ARSENOPYRITE MELTING DURING METAMORPHISM OF SULFIDE ORE DEPOSITS

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ABSTRACT

Arsenopyrite is present as a minor phase in many different types of ore deposits. Here we investigate a number of ore deposits metamorphosed to mid-amphibolite facies and above to show that in some environments, arsenopyrite is likely to melt during metamorphism, but in others it will persist until it is converted to löllingite + pyrrhotite. The fate of arsenopyrite is governed by the sulfur fugacity imposed by the surrounding mineralogy during metamorphism. At the Hemlo gold deposit, Canada, which contains a range of disseminated sulfides, the breakdown of barite promoted conditions of high \(f(S_2)\) and melting of arsenopyrite during prograde metamorphism. On the other hand, at several massive sulfide deposits including Osborne Lake, Montauban and Geco in Canada, high \(f(S_2)\) conditions were instead generated through pyrite breakdown on the pyrite–pyrrhotite buffer, also causing arsenopyrite to melt in favorable parts of the deposits. In contrast, metamorphic processes that inhibit high \(f(S_2)\) through consumption of sulfur promote the solid-state conversion of arsenopyrite to löllingite and pyrrhotite rather than melting. In most mineral deposits, the strongest influence on sulfur fugacity is the pyrite-to-pyrrhotite reaction, which buffers \(f(S_2)\) to increasingly elevated values as temperature increases. Once pyrite is consumed, however, \(f(S_2)\) no longer is maintained at elevated values. If rocks hosting arsenopyrite are able to conserve pyrite to middle-amphibolite-facies conditions (beyond 491°C at 1 bar, or ~560°C at 5 kbar), arsenopyrite melting will occur. If not, arsenopyrite melting is unlikely, though still possible. Of the mechanisms that promote pyrite decomposition at metamorphic conditions below arsenopyrite melting, sequestration of sulfur by iron silicates or oxides (or both) to form pyrrhotite may be the most effective in many types of deposit. At the Calumet deposit and in some parts of the Geco deposit, this process was found to be effective in converting pyrite to pyrrhotite in magnetite-rich rocks. Pyrite consumption and low-\(f(S_2)\) conditions are also promoted to a small extent by incorporation of sulfur in hydrothermal fluids, such as an introduced fluid or those generated by dehydration reactions, this effect becoming more significant as temperature rises. Deposits where arsenopyrite is likely to melt during metamorphism include pyrite-rich massive sulfide deposits as well as disseminated deposits lacking abundant iron silicates and oxides. The As-rich melts that result are highly effective in incorporating and mobilizing other metals, particularly gold and silver, as demonstrated at the Challenger deposit (Australia) and at Hemlo, Ontario.

Keywords: arsenopyrite, sulfide melt, metamorphism, ore deposits, mobilization, gold.

SOMMAIRE

L’arsénopyrite est présente en quantités mineures dans plusieurs sortes de gîtes minéraux. Nous examinons ici quelques gisements ayant subi un degré de métamorphisme au faciès amphibolite moyen ou à un faciès plus élevé, afin de montrer que dans certains milieux, l’arsénopyrite est apte à fondre au cours du métamorphisme, quoique dans d’autres, elle peut persister jusqu’au point où elle se déstabilise pour former lollingite + pyrrhotite. Son sort dépend de la fugacité du soufre imposée par l’assemblage de minéraux dans le milieu pendant le métamorphisme. Dans le gisement d’or de Hemlo, en Ontario, dans lequel on trouve une variété de sulfures disséminés, la déstabilisation de la barite provoque une fugacité élevée du soufre, et la fusion de l’arsénopyrite lors du métamorphisme prograde. Par ailleurs, à plusieurs autres gisements de sulfures massifs, par exemple ceux de Osborne Lake, Montauban et Geco au Canada, les conditions de \(f(S_2)\) élevée sont apparues à cause de la déstabilisation de la pyrite en traversant le tampon pyrite–pyrrhotite, et ont aussi mené à la fusion de l’arsénopyrite dans les parties favorables de ces gisements. En revanche, les processus métamorphiques qui empêchent la hausse de la fugacité de soufre causeront la perte

