light one cannot know if any particular measurement is normal to the interface, a population of measurements will occupy a wide distribution around the average value (Smith 1948). As a result, the interfacial angles between galena and sphalerite-sphalerite boundaries reported by Stanton (1965) range from 50° to 150°. Despite this huge range of uncertainty, we conclude that the population of interfacial angles from Broken Hill clearly indicates that the galena and sphalerite did not equilibrate in the solid



B Cp Ga Sph <u>100 µ</u>, state. Of the 60 grain boundaries measured, 96% are lower than the average value for boundaries where the surface energy has equilibrated in the solid state, and 43% lie below the lowest angles reported by Stanton (1965) (Fig. 3). Furthermore, 48% of the measured angles from Broken Hill lie below 60°, an angle below which galena would have crystallized out of a phase that wets the sphalerite–sphalerite grain edges, whereas only 2% of the samples measured by Stanton (1965) have an angle that low. We interpret the wide range of low interfacial angles displayed in Figure 3 to reflect that galena in this rock crystallized from a melt–crystal mixture, the surface energy of which increased during crystallization.

# Remobilization of Sulfide Minerals During Metamorphism

The recognition that the Broken Hill orebody may have melted during metamorphism has led us to assess whether melting may have occurred in other orebodies. It has long been recognized that metamorphism and deformation result in mobilization or remobilization of sulfide orebodies (Ramdohr 1953, Vokes 1969, Plimer 1987, Marshall et al. 2000). However, the question of just what the terms "mobilization" and "remobilization" mean is a matter of considerable debate (Mookherjee 1976, Marshall & Gilligan 1987). Marshall et al. (2000) noted that the term "remobilization" describes a spectrum of processes ranging from solid-state movement of sulfides due to deformation, through H2O-enhanced diffusion during deformation, to a chemical transfer in a liquid state. Marshall et al. (2000) also distinguished between internal remobilization, wherein material is remobilized within a deposit, and external remobiliza-



FIG. 2. Photomicrographs of textures from the ore package at the Western A lode, Broken Hill. A. Multiphase sulfide inclusion in garnet. B. Low interfacial angles between galena and sphalerite. Arg: argentite, Ch: chlorite, Cp: chalcopyrite, Ga: galena, Gar: garnet, Po: pyrrhotite, Sph: sphalerite.



tion, in which material is moved into country rock surrounding the deposit.

The behavior of various sulfide minerals during deformation, and the textures formed by these processes, are well described (*e.g.*, Cox 1987, Craig & Vokes 1993). However, the process by which remobilization changes the relative abundances of minor metals is still not well characterized. In the amphibolite facies, elements such as Ag, As, Au and Sb, which are dissolved in the major sulfides at low grades, become concentrated in pockets to produce a wide variety of rare sulfides, sulfosalts, and alloys (Cook 1996). The process by which this remobilization, which is mostly internal, occurs is rarely specified, but both hydrothermal and melting processes have been suggested (Lawrence 1967, Vokes 1971, Cook 1992, Marshall *et al.* 2000).

### LOW-MELTING-POINT CHALCOPHILE ELEMENTS

A distinctive feature of the remobilized portions of sulfide orebodies is that they may contain high abundances of Ag, As, Bi, Hg, Se, Sb, Sn, Tl or Te (Basu et al. 1981, 1983, Hofmann 1994, Cook 1996). These elements all have melting points below 1000°C, and most are chalcophile. Although Sn is often classified as siderophile, it may occur in remobilized ore deposits as stannite (Cu<sub>2</sub>FeSnS<sub>4</sub>), clearly a sign of chalcophile behavior. These elements all cluster in the same area of the periodic table (Fig. 4); we will refer to them collectively as Low-Melting-Point Chalcophile Elements (LMCE). Although Au melts at high T, it is typically associated with the LMCE in polymetallic melts (Tomkins 2002). A number of other metals have low melting points, but most of those are lithophile and are invariably found in nature bound with oxygen. As a result, their low melting point has no geological signifi-

actinides

Th Pa

cance. In contrast, many of the LMCE are found in their native state, and as a result their occurrence is important to evaluating the presence of low-temperature metal-rich melts in nature.

# THE STABILITY OF MELTS IN EXPERIMENTAL SYSTEMS

Experimental sulfide petrology was a particularly active field of research from the mid-1960s into the 1980s. During this time, both the solidus and subsolidus relations in the most common ternary systems were determined. Experimental data on more complex systems, however, are sparse. Most of these experiments were run at 1 atmosphere; except where noted otherwise, therefore, the temperatures given below are for one-bar conditions.

#### The system Cu-Fe-Pb-Zn-(Ag)-S

The most common sulfides in nature occur in the system Cu–Fe–Pb–Zn–S. In the system Cu–Pb–S, the lowest-temperature melt forms at 510°C in the assemblage chalcocite–galena (Craig & Kullerud 1968a). Addition of small amounts of Zn and Fe to the system does not suppress melting temperature, meaning that this is the minimum melting temperature for the system Cu–Fe–Pb–Zn–S (Craig & Kullerud 1968a). Addition of Fe raises the melting temperature; bornite + galena melts at 609°C, and the assemblage chalcopyrite + galena melts at 630°C (Craig & Kullerud 1967). The quaternary cotectic is terminated at 716°C, the minimum melting temperature for pyrite + galena in the system Fe–Pb–S (Brett & Kullerud 1967).

In the system Cu–Fe–S, the first melt forms on the join Cu–S at 813°C (Kullerud 1968). It propagates into

Η		lithophile element													He		
Li	Be		siderophile element							В	C	N	0	F	Ne		
Na	Mg		chalcophile element							Al	Si	Р	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Ι	Xe
Cs	Ba	La	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	T1	Pb	Bi	Ро	At	Rn
Fr	Ra	Ac															
lantha	nides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dv	Ho	Er	Tm	Yh	I u		

FIG. 4. Periodic table showing the low-melting elements. Dark shading shows the lowmelting-point chalcophile elements. Although usually considered siderophile, Sn is commonly found as a sulfide in metamorphosed ore deposits.

U Np Pu AmCm Bk Cf Es Fm Md No Lr

the ternary system with increasing T. The bulk composition of chalcopyrite (intermediate solid-solution, *iss*, at that temperature) melts incongruently at 880°C (Dutrizac 1976).

First melting in the assemblage pyrrhotite (FeS) – galena – sphalerite occurs at 800°C at 1 bar and at 830°C at 5 kilobars. The melt produced is Pb- and Fe-rich, with a composition  $PbS_{62.5}FeS_{30.5}ZnS_7$ . The temperature of initial melting is lowered to 795°C at 5 kilobars where the starting pyrrhotite composition is  $FeS_{0.96}$ , close to the pyrrhotite composition found at Broken Hill. The addition of only 1 wt.% Ag<sub>2</sub>S lowers the melting point by another 28°C (Mavrogenes *et al.* 2001).

First melting in the system Ag–Pb–S occurs on the Ag–Pb join at 304°C (Craig 1967). The most important melting reaction in the natural system involves the assemblage Ag<sub>2</sub>S–PbS, which occurs at 605°C. The melt produced by this reaction has the composition  $Ag_{21}Pb_{34}$  S<sub>45</sub> (Van Hook 1960).

## The system Cu-(Fe)-Ni-S

At low temperatures, the system Cu–Ni–S has two fields occupied by ternary melts. One is a sulfur-poor melt that appears at 572°C, and another is a sulfur-rich melt that appears at 780°C (Kullerud & Moh 1968). The low-T melt forms in the presence of the assemblage chalcocite, Ni<sub>3+4</sub>S<sub>2</sub> (a high-T, nonstoichiometric form of heazlewoodite) and a Fe–Ni alloy, an uncommon natural assemblage. The most common, Ni–Cu-bearing high-T assemblage in nature is chalcopyrite solid-solution and monosulfide solid-solution (a solid solution between NiS and FeS). This assemblage does not melt until 850°C (Craig & Kullerud 1968b).

## Melting relations in S-bearing systems with low melting-point chalcophile elements

*The system* As–Sb–S: Apart from the melting of pure S (which occurs at 113°C), the first melt in the system Fe–As–S appears at 281°C. It forms at a eutectic between realgar (AsS) and orpiment (As<sub>2</sub>S<sub>3</sub>). The melt field expands rapidly with increasing T; by 321°C, the whole join from realgar to sulfur has melted (Hall & Yund 1964). By 500°C, most of the area bounded by stibnite (Sb<sub>2</sub>S<sub>3</sub>), realgar, and sulfur has melted (Fig. 5).

The systems Fe–As–S and Fe–Sb–S: With respect to melting of massive sulfide deposits, the most important reactions in this system are those that involve arsenopyrite. At 491°C, arsenopyrite + pyrite react to form melt + pyrrhotite. The melt produced by this reaction lies on the As–S join and has the composition  $As_{29}S_{71}$  (Clark 1960) (Fig. 6). Arsenopyrite melts incongruently at 702°C to pyrrhotite + löllingite (FeAs) + a binary As–S melt (As<sub>48</sub>S<sub>52</sub>) (Clark 1960).

In the system Fe–Sb–S, the first melting reaction involving a commonly found assemblage is: pyrite + stibnite = pyrrhotite + melt, which occurs at 545°C. The melt produced by this reaction contains only 1 wt.% Fe and, hence lies near the Sb–S plane (Barton 1971). Thus, melts formed initially within the system Fe–As–Sb–S, be it by reaction between pyrite + arsenopyrite or between pyrite + stibnite, could have a wide range in As:Sb ratio but will contain very limited amounts of Fe.

The systems Cu–As–S and Cu–Sb–S: As with the system Fe–As–S, the first melt in the system Cu–As–S appears on the join As–S at 281°C. This melt remains Cu-poor until around 500°C; above this temperature, increasing T causes the field of liquid to expand to more Cu-rich compositions (Fig. 7A). Tennantite (Cu<sub>12.31</sub> As<sub>4</sub>S<sub>13</sub>) and enargite (Cu<sub>3</sub>AsS<sub>4</sub>), the major ternary minerals in this system, melt at around 665°C (Maske & Skinner 1971).

In the system Cu–Sb–S, the first melts form on the join Sb–S. One melt, which is slightly more S-rich than stibnite, forms at 496°C, whereas another, slightly more Sb-rich than stibnite, develops at 518°C (Skinner *et al.* 1972). As with the system Cu–As–S, melt in the system Cu–Sb–S becomes progressively more Cu-rich with increasing T (Fig. 7B). The important ternary phase in this system is tetrahedrite, the composition of which is approximated by the formula Cu<sub>12+x</sub>Sb<sub>4+y</sub>S<sub>13</sub>, (where 0 < x < 1.92 and -0.02 < y < 0.27: Skinner *et al.* 1972). Tetrahedrite breaks down at 543°C to digenite (Cu<sub>3</sub>SbS<sub>3</sub>). Skinnerite, which has a composition close to that of tetrahedrite, melts at 608°C (Skinner *et al.* 1972).

*The systems Pb–As–S and Pb–Sb–S*: Unlike the other ternary systems described here, ternary liquidus diagrams are not available for the system Pb–As–S. However, a pseudobinary diagram along the join PbS–As<sub>2</sub>S<sub>3</sub>



FIG. 5. Phase relations in the system As–Shb–S at 500°C and one bar, after Luce *et al.* (1977). X: a synthetic phase (approx. AsSb<sub>2</sub>S<sub>2</sub>).

join (Chang & Bever 1973) provides all the information needed for this discussion (Fig. 8A). The first melt in the system Pb–As–S forms at 305°C and has only a small amount of Pb. The melt becomes progressively more Pb-rich with increasing T. By 600°C, all of the Pb–As sulfosalts have melted, and a ternary Pb–As–S melt coexists with galena. The first melt in the system Pb–Sb–S forms in the metal-rich portion of the system at 240°C and has the approximate composition  $Pb_{72}Sb_{16}S_{12}$  (Craig *et al.* 1973). The geologically more reasonable melts form on the join Sb–S. As with the system Cu–Sb–S, the first melts form on either side of stibnite, at 496° and 518°C. These melts propagate into the ternary system along



FIG. 6. Chemographic diagrams showing the melting reaction pyrite + arsenopyrite = melt + pyrrhotite. A. Phase relations below 490°C and one bar. B. Phase relations above 490°C and one bar (after Clark 1960). Asp: arsenopyrite, Löl: löllingite, Po: pyrrhotite, Py: pyrite.



FIG. 7. Phase relations in the systems Cu–As–S (A) and Cu–Sb–S (B) at 600°C and one bar. Ruled fields show the size of the melt fields in these systems at 500°C and one bar. Data from Skinner *et al.* (1972) and Maske & Skinner (1971).

cotectics that lie on either side of the  $PbS-Sb_2S_3$  binary (Fig. 8B). The mineral boulangerite ( $Pb_5Sb_4S_{11}$ ), the most common Pb sulfosalt, is consumed by melt at 638°C (Craig *et al.* 1973). Above this temperature, galena coexists with a ternary Pb–Sb–S melt.

*The systems* Ag–As–S and Ag–Sb–S: The first melt in the system Ag–As–S appears at 280°C. It lies nearly on the As–S join with the composition (Ag<sub>1.6</sub>As<sub>39</sub>S<sub>59.4</sub>). By 495°C, the melt has propagated from the As–S join to consume the four ternary minerals in this system: proustite or xanthoconite (Ag<sub>3</sub>AsS<sub>3</sub>) and smithite or trechmannite (AgAsS<sub>2</sub>) (Roland 1970) (Fig. 9A).

The first melt in the system Ag–Sb–S forms at 450°C. The first melt is ternary and Sb-rich, but con-



FIG. 8. A. Phase relations at one bar in the system As<sub>2</sub>S<sub>3</sub>–PbS. Data from Chang & Bever (1973). B. Phase relations in the system Pb–Sb–S at 635°C. Ruled fields show the composition of the melt at 500°C. Data from Craig *et al.* (1973).



FIG. 9. Phase relations in the system Ag–As–S (A) and Ag–Sb–S (B) at 500°C. Data from Keighin & Honea (1969) and Roland (1970).

tains a significant amount of Ag (Keighin & Honea 1969). By 510°C, all the ternary phases in the system have melted, and there is a large field for melt within the ternary system (Fig. 9B).

The system  $Cu_2S$ -PbS-Sb<sub>2</sub>S<sub>3</sub>: The system  $Cu_2S$ -PbS-Sb<sub>2</sub>S<sub>3</sub> is one of the few quaternary systems that has been studied experimentally (Hoda & Chang 1975, Pruseth *et al.* 1995). At 500°C, the system has a thermal divide between galena and chalcostibite, and two fields for melt (Fig. 10). The Cu-rich eutectic lies at 477°C, whereas the Sb-rich eutectic lies at 461°C.

Other systems with LCMEs: Polymetallic melts may survive down to very low temperatures in systems involving Te, Bi, and Tl. For example, melts are present in the Au–Ag–Te system down to  $T < 335^{\circ}$ C (Cabri 1965). Similarly, a melt is present down to approximately 400°C in the Te-rich portion of the system Au– Bi–Te, and down to below 300°C on the Bi-rich portion of the system (Gather & Blachnik 1974). The first melt appears in the Au–Tl system at 131°C, and melts are present down to temperatures below 300°C in many other Tl-bearing systems (Moh 1991).

### The effect of pressure

Changes in pressure will have two possible effects on the 1-bar phase equilibria discussed above. First, increasing pressure may change the stable assemblages found in subsolidus conditions, and second, for most systems, it will increase the temperature of melting.

Sulfosalts have notoriously complex phase-relations, which is a reflection of the very low differences in free energy between the various sulfosalt minerals (Barton 1970). Thus it is possible that high-pressure phase relations are different from phase relations depicted in 1 bar experiments. Unfortunately, thermodynamic data are lacking for most of the sulfosalts, so it is impossible to



FIG. 10. Phase relations in the system Cu<sub>2</sub>S–PbS–Sb<sub>2</sub>S<sub>3</sub> at 500°C and one bar. Data from Pruseth *et al.* (1995).

calculate the high-pressure phase relations. Thus we may not be able to use relations depicted in the 1-bar experiments to predict the exact melting reactions that occur in nature. For this reason, we cannot determine the significance of many distinctive textures among sulfosalts that are described in the literature.