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de soufre pour promouvoir la conversion à l’état solide de l’arsénopyrite en lollingite et pyrrhotite plutôt que la fusion. Dans la plupart des gîtes minéraux, l’influence la plus forte sur la fugacité du soufre est la réaction de pyrite à pyrrhotite, qui tamponne la valeur de \( f(S_2) \) à des niveaux toujours plus élevés à mesure qu’augmente la température. Une fois la pyrite éliminée, toutefois, la valeur de \( f(S_2) \) n’est plus maintenue à un niveau élevé. Si les roches contenant l’arsénopyrite peuvent conserver la pyrite jusqu’aux conditions du faciès amphibolite moyen (au delà de 491°C à 1 bar, ou ~560°C à 5 kbar), on peut s’attendre à voir fondre l’arsénopyrite. Sinon, il est peu probable que l’arsénopyrite puisse fondre, quoique la possibilité existe toujours. Parmi les mécanismes qui promeuvent la déstabilisation de la pyrite à des conditions métamorphiques en dessous des conditions de fusion de l’arsénopyrite, l’incorporation du soufre par des silicates ou des oxydes de fer (ou les deux) pour former la pyrrhotite pourraient bien être le moyen le plus efficace dans plusieurs types de gisement. Dans le cas du gisement de Calumet et dans certaines parties du gisement de Geco (les deux au Canada), ce processus s’avère efficace dans la conversion de pyrite en pyrrhotite dans les roches riches en magnétite. L’élimination de la pyrite et l’établissement des conditions de faible \( f(S_2) \) seraient aussi favorisés à un degré moindre par la répartition du soufre dans un fluide hydrothermal, par exemple une phase fluide introduite ou bien générée par une réaction de déshydratation, cet effet revêtant une importance plus grande à mesure qu’augmente la température. Parmi les gisements dans lesquels l’arsénopyrite est disposée à fondre au cours du métamorphisme, notons les gisements de sulfures massifs riches en pyrite et les gisements disséminés dépourvus de silicates et d’oxydes de fer répandus. Les liquides riches en arsenic qui peuvent apparaître seront très efficaces pour incorporer et mobiliser certains autres métaux, en particulier l’or et l’argent, comme le démontrent le gisement de Challenger en Australie, et celui de Hemlo, en Ontario.

(Traduit par la Rédaction)

**Mots-clés:** arsénopyrite, bain fondu sulfuré, métamorphisme, gîte minéral, mobilisation, or.

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**INTRODUCTION**

Arsenic-bearing sulfide melts are recognized to have formed during metamorphism in a number of different ore deposits (Hofmann 1994, Tomkins & Mavrogenes 2002, Frost et al. 2002a, Tomkins et al. 2004). Furthermore, it has been suggested that gold and other metals may be sequestered by these As-bearing melts, making recognition of the controls and behavior of these melts of economic importance. The arsenic in these melts could come from the breakdown of several minerals, the most common being arsenopyrite, tennantite, realgar and orpiment. Of these, orpiment, realgar and tennantite melt at 310°, 318° and 665°C, respectively (at 1 bar; Massalski et al. 1990, Maske & Skinner 1971), but a temperature increase alone is not enough to induce melting of arsenopyrite. The stability of arsenopyrite also depends on sulfur fugacity (Barton 1969), and thus also on related chemical parameters such as oxygen fugacity.

Tomkins et al. (2004) showed sulfide melts to be highly mobile during deformation. Thus, there is potential for segregation of these melts, possibly leading to new metal-rich accumulations. Melting of arsenopyrite may be critical to the early onset of melting in massive sulfide deposits (Frost et al. 2002a); without it, melting may not occur in these deposits until the granulite facies is reached. In addition, because arsenopyrite is commonly associated with gold, it is important to understand the physical and chemical processes that lead to or inhibit the melting of arsenopyrite during metamorphism.