Because melting usually involves an increase in volume, it is reasonable to assume that the melting temperatures will increase with increasing pressure. This appears true for S-bearing systems. For example, the temperature of the eutectic for the assemblages FeS–PbS–ZnS increases by 6°C/kbar (Mavrogenes *et al.* 2001), and the peritectic reaction arsenopyrite + pyrrhotite = löllingite + melt increases by 10°C/kbar (Clark 1960). The reaction arsenopyrite + pyrite = melt + pyrrhotite, which may be an important melting reaction in nature, increases by 17°C/kbar. This means that it will occur at conditions of the lower amphibolite facies (*i.e.*, 500° < T < 600°C) at pressures below 7 kilobars and in the upper amphibolite facies (*i.e.*, above 600°C) at higher P (Fig. 11).

The melting temperature of the LCMEs show a variable dependence on pressure. The melting temperature of Te, Se, and As increases with increasing pressure, with the pressure dependence ranging from  $1.5^{\circ}$ C/kbar for Te to  $18^{\circ}$ C/kbar for Se (Liu & Bassett 1986). In contrast, the melting temperature of Sb and Bi decreases with increasing pressure, with pressure dependencies of  $-0.2^{\circ}$ C/kbar for Sb and  $-4.5^{\circ}$ C/kbar for Bi (Liu & Bassett 1986). Thus for Sb- and Bi-bearing systems, increasing P may actually decrease melting temperature.



FIG. 11. P–T diagram showing the relative positions of the reaction arsenopyrite + pyrite = pyrrhotite + melt, the boundary between greenschist and the amphibolite facies, and the solidus for  $H_2O$ -saturated granite. Abbreviations as in Figure 6. Data from Clark (1960), Spear (1993) and Clarke (1992).

## The effect of minor components

Many natural occurrences of sulfosalts contain many more components than the experimental systems described above. This situation makes it difficult to estimate the melting temperature of most natural assemblages, even if experimental information is available for one or more phases in them. In most chemical systems, the addition of a new component will decrease the minimum temperature of melting. For example, the addition of 1% Ag decreases the minimum melting of the system FeS-PbS-ZnS by 28°C (Mavrogenes et al. 2001). Similarly, the addition of small amounts of Pb will decrease the melting temperature of the assemblage skinnerite + chalcocite from 608°C (Skinner et al. 1972) to 477°C (Hoda & Chang 1975). We have no constraints on the effect that small amounts of Bi, Te, Tl, elements that remain molten to very low T, might have on the melting temperatures of sulfides or sulfosalts. We also do not know whether volatile components (H<sub>2</sub>O, F, Cl) will dissolve into polymetallic melts and hence decrease the melting temperature further. Experimental work has shown that addition of H2O to sulfide systems does not affect melting temperature, indicating that H<sub>2</sub>O is not compatible with low-T sulfide melts (Craig & Kullerud 1968a, Naldrett & Richardson 1968). There is, however, no experimental evidence on the effect of H2O on melting temperature in As- and Sb-rich systems. We consider it likely that the freezing-point depression caused by minor components will overwhelm the pressure effect, and that the temperatures we quote from 1-bar experiments are conservative.

# A MODEL FOR THE FORMATION OF POLYMETALLIC MELTS

It is obvious from the phase diagrams discussed above that many minerals containing LCMEs will melt at conditions attained in the amphibolite facies, and some may melt at conditions of the greenschist facies or lower. This means that the presence of a polymetallic melt must be considered a possible cause for remobilization in a massive sulfide body that has been metamorphosed at temperatures of the amphibolite facies or higher. This statement is particularly true if the remobilized portion of the orebody lacks any sign of deformation or of low-temperature hydrothermal alteration.

Clearly the temperature at which a sulfide orebody begins to melt is dependent on the mineral assemblage in the protolith. An orebody containing abundant minerals with Te, Bi, or Tl, such as some epithermal gold deposits, may begin to melt at temperatures of the greenschist facies. If the LMCE in a deposit are dissolved as trace components in the main sulfides, the deposit may not melt even at temperatures of the upper amphibolite facies. In those deposits that contain the assemblage pyrite–arsenopyrite, melting will likely begin at temperatures between 500° and 600°C, depending on the pressure (Fig. 11).

If the melt generated by this reaction wets the edges of sulfide grains, as suggested by the low interfacial angles of galena against sphalerite-sphalerite pairs from Broken Hill (Fig. 2B), then the LMCE that are present in trace amounts in the host sulfides may diffuse into the melt. Sulfides have notoriously high diffusion-coefficients, so that reaction between the melt and residual sulfides is likely to be very efficient. For example, Clark (1960) noted that at 600°C. Au readily diffuses out of arsenopyrite and into the melt. The early-formed polymetallic melts will be very poor in Fe, but they may contain significant amounts of Sb and Ag (Figs. 5, 9). The Sb may have originally been dissolved in arsenopyrite, pyrite, or sphalerite (Ramdohr 1980, Ashley et al. 2000). The Ag may have been dissolved initially in galena, pyrite, arsenopyrite, or chalcopyrite (Amcoff 1984, Dalstra et al. 1997, Ashley et al. 2000). The initial melt may also contain significant amounts of Tl, as indicated by the fact that at temperatures of 200°C, many Tl-bearing systems contain polymetallic melt (Moh 1991). The Tl may have originally been in pyrite (Murao & Itoh 1992), but it has also been reported as a minor element in sphalerite (Ramdohr 1980). Other elements that may dissolve into these low-T polymetallic melts include Au, Bi, Hg, Se, Sn, and Te. The Au may have originally been dissolved as a trace element in pyrite, chalcopyrite, or arsenopyrite (Cook & Chryssoulis 1990, Dalstra et al. 1997, Ashley et al. 2000). A good example of these lowest-T melts are the multiphase inclusions in quartz from Lengenbach, Switzerland, which are enriched in As, Pb, and Tl (Hofmann 1994).

Progressive melting with increasing T, perhaps in the range of  $600^{\circ}$ – $700^{\circ}$ C, will enrich the polymetallic melts in Cu and Pb (Figs. 7, 8). Further increase in T (to  $700^{\circ}$ – $800^{\circ}$ C) will enrich the melt in Fe, Zn, Mn, and Si, as indicated by the presence of rhodonite, pyrrhotite, and sphalerite in the polymetallic melts from Broken Hill. The presence of Si in these high-temperature melts may also allow these melts to accommodate H<sub>2</sub>O and F.

Ore deposits that do not contain arsenopyrite may not melt until the upper limits of metamorphism. We have already noted that deposits containing galena + sphalerite (such as those at Broken Hill) are likely to have melted in the granulite facies (Mavrogenes *et al.* 2001), and that the assemblage chalcopyrite + galena will melt at upper-amphibolite-facies conditions (Craig & Kullerud 1967). The occurrence of polymetallic melts with the assemblage pyrrhotite – chalcopyrite – sphalerite at the margin of dikes in the Geco mine (Mookherjee & Dutta 1970) suggests that there are other minimummelt compositions possible among major-element sulfides. Such melts may not necessarily be enriched in LMCE.

Regardless of its original composition and temperature at which it formed, any polymetallic melt may undergo extensive differentiation during cooling. This may allow it to persist down to very low temperatures. At present, we cannot determine the liquid line of descent for a complex polymetallic melt. In part, experimental work in the complex multicomponent system is lacking. However, even with adequate experimental work, the liquid line of descent of polymetallic melts will be difficult to determine. The complex systems, like the simple ternary systems, probably contain thermal divides that cause melts to evolve to very different compositions depending on minor changes in bulk composition (cf. Roland 1970). As melt pockets become isolated during cooling, each pocket of melt may thus follow a distinct line of descent, depending on the phases that surround it. This possibility may explain the huge range of mineral assemblages with LMCE found in metamorphosed ore deposits (Cook 1996, Basu et al. 1981, 1983).

### CHARACTERISTIC FEATURES OF MELTED SULFIDE BODIES

From the discussion above, we contend that many massive sulfide bodies may undergo partial melting during metamorphism at conditions of the amphibolite facies. We recognize five features that may indicate that melting has occurred: 1) irregularly distributed areas with abundant LMCEs, 2) multiphase sulfide inclusions in gangue, 3) low grain-boundary angles, 4) sulfide minerals filling fractures, 5) the presence of a Mn- or Ca-rich selvage around the orebody.