Experiments in the system Fe–As–S were first conducted by Clark (1960a, b), who recognized that arsenopyrite could melt during amphibolite-facies metamorphism. However, Barton (1969) showed that the stability of arsenopyrite is dependent on \( f(S_2) \).

Improvements on the understanding of the stability field of arsenopyrite in log \( f(S_2) \)–T–P space were subsequently made by Kretschmar & Scott (1976) and Sharp et al. (1985). In this study, we review the metamorphic reactions by which melting of arsenopyrite can occur, as well as reactions that inhibit melting. Geological environments where some of these reactions may have taken place are then discussed.

**METAMORPHIC REACTIONS RELEVANT TO ARSENOPYRITE MELTING**

Arsenopyrite typically coexists in ore deposits with other sulfide minerals. Pyrite or pyrrhotite (or both) are almost invariably present, and it is these two minerals that are likely to control the stability of arsenopyrite during metamorphism in most deposits. Therefore, in this section we first review metamorphic processes that affect the stability of pyrite and pyrrhotite, so that we can then address the stability of arsenopyrite from the perspective of whole-rock composition.

**The system Fe–S**

The simplest desulfidation-type reaction that proceeds during prograde metamorphism of a sulfide ore deposit is one that has been recognized for many years, that of pyrite breaking down to form pyrrhotite (Toulmin & Barton 1964, Craig & Vokes 1993; Fig. 1):

\[
2\text{FeS}_2 = 2\text{FeS} + \text{S}_2
\]  
(1).

Because pyrite is common in many sulfide deposits, reaction (1) exerts the major influence on \( f(S_2) \) conditions during metamorphism. This reaction is referred to as the pyrite–pyrrhotite (Py–Po) buffer because \( f(S_2) \)–T
conditions are restricted to the pyrite–pyrrhotite curve while both minerals are in equilibrium. In general, prograde metamorphism of pyrite-rich rocks in a closed system will lead to formation of pyrrhotite and liberation of sulfur through reaction (1), thus driving up sulfur fugacity.

However, in natural rocks, two coupled processes compete with the \( f(S_2) \) buffering effect of reaction (1). In one process, \( H_2O \) produced from metamorphically induced dehydration of silicates dissolves \( S \) and other components, leading to consumption of pyrite to maintain equilibrium proportions of \( H_2O, CO_2, CH_4, CO, O_2, H_2, H_2S, SO_2 \) and \( S_2 \) in the fluid (Connolly & Cesare 1993):

\[
2FeS_2 + 2H_2O = 2FeS + 2H_2S + O_2 \quad (2),
\]

\[
FeS_2 + 2H_2O = FeS + SO_2 + 2H_2 \quad (3).
\]

This process, which is insignificant at low temperatures owing to the low concentration of sulfur in metamorphic fluids on the Py–Po buffer, becomes increasingly significant as temperature rises, and is particularly applicable at low \( f(O_2) \) conditions where high \( X(H_2S) \) fluids can be generated (see Fig. 5d of Connolly & Cesare 1993).

In the second process, iron from silicates and oxides combines with the sulfur released from pyrite to form pyrrhotite (e.g., Tracy & Robinson 1988). This reaction is coupled to the first process in that hydrothermal fluids would facilitate interaction between sulfur and Fe-oxides and ferromagnesian silicates. Sulfur consumption is likely to be more effective where Fe is liberated through destruction of the silicate or oxide rather than through diffusion. This is the case with reactions involving oxides, which are consequently likely to be relatively efficient. Important silicate reactions include those where one ferromagnesian silicate is consumed to make another, for example:

\[
(\text{Fe,Mg})\text{-Chl} + \text{Ep} + \text{Qtz} + \text{FeS}_2 = \text{Mg-Amp} + \text{An} + \text{FeS} + O_2 + H_2O \quad (4),
\]