# Irregularly distributed areas with abundant LMCEs

Because the low melting-point elements will tend to be concentrated during differentiation of a polymetallic melt, the strongest evidence for the presence of a melt during peak metamorphism would be the presence of isolated concentrations of sulfosalts and other LMCEbearing minerals in orebodies metamorphosed to the middle or upper amphibolite facies. This is particularly true if one finds a mineral or assemblage that would have been molten at temperatures of peak metamorphism and if there is no obvious low-temperature process by which these minerals could have formed.

Perhaps the best example of LMCE-enriched melt comes from Lengenbach, Switzerland. Hofmann (1994) and Hofmann & Knill (1996) interpreted the spectacular As, Pb, and Tl sulfosalts in this deposit as having crystallized from a melt that was present at peak conditions of metamorphism (3 kilobars, 500–520°C). Lowmelting Ag-dominant sulfosalts are described from the Pinnacles mine at Broken Hill, Australia (McQueen 1984), which is hosted in granulite-grade gneisses. Realgar and native Bi are reported from Sulitjelma, Norway (Cook 1996). Both of these phases would have been molten at 350°C (Hansen & Anderko 1958). Powell & Pattison (1997) described the assemblage stibnite – native antimony at Hemlo, Ontario. This assemblage would melt at 530°C (Hansen & Anderko 1958). Native Pb, which melts at 327°C (Hansen & Anderko 1958), is described from Aguilar, Argentina (Gemmell *et al.* 1992).

#### Sulfide inclusions in gangue

Multiphase sulfide inclusions within the country rock are a strong indication that a sulfide melt was present. It is possible, and even likely, that silicates growing during metamorphism may include adjacent sulfides. However, the possibility that a sulfide inclusion was trapped in a liquid phase becomes increasingly more likely if it contains many phases (Fig. 2A). For example, up to five phases are reported in sulfide inclusions at Broken Hill (Sloan 2000). If the inclusion is much richer in LMCE than the associated orebody, then it is also likely that it was trapped as a liquid.

Perhaps the best examples of this texture are the polyphase As–Pb–Tl–S-bearing inclusions in quartz from Lengenbach (Hofmann 1994). Hofmann (1994, Fig. 1D) showed an inclusion containing interstitial orpiment. This inclusion would have begun to melt at 310°C, well below the temperature of regional metamorphism (which was 500°–520°C: Hofmann & Knill 1996).

Another good example of multiphase inclusions that must have been incorporated as a melt is the occurrence of isolated inclusions of native Au – maldonite – native Bi – arsenopyrite in cordierite, garnet, and perthitic Kfeldspar at the Challenger deposit (Tomkins 2002). Maldonite – Bi melts at 241°C, and maldonite melts incongruently to Au + melt at 373°C (Hansen & Anderko 1958). These phases could not have been introduced to the phenocryst by hydrothermal fluids at temperatures below their melting temperature because this would have produced massive retrogression in the phenocrysts. Therefore, Tomkins (2002) concluded that the only way these inclusions could have been trapped would have been as a melt.

#### Low grain-boundary angles

Sulfides that have equilibrated in the solid state should have mutual grain-boundary angles that range from 100° to 140° (Stanton 1965). As noted above, sulfide interfaces that have angles much lower than this are likely to have formed from a melt that had a low surface-energy relative to the solid phases (Fig. 2B). A good example of this is shown in Figure 1A from Powell & Pattison (1997). This photomicrograph shows small grains of native antimony that have low interfacial angles against stibnite. As noted above, this assemblage would have melted at 530°C, well below the ambient temperature of the deposit.

# Sulfide minerals filling fractures

One textural feature that is characteristic of silicate melts is the formation of dikes, *i.e.*, melt-filled fractures. It may be difficult to distinguish between fracture-fillings that formed from melt and those formed by hydrothermal veins, because both polymetallic melts and hydrothermal fluids may be focussed into the same fracture. For this reason, this characteristic is not a diagnostic one, although clearly, those polymetallic dikes formed from melts alone would lack the halo of alteration typically associated with hydrothermal veins. At a smaller scale, some microfractures strongly suggest the participation of a sulfide melt, particularly if there is no sense of shear across the fracture and if the minerals present would have melted at low T. Such textures are seen at the Edwards Pb-Zn deposit, Balmat district, New York, which was metamorphosed to the granulite facies (Serviss et al. 1986). Figure 5D of Serviss et al. (1986) shows a veinlet containing the assemblage freibergite + silver cutting gangue. As noted above, silver sulfosalts should melt at temperatures ca. 500°C, well below the temperatures of the granulite facies. Another possible example comes from the Sulitjelma deposit in Norway. Figure 10D in Cook (1996) shows fractures that are filled with the assemblage pyrargyrite, native Sb and an Sb-Ag intergrowth. This assemblage should be molten at temperatures below 500°C, at the lower limits of the temperature of regional metamorphism (500-600°C).

# Mn- or Ca-rich selvage

As noted above, a reaction halo consisting of Ca-Mn garnet, rhodonite, bustamite, hedenbergite, or wollastonite occurs around the Broken Hill orebody. Such selvages are also found around the orebodies at Cannington (Bodon 1998), Aguilar (Gemmell et al. 1992) and Balmat (Brown et al. 1980). All of these deposits have been metamorphosed at upper amphibolite or granulite grades. Thus, the lack of these selvages around less metamorphosed deposits indicates that they are a feature restricted to deposits metamorphosed to the highest grades. It is important to note that a Mn-rich selvage is not a diagnostic feature, since Mn-rich rocks may form from sedimentary processes (Spry et al. 2000). The Mn-rich selvage formed by melt processes should: 1) lack compositional layering, 2) cut the regional fabric, and 3) be markedly high in variance; in many places at Broken Hill, they consist of only a single mineral.

# OREBODIES THAT MAY HAVE UNDERGONE PARTIAL MELTING

Using the criteria above, we have recognized 26 metamorphosed ore deposits around the world that contain LCME minerals, which may have been concentrated due to partial melting (Table 1, Fig. 12). In this compilation, we have included mainly deposits that have been subjected to regional metamorphism. We have included three contact-metamorphic deposits. In two deposits [Aguilar: Gemmell *et al.* (1992); Union Hill, Australia: Hack *et al.* (1998)], the ore apparently was present before the thermal maximum. In the other deposit (Lucky Draw: Sheppard *et al.* 1995), the temperature of the ore deposition is well constrained. We cannot be certain that all of the deposits listed on Table 1 melted because we cannot be sure from the descriptions in the literature whether or not the LCME-rich areas in these

TABLE 1. METAMORPHOSED SULFIDE ORE DEPOSITS THAT MAY HAVE MELTED

Deposit	P kbar	T or metamorphic grade	Low I.A.	S. incl.	Tab. bodies	Mn selv.	Refer- ence					
Pb and Zn deposits												
Aggenevs		granulite				?	1					
Aguilar	1-2	pyroxene hornfels		×		×	2					
Bleikvassli	8	600°C					3.4					
Bluebell	5	620°C		×	×	×	5,6					
Bodenmais 3		730°C					7.8					
Broken Hill	-	granulite	×	×	×	×	9, 10					
Cannington	4-6	640-690°C				×	11					
Edwards		granulite			×	×	12					
Gorevsk		amphibolite					13					
Langenbach	3	500-520°C	×	×	×		14.15					
Rainura-Dariha	55	550°C					16					
Sterling Hill	4-5	700-800°C				?	17					
Taivaliärvi		unner amphibolite			×		18					
t ui vuijui vi		apper ampinoonie										
		Cu-rich depe	osits									
Geco	5-7	620-680°C		×			19, 20, 21					
Outokumpu		amphibolite			×		22					
Pyhäsalmi		sillimanite			×		23					
Sulitielma	68	520-550°C					24					
Tunaberg	2-3	550-600°C		×			25					
0		An denesi	**									
		Au ueposi	13									
Big Bell	4–5	650-700°C					26, 27					
Chalice	3-4	500°C					28					
Challenger	7-8	800°C		×			29					
Hemlo	6-7	600-650°C					30, 31					
Lucky Draw	2	550°C			×		32					
Renco		granulite					33					
Union Hill	1–2	>500°C					34					
		Au and base-meta	l depos	its								
Calumet Island		upper amphibolite				×	35, 36					
Montauban	5	630–650°C			×	?	37, 38					

Column headings: Low I.A.: low interfacial angles; S. incl.: sulfide inclusions; Tab. bodies: tabular bodies (*i.e.*, fracture fillings); Mn selv.: Mn- and Ca-enriched selvage. References: I Ryan et al. (1986), 2 Gemmell et al. (1992), 3 Rosenberg et al. (1997), 4 Cook et al. (1998), 5 Ohmoto & Rye (1970); 6 Höy (1980), 7 Schreyer et al. (1964), 8 Dill (1990), 9 Mavrogences et al. (2001), 10 Sloan (2000), 11 Bodon (1998), 12 Serviss et al. (1986), 13 Smirnov (1977), 14 Hofmann (1994), 15 Hofmann & Knill (1996), 16 Basu et al. (1983), 17 Jenkins & Misiur (1994), 18 Papunen et al. (1983), 19 Petersen & Friesen (1982), 20 Friesen et al. (1982), 21 Suffel et al. (1971), 22 Mikkola & Vaisanen (1972), 23 Helovuori (1973), 24 Cook (1996), 25 Dobbe & Cont (1993), 26 Wilkins (1993), 27 Phillips & de Nooy (1988), 28 Bucci et al. (2000), 29 Tomkins (2002), 30 Powell & Pattison (1977), 31 Powell et al. (1998), 32 Sheppard et al. (1995), 33 Börnke & Varndell (1986), 34 Hack et al. (1998), 35 Williams (1990a), 36 Williams (1990b), 37 Bernier et al. (1987), 38 Stamatelopoulou-Seymour & MacLean (1984).

deposits are found in retrograde horizons. In the discussion below, we have concentrated on those deposits where melting is most likely to have occurred. We have found three distinct compositional types of deposits in which melting may have occurred: 1) Pb- and Zn-rich deposits, 2) Cu-rich deposits, and 3) Au-rich deposits.

## Pb- and Zn-rich deposits

The largest number of deposits that may have melted are Pb–Zn deposits. This is probably because, as noted above, galena-bearing assemblages melt at a lower T than galena-absent assemblages dominated by chalcopyrite. These deposits may have originally been SEDEX deposits, which are hosted in metamorphosed pelitic and psammitic rocks (*e.g.*, Broken Hill: Parr & Plimer 1993), or MVT deposits, which are hosted in metamorphosed carbonates (*e.g.*, Bluebell: Ohmoto & Rye 1970). The Pb:Zn ratios in these deposits range from Pb-rich (Broken Hill: Parr & Plimer 1993) to Zn-rich with only minor Pb (Taivaljärvi: Papunen *et al.* 1989).

The deposit of this type that is most likely to have melted is Broken Hill. This inference is based upon the fact that the temperature of the regional metamorphism is greater than the melting temperature of the bulk ore (Mavrogenes *et al.* 2001). This hypothesis is also consistent with textural features noted above. Another deposit that almost certainly melted is the contact-metamorphosed Aguilar deposit in Argentina. In addition to the stratabound sulfide in the country rocks, the deposit also contains sulfides in fissure veins. These veins are most abundant in the pyroxene-hornfels facies, near the contact with a granitic stock (Gemmell *et al.* 1992), where they contain native Pb that is rimmed by galena. As noted above, native Pb would melt at 327°C, well below the 650°C temperature of metamorphism. The Edwards deposit in New York, which was metamorphosed in the granulite facies, probably also melted. As noted above, it contains veinlet of silver + freibergite, an assemblage that would have been molten at the peak temperature.

Other deposits of interest are the small carbonatehosted MVT deposits of the Kootenay Arc, which extend from northwestern Washington State into southcentral British Columbia. In the southern portion of this belt, which has been only weakly metamorphosed, the deposits are stratabound and mineralogically simple (pyrite – sphalerite – galena  $\pm$  pyrrhotite). In contrast, in the northern portion of the belt, where Bluebell mine occurs, the metamorphic grade reached the upper amphibolite facies. The Pb–Zn ore deposits in this area are transgressive and mineralogically complex. In addition



FIG. 12. Map showing the locations of metamorphosed ore deposits that may have melted. 1 Broken Hill, 2 Cannington, 3 Lucky Draw, 4 Union Hill, 5 Challenger, 6 Big Bell and Chalice, 7 Rajpura–Dariba, 8 Gorevsk, 9 Aggeneys, 10 Renco, 11, Lengenbach, 12 Bodenmais, 13 Pyhäsalmi, 14 Outokumpu, 15 Taivaljärvi, 16 Sulitjelma, 17 Bleikvassli, 18 Tunaberg, 19 Sterling Hill, 20 Edwards, 21 Calumet Island, 22 Montauban, 23 Hemlo, 24 Geco, 25 Bluebell, 26 Aguilar. Sources of data are listed in Table 1.

to the minerals found in the low-temperature deposits, the high-temperature deposits also contain chalcopyrite, arsenopyrite, argentian tetrahedrite and other Ag-dominant minerals (Ohmoto & Rye 1970). We contend that the transgressive orebodies probably melted and that Ag, Sb, and As were concentrated in the partial melt.

#### Cu-rich massive sulfide deposits

A small number of massive sulfide deposits consisting of chalcopyrite – sphalerite – pyrite  $\pm$  pyrrhotite and hosted in amphibolites, cordierite-anthophyllite gneisses, or in felsic schists or gneisses may have melted. Minor phases include galena and many LMCE-bearing sulfosalts [Pyhäsalmi: Helovuori (1979); Sulitjelma: Cook (1996)]. The strongest candidate for melting is the Cu-Co deposit at Tunaberg in the Bergslagen district of Sweden. This deposit was metamorphosed at 3 kilobars and 550-600°C (Dobbe & Oen 1993). It contains abundant low-melting minerals, including native Bi (Dobbe & Zakrzewski 1998), which melts at 271°C (Hansen & Anderko 1958). Also present are inclusions of Bi and Bi-Te alloys in galena (Dobbe 1993), which would melt at 266°C (Hansen & Anderko 1958) and Ag-Bi intergrowths (Dobbe & Oen 1993), which would melt at 262°C (Hansen & Anderko 1958). Several other deposits in the Bergslagen district, which contain silver in Sb- and Bi-rich ores (Jeppsson 1987) may also have melted.

Another intriguing series of such deposits are those at Sulitjelma, Norway. These deposits are hosted by mafic rocks that were metamorphosed at temperatures between 520° and 550°C (Cook 1996) and contain a number of LCME minerals that melt at very low temperatures. Low-melting minerals listed by Cook (1996) include pyrargyrite, which melts at 485°C (Keighin & Honea1969), aurostibite, which melts at 460°C (Hansen & Anderko 1958), realgar, which melts at 321°C (Hansen & Anderko 1958), and native Bi, which melts at 271°C (Hansen & Anderko 1958). Cook (1996) interpreted these minerals to have formed by decomposition of an earlier phase. It is possible that this phase was a polymetallic melt, rather than a solid.

#### Disseminated Au deposits

A number of disseminated gold deposits from highgrade metamorphic terranes have assemblages that clearly would have melted at peak temperatures. Perhaps the most striking is the Challenger deposit in South Australia, which occurs in granulite-grade gneisses and contains phases that would be molten below 400°C. Another deposit that apparently melted is the Lucky Draw deposit in Australia. This deposit is hosted in contact-metamorphosed metasedimentary rocks that were metamorphosed at 2 kilobars and temperatures around 600°C. The ore was emplaced during a later retrogressive event at T  $\approx$  550°C. The presence of abundant lowmelting minerals in the ore led Sheppard *et al.* (1995) to conclude that the ore may have been concentrated as a melt.

Other Au deposit from high-grade rocks that may have melted include the Renco deposit in Zimbabwe and the Hemlo deposit in Ontario. The gold in the Renco deposit was emplaced into amphibolite-grade shear zones that cut granulite-grade gneisses. Deposition occurred at a temperature around 600°C (Kisters et al. 1998), but the presence of maldonite and native Bi in the ore (Bömke & Varndell 1986, Tabeart 1987) indicates that least some of the ore would have been molten at this temperature. The Hemlo deposit was metamorphosed at temperatures around 600°C, yet contains lowmelting minerals such as orpiment and cinnabar (Powell & Pattison 1997). These phases occur as intimate intergrowths that may be the result of exsolution (Powell & Pattison 1997). We conclude that they may also be the result of crystallization of a residual melt phase.

Some of the disseminated Au deposits, such as Hemlo, appear to be metamorphosed epithermal deposits (Powell *et al.* 1999). In such deposits, the enrichment of LMCE may have formed before metamorphism. In other deposits, it is unclear whether the LMCE enrichment was premetamorphic or whether it is the product of melting. Two deposits, Montauban and Calumet Island, both in the Grenville Province of Quebec, involve a disseminated Au deposit that is peripheral to a metamorphosed massive sulfide deposit (Bernier *et al.* 1987, Williams 1990a). Could these gold deposits have formed by expulsion of Au-bearing partial melt from a VMS restite? It is certainly a matter that deserves further study.

## CONCLUSIONS

The recognition that sulfide ore deposits may have melted during metamorphism has some important geological implications. First, it provides another process for remobilization and concentration of trace metals during metamorphism. Second, it provides a means to interpret orebodies and textures that have previously been cryptic. For example, the melting of sulfides could explain why an orebody considered to be premetamorphic on the basis of geochemical evidence lacks structural features that developed at the time of metamorphism. Furthermore, because polymetallic melts may remain liquid to conditions well below those of peak metamorphism, this model obviates the need to call upon an external process to explain textural features and assemblages that formed at lower temperatures than those of peak metamorphism. The recognition of former sulfide melts at Broken Hill (Mavrogenes et al. 2001) and Lengenbach (Hofmann 1994) has led to a radical new interpretation for the origin of these ore deposits.

Finally, the partial melting of sulfide orebodies in medium- to high-grade metamorphic terranes may have a critical effect on the concentrations of precious metals in these deposits. In deposits where the precious metals Ag and Au are distributed as trace components in major sulfides, one can simply use statistical methods to determine the amount of precious metals present. However, if the deposit has undergone melting during metamorphism, these metals may have been concentrated in small areas of high-grade ore rather than being widely disseminated. Clearly, the presence or absence of such concentrated pockets or precious metals is critical to an evaluation of the economic viability of massive sulfide orebodies in metamorphic terranes. For example, at Broken Hill, the outlying orebodies, known as droppers, are enriched in silver relative to the main orebody (Maiden 1976). This is also seen at the Edwards mine, where silver is concentrated in a few very-highgrade zones (Serviss et al. 1986). An unfocussed drilling project may miss such high-grade ores and hence, will underestimate the value of the deposit.

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#### References

- AMCOFF, O. (1984) Distribution of silver in massive sulfide ores. *Mineral. Deposita* 19, 63-69.
- ASHLEY, P.M., CREAGH, C.J. & RYAN, C.G. (2000): Invisible gold in ore and mineral concentrates from the Hillgrove gold-antimony deposits, NSW, Australia. *Mineral. Deposita* 35, 285-301.
- BARTON, P.B., JR. (1970): Sulfide petrology. *Mineral. Soc. Am., Spec. Pap.* 3, 187-198.

\_\_\_\_\_ (1971): The Fe–Sb–S system. *Econ. Geol.* **66**, 121-132.

- BASU, K., BORTNIKOV, N.S., MOOKHERJEE, A., MOZGOVA, N.N. & TSEPIN, A.I. (1981): Rare minerals from Rajpura–Dariba, Rajasthan, India. II. Intermetallic compound Ag<sub>74.2</sub>Au<sub>16.4</sub> Hg<sub>9.4</sub>. Neues Jahrb. Mineral., Abh. 141, 217-223.
  - L.N. (1983): Rare minerals from Rajpura–Dariba, Rajasthan, India. IV. A new Pb–Ag–Tl–Sb sulphosalt, rayite. *Neues Jahrb. Mineral., Monatsh.*, 296-304.
- BERNIER, L., POULIOT, G. & MACLEAN, W.H. (1987): Geology and metamorphism of the Montauban North Gold Zone: a

metamorphosed polymetallic exhalative deposit, Grenville Province, Quebec. *Econ. Geol.* **82**, 2076-2090.

- BODON, S.B. (1998): Paragenetic relationships and their implications for ore genesis at the Cannington Ag-Pb-Zn deposit, Mount Isa Inlier, Queensland, Australia. *Econ. Geol.* 93, 1463-1488.
- BÖMKE, F.C. & VARNDELL, B.J. (1986): Gold in granulites at Renco mine, Zimbabwe. *In* Mineral Deposits of Southern Africa (C.R. Anhaeusser, & S. Maske, eds.). Geological Society of South Africa, Johannesburg, South Africa (221-230).
- BRETT, R. & KULLERUD, G. (1967): The Fe-Pb-S system. *Econ. Geol.* **62**, 354-369.
- BROWN, P.E., ESSENE, E.J. & PEACOR, D.E. (1980): Phase relations inferred from field data for Mn pyroxenes and pyroxenoids. *Contrib. Mineral. Petrol.* 74, 417-425.
- BUCCI, L.A., HAGEMANN, S.G., GROVES, D.I. & MCNAUGHTON, N.J. (2000): Two-stage gold mineralisation at the Archean Chalice gold deposit, Yilgarn Craton, Western Australia. *Geol. Soc. Aust.* 59, 64 (abstr.).
- CABRI, L.J. (1965): Phase relations in the Au–Ag–Te system and their mineralogical significance. *Econ. Geol.* 60, 1569-1606.
- CHANG, L.L.Y. & BEVER, J.E. (1973): Lead sulfosalts minerals: crystal structures, stability relations, and paragenesis. *Minerals Sci. Eng.* 5, 181-191.
- CLARK, L.A. (1960): The Fe–As–S system: phase relations and applications. *Econ. Geol.* 55, 1345-1381, 1631-1652.
- CLARKE, D.B. (1992): *Granitoid Rocks*. Chapman Hill, London, U.K.
- COOK, N.J. (1992): Antimony-rich mineral parageneses and their association with Au minerals within massive sulfide deposits at Sulitjelma, Norway. *Neues Jahrb. Mineral.*, *Monatsh.*, 97-106.
  - \_\_\_\_\_ (1996): Mineralogy of the sulphide deposits at Sulitjelma, northern Norway. *Ore Geol. Rev.* **11**, 303-338.
  - & CHRYSSOULIS, S.J. (1990): Concentrations of "invisible gold" in the common sulfides. *Can. Mineral.* 28, 1-16.
  - \_\_\_\_\_, SPRY, P.G. & VOKES, F.M. (1998): Mineralogy and textural relationships among sulphosalts and related minerals in the Bleikvassli Zn–Pb–(Cu) deposit, Nordland, Norway. *Mineral. Deposita* 34, 35-56.
- Cox, S.F. (1987): Flow mechanisms in sulfide minerals. Ore Geol. Rev. 2, 133-171.
- CRAIG, J.R. (1967): Phase relations and mineral assemblages in the Ag–Bi–Pb–S system. *Mineral. Deposita* 1, 278-306.
  - \_\_\_\_\_, CHANG, L.L.Y. & LEES, W.R. (1973): Investigations in the Pb–Sb–S system. *Can. Mineral.* **12**, 199-206.

& KULLERUD, G. (1967): The Cu–Fe–Pb–S system. *Carnegie Inst. Wash., Yearbook* **65**, 344-352.

& \_\_\_\_\_\_ (1968a): Phase relations and mineral assemblages in the copper – lead – sulfur system. *Am. Mineral.* **53**, 145-161.

\_\_\_\_\_ & \_\_\_\_\_ (1968b): The Cu–Fe–Ni–S system. Carnegie Inst. Wash., Yearbook 66, 413-417.

- & VOKES, F.M. (1993): The metamorphism of pyrite and pyritic ores: an overview. *Mineral. Mag.* 57, 3-18.
- DALSTRA, H.J., BLOEM, E.J.M. & RIDLEY, J.R. (1997): Gold in amphibolite facies terrains and its relationship to metamorphism, exemplified by syn-peak metamorphic gold in the Transvaal deposit, Yilgarn Block, Western Australia. Chron. Rech. Minières 529, 3-24.
- DILL, H.G. (1990): Chemical basin analysis of metalliferous "Variegated Metamorphics" of the Bodenmais ore district (F.R. of Germany). Ore Geol. Rev. 5, 151-173.
- DOBBE, R.T.M. (1993): Bismuth tellurides (joseite-B, bismuthian tsumoite) in a Pb–Zn deposit from Tunaberg, Sweden. Eur. J. Mineral. 5, 165-170.
- & OEN, I.S. (1993): Sulphosalt mineralogy and paragenetic relations in Zn-Pb ores from Tunaberg, Bergslagen, Sweden. *Neues Jahrb. Mineral.*, *Abh.* **165**, 123-142.
- & ZAKRZEWSKI, M.A. (1998): Oenite, CoSbAs, a new mineral species from the Tunaberg Cu–Co sulfide skarns, Bergslagen, Sweden. *Can. Mineral.* 36, 855-860.
- DUTRIZAC, J.E. (1976): Reactions in cubanite and chalcopyrite. *Can. Mineral.* **14**, 172-181.
- FRANCHETEAU, J., NEEDHAM, H.D., CHOUKROUNE, P., JUTEAU, T., and 11 others (1979): Massive deep-sea sulphide ore deposits discovered by submersible on the East Pacific Rise. *Nature* 277, 523-528.
- FRIESEN, R.G., PIERCE, G.A. & WEEKS, R.M. (1982): Geology of the Geco base metal deposit. *In* Precambrian Sulphide Deposits (R.W. Hutchinson, C.D. Spence & J.M. Franklin, eds.). *Geol. Assoc. Can., Spec. Pap.* 25, 343-363.
- GATHER, B. & BLACHNIK, R. (1974): Das System Gold-Wismut-Tellur. Z. Metallkunde 65, 653-656.
- GEMMELL, J.B., ZANTOP, H. & MEINERT, L.D. (1992): Genesis of the Aguilar zinc–lead–silver deposit, Argentina: contact metasomatic vs. sedimentary exhalative. *Econ. Geol.* 87, 2085-2112.
- HACK, A.C., MAVROGENES, J.A., HOSKIN, P.O. & SCOTT, R.J. (1998): A turbidite hosted, gold (–bismuth) quartz vein deposit, Union Hill mine, Maldon, central Victoria. *Geol. Soc. Aust.* 49, 194 (abstr.).
- HALL, H.T. & YUND, R.A. (1964): Equilibrium relations among some silver sulfosalts and arsenic sulfides. *Trans. Am. Geophys. Union* 45, 122 (abstr.).

- HANSEN, M. & ANDERKO, K. (1958): Constitution of Binary Alloys. McGraw Hill, New York, N.Y.
- HELOVUORI, O. (1979): Geology of the Pyhäsalmi ore deposit, Finland. Econ. Geol. 74, 1084-1101.
- HODA, S.N. & CHANG, L.L.Y. (1975): Phase relations in the pseudo-ternary system PbS–Cu<sub>2</sub>S–Sb<sub>2</sub>S<sub>3</sub> and the synthesis of meneghinite. *Can. Mineral.* **13**, 388-393.
- HOFMANN, B.A. (1994): Formation of a sulfide melt during Alpine metamorphism of the Lengenbach polymetallic sulfide mineralization, Binntal, Switzerland. *Mineral. Deposita* 29, 439-442.
- & KNILL, M.D. (1996): Geochemistry and genesis of the Lengenbach Pb–Zn–As–Tl–Ba-mineralisation, Binn Valley, Switzerland. *Mineral. Deposita* **31**, 319-339.
- Höy, T. (1980): Geology of the Riondel area, central Kootenay Arc, southeastern British Columbia. B.C. Ministry of Energy Mines and Petroleum Resources, Bull. 73.
- HUTCHINSON, R.W. (1965): Genesis of Canadian massive sulphides reconsidered by comparison to Cyprus deposits. *Can. Inst. Mining Metall. Bull.* **58**(641), 972-986.
- JENKINS, R.E. II & MISIUR, S.C. (1994): A complex base-metal assemblage from the Sterling mine, New Jersey. *Mineral. Rec.* 25, 95-104.
- JEPPSSON, M. (1987): Mineral chemistry of silver in antimony and bismuth rich sulfide ores in Bergslagen, central Sweden. *Neues Jahrb. Mineral.*, *Monatsh.*, 205-216.
- KEIGHIN, C.W & HONEA, R.M. (1969): The system Ag–Sb–S from 600°C and 200°C. *Mineral. Deposita* 4, 153-171.
- KISTERS, A.F.M., KOLB, J. & MEYER, F.M. (1998): Gold mineralization in high-grade metamorphic shear zones of the Renco mine, southern Zimbabwe. *Econ. Geol.* 93, 587-601.
- KULLERUD, G. (1968): High-temperature phase relations in the Cu–Fe–S system. *Carnegie Inst. Wash.*, Yearbook 66, 404-409.
- & Мон, G. (1968): High-temperature phase relations in the Cu-Ni-S system. Carnegie Inst. Wash., Yearbook 66, 409-413.
- LAWRENCE, L.J. (1967): Sulphide neomagmas and highly metamorphosed sulphide deposits. *Mineral. Deposita* 2, 5-10.
- LIU, LIN-GUN & BASSETT, W.A. (1986): Elements, Oxides, and Silicates: High Pressure Phases with Implications for the Earth's Interior. Oxford University Press, New York, N.Y.
- LUCE, F.D., TUTTLE, C.L. & SKINNER, B.J. (1977): Studies of sulfosalts of copper. V. Phases and phase relations in the system Cu–Sb–As–S between 350° and 500°C. *Econ. Geol.* 72, 271-289.

- MAIDEN, K.J. (1976): Piercement structures formed by metamorphic mobilisation of the Broken Hill orebody. *Proc. Aust. Inst. Mining Metall.* 257, 1-8.
- MARSHALL, B. & GILLIGAN, L.B. (1987): An introduction to remobilization: information from ore-body geometry and experimental considerations. *Ore Geol. Rev.* 2, 87-131.
- \_\_\_\_\_, VOKES, F.M. & LAROCQUE, A.C.L. (2000): Regional metamorphic remobilization: upgrading and formation of ore deposits. *Rev. Econ. Geol.* 11, 19-38.
- MASKE, S. & SKINNER, B.J. (1971): Studies of the sulfosalts of copper. I. Phases and phase relations in the system Cu–As– S. Econ. Geol. 66, 901-918.
- MAVROGENES, J.A., MACINTOSH, I.W. & ELLIS, D.J. (2001): Partial melting of the Broken Hill galena–sphalerite ore – experimental studies in the system PbS–FeS–ZnS–(Ag<sub>2</sub>S). *Econ. Geol.* 96, 205-210.
- MCQUEEN, K.G. (1984): Meneghinite, boulangerite and associated minerals from the Pinnacles mine, Broken Hill, New South Wales. *Neues Jahrb. Mineral.*, *Monatsh.*, 323-336.
- MIKKOLA, A.K. & VÄISÄNEN, S.E. (1972): Remobilization of sulphides in the Outokumpu and Vihanti ore deposits, Finland. Proc. 24th Int. Geol. Congress, Sect. 4, 488-497.
- MOH, G.H. (1991): Thallium and gold: observations and experimental contributions to mineralogy, geochemistry and crystal chemistry. *Neues Jahrb. Mineral.*, *Abh.* 163, 197-270.
- MOOKHERJEE, A. (1976): Ores and metamorphism: temporal and genetic relationships. *In* Handbook of Stratabound and Stratiform Ore Deposits 4 (K.H. Wolf, ed.). Elsevier, New York, N.Y. (203-260).
- \_\_\_\_\_ & DUTTA, N.K. (1970): Evidence of incipient melting of sulfides along a dike contact, Geco mine, Manitouwadge, Ontario. *Econ. Geol.* 65, 706-713.
- MURAO, S. & ITOH, S. (1992): High thallium content in Kurokotype ore. J. Geochem. Explor. 43, 223-231.
- NALDRETT, A.J. (1997): Key factors in the genesis of Noril'sk, Sudbury, Jinchuan, Voisey's Bay and other world-class Ni– Cu–PGE deposits: implications for exploration. Aust. J. Earth Sci. 44, 283-315.
  - & RICHARDSON, S.W. (1968): Effect of water on the melting of pyrrhotite-magnetite assemblages. *Carnegie Inst. Wash., Yearbook* 66, 429-431.
- OHMOTO, H. & RYE, R.O. (1970): The Bluebell mine, British Columbia. I. Mineralogy, paragenesis, fluid inclusions, and isotopes of hydrogen, oxygen, and carbon. *Econ. Geol.* 65, 417-437.
- PAPUNEN, H., KOPPEROINEN, T. & TUOKKO, I. (1989): The Taivaljärvi Ag–Zn deposit in the Archean greenstone belt, eastern Finland. *Econ. Geol.* 84, 1262-1276.

- PARR, J.M. & PLIMER, I.R. (1993): Models for Broken Hilltype lead – zinc – silver deposits. *In Mineral Deposit* Modeling (R.V. Kirkham, W.D. Sinclair, R.I. Thorpe & J.M. Duke, eds.). *Geol. Assoc. Can., Spec. Pap.* **40**, 253-288.
- PETERSEN, E.U. & FRIESEN, R.G. (1982): Metamorphism of the Geco massive sulfide deposit, Manitouwadge, Ontario. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* 7, 73.
- PHILLIPS, G.N. & DE NOOY, D. (1988): High-grade metamorphic processes which influence Archean gold deposits, with particular reference to Big Bell, Australia. J. Metamorph. Geol. 6, 95-114.
- PLIMER, I.R. (1987): Remobilization in high-grade metamorphic environments. Ore Geol. Rev. 2, 231-245.
- POWELL, W.G. & PATTISON, D.R.M. (1997): An exsolution origin for low-temperature sulfides at the Hemlo gold deposit, Ontario, Canada. *Econ. Geol.* 92, 569-577.
- \_\_\_\_\_\_\_ & JOHNSTON, P. (1999): Metamorphic history of the Hemlo gold deposit from Al<sub>2</sub>SiO<sub>5</sub> mineral assemblages, with implications for the timing of metamorphism. *Can. J. Earth Sci.* **36**, 33-46.
- PRUSETH, K.L., MISHRA, B. & BERNHARDT, H.-J. (1995): Phase relations in the Cu<sub>2</sub>S–PbS–Sb<sub>2</sub>S<sub>3</sub> system: an experimental appraisal and application to natural polymetallic sulfide ores. *Econ. Geol.* **90**, 720-732.
- RAMDOHR, P. (1950): Die Lagerstätte von Broken Hill in New South Wales im Lichte der neuen geologischen Erkenntnisse und erzmikroskopischer Untersuchungen. *Heidelb. Beitr. Mineral. Petrogr.* 2, 291-333.
  - (1953): Über metamorphose und sekundäre Mobilisierung. Geol. Rundsch. 42, 11-19.
  - \_\_\_\_\_ (1980): The Ore Minerals and their Intergrowths. Pergamon Press, New York, N.Y.
- ROLAND, G.W. (1970): Phase relations below 575°C in the system Ag–As–S. Econ. Geol. 65, 241-252.
- ROSENBERG, J.L., SPRY, P.G., JACOBSON, C.E., COOK, N.J. & VOKES, F.M. (1997): Metamorphic pressure – temperature determinations at the Bleikvassli Zn–Pb–(Cu) deposit, Nordland, Norway. *Geol. Soc. Am., Abstr. Programs* 29, 69.
- RYAN, P.J., LAWRENCE, A.L. LIPSON, R.D., MOORE, J.M., PATERSON, A., STEDMAN, D.P. & VANZYL, D. (1986): The Aggeneys base metal sulfide deposits, Namaqualand district. *In* Mineral Deposits of Southern Africa (C.R. Anhaeusser & S. Maske, eds.). Geological Society of South Africa, Johannesburg, South Africa (1147-1473).
- SCHREYER, W., KULLERUD, G. & RAMDOHR, P. (1964): Metamorphic conditions of ore and country rock of the Bodenmais, Bavaria, sulfide deposit. *Neues Jahrb. Mineral., Abh.* 101, 1-26.

- SERVISS, C.R., GROUT, C.M. & HAGNI, R.D. (1986): The mineralogy of a silver-rich area in the Edwards zinc–lead mine, New York. *Can. Mineral.* 24, 239-245.
- SHEPPARD, S., WALSHE, J.L. & POOLEY, G.D. (1995): Noncarbonate, skarnlike Au–Bi–Te mineralization, Lucky Draw, New South Wales, Australia. *Econ. Geol.* **90**, 1553-1569.
- SKINNER, B.J. & JOHNSON, C.A. (1987): Evidence for movement of ore materials during high-grade metamorphism. *Ore Geol. Rev.* 2, 191-204.
- \_\_\_\_\_, LUCE, F.D. & MAKOVICKY, E. (1972): Studies of the sulfosalts of copper. III. Phases and phase relations in the system Cu–Sb–S. *Econ. Geol.* 67, 924-938.
- SLOAN, M.C. (2000): Relationships Between the Ore and Enclosing Rocks at Broken Hill, NSW. Honours thesis, Australian National Univ., Canberra, Australia.
- SMIRNOV, V.I. (1977): Ore Deposits of the USSR 2. Pitman, London, U.K. (245-249).
- SMITH, C.S. (1948): Grains, phases and interfaces: an interpretation of microstructure. *Trans. Am. Inst. Mining Metall. Eng.* 175, 15-51.
- SPEAR, F.S. (1993): Metamorphic Phase Equilibria and Pressure – Temperature – Time Paths. Mineralogical Society of America, Washington, D.C.
- SPRY, P.G., PETER, J.M. & SLACK, J.F. (2000): Meta-exhalites as exploration guides to ore. *Rev. Econ. Geol.* 11, 163-201.
- SPURR, J.E. (1923): The Ore Magmas. McGraw Hill, New York, N.Y.
- STAMATELOPOULOU-SEYMOUR, K. & MACLEAN, W.H. (1984): Metamorphosed volcanogenic ores at Montauban, Grenville Province, Quebec. Can. Mineral. 22, 595-604.
- STANTON, R.L. (1965): Mineral interfaces in stratiform ores. Trans. Inst. Mining Metall. 74, 45-79.

- SUFFEL, G.G., HUTCHINSON, R.W. & RIDLER, R.H. (1971): Metamorphism of massive sulphides at Manitouwadge, Ontario, Canada. Soc. Mining Geol. Japan, Spec. Issue 3, 235-240.
- TABEART, F. (1987): Controls to deposition of gold, copper, and bismuth at Renco mine, Zimbabwe. *In* African Mining (E.L. Dempster & K.A. Viewing, eds.). Institution of Mining and Metallurgy, London, U.K. (347-363).
- TOMKINS, A.G. (2002): Evolution of the Granulite-Hosted Challenger Gold Deposit, South Australia: Implications for Ore Genesis. Ph.D. thesis, Australian National Univ., Canberra, Australia.
- VAN НООК, H.J. (1960): The ternary system Ag<sub>2</sub>S–Bi<sub>2</sub>S<sub>3</sub>–PbS. *Econ Geol.* **55**, 759-788.
- VOKES, F.M. (1969): A review of the metamorphism of sulfide deposits. *Earth Sci. Rev.* 5, 99-143.
- (1971): Some aspects of the regional metamorphic mobilization of preexisting sulphide deposits. *Mineral. Deposita* **6**, 122-129.
- WILKINS, C. (1993): A post-deformational, post-peak metamorphic timing for mineralization at the Archean Big Bell gold deposit, Western Australia. Ore Geol. Rev. 7, 439-483.
- WILLIAMS, P.J. (1990a): The gold deposit at Calumet, Quebec (Grenville Province): an example of the problem of metamorphic versus metamorphosed ore. *In* Regional Metamorphism of Ore Deposits and Genetic Implications (P.G. Spry & L.T. Bryndzia, eds.). VSP, Zeist, Utrecht, The Netherlands (1-25).
- (1990b): Evidence for a late metamorphic origin of disseminated gold mineralization in Grenville gneisses at Calumet, Quebec. *Econ. Geol.* **85**, 164-171.
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