or, rewritten with formulae,

\[
(\text{Fe,Mg,Al})_6(\text{Si,Al})_4\text{O}_{10}(OH)_8 + 2 \text{Ca}_2(\text{Al,Fe})\text{Al}_2\text{O}(\text{Si}_2\text{O}_3)(\text{Si}_2\text{O}_7)(\text{OH})_2 + \text{Si}_2\text{O}_3 + \text{FeS}_2 = \text{Ca}_3(\text{Mg,Al})_3(\text{Si,Al})_3\text{O}_{12}(\text{OH})_2 + 2 \text{CaAl}_2\text{Si}_2\text{O}_8 + 2 \text{FeS} + O_2 + 4 H_2O
\]
Reactions such as (4) may be particularly effective at minimizing high $(S_2)$ conditions because they involve the consumption of sulfur associated with both dehydration and sequestration of Fe from silicates. Many authors have also proposed that high $(S_2)$ conditions may destabilize some ferromagnesian silicates (e.g., Tracy & Robinson 1988).

There is some question concerning the metamorphic conditions at which Fe sequestration from silicates becomes relevant. Previous investigators of metamorphosed pyritic–graphitic sediments suggested that there is no noticeable sulfdation of silicates at 460–550°C and 3 kbar (Ferry 1981), whereas sulfdation becomes noticeable at ~540°C and 6 kbar (Nesbitt 1979), ~580°C and 6.6 kbar (Mohr & Newton 1983), and ~600°C and 5.5 kbar (Hutcheon 1979). At 650–725°C and 6 kbar, Tracy & Robinson (1988) noted clear evidence of extensive sulfdation of silicates. These authors used the $\text{Fe/(Fe + Mg)}$ ratio of ferromagnesian silicates to monitor this process. Although the sulfdation of ferromagnesian silicates depends critically on fluid : rock ratios, such that every geological domain may behave differently, these previous studies do provide limited constraints on the metamorphic conditions required.

The consequence of these coupled sulfur-consuming processes is that in disseminated sulfide deposits, which may contain significant silicates or oxides of Fe and abundant H$_2$O-bearing silicates, pyrite can be completely consumed during metamorphism at moderate temperatures. On the other hand, disseminated sulfide deposits that initially lack these sulfur-scavenging reactants may preserve pyrite to higher metamorphic grades. Similarly, massive sulfide deposits that characteristically contain only sparsely distributed hydrous silicates and Fe-oxides and silicates may retain pyrite until high metamorphic temperatures are reached, resulting in high $(S_2)$ conditions at mid-amphibolite facies and above. It is important to note that influx of an external hydrothermal fluid at amphibolite-facies conditions would result in pyrite consumption to maintain fluid equilibrium.

The system Fe–As–S

The stability field of arsenopyrite, in log $(S_2)$–T space, is highlighted on Figure 2. This diagram also indicates the position of several metamorphic reactions that govern the formation and consumption of arsenopyrite. Each of the solid black diagonal lines on this diagram represents a desulfdation reaction, where sulfur is released by the reactant phases as temperature increases. The dashed bold line represents the boundary between regions where solid As (+ S) is stable and where As–S liquid is stable. Also shown on Figure 2 are the various paths that fluid composition may follow during metamorphism of arsenopyrite-bearing deposits. The paths and the reactions that control them are discussed in detail below.

Many types of ore deposits form through precipita-
tion of sulfides in the stability field of arsenopyrite + pyrite. If, during metamorphism, sulfur is added to the chemical system, either through breakdown of another sulfur-bearing phase or through introduction of an external sulfur-rich fluid, the following incongruent reaction depicting arsenopyrite melting may occur (Path A, Fig 2):

$$\text{FeAsS} + (S_2) = \text{FeS}_2 + \text{As}–\text{S(melt)} (5).$$

Alternatively, if the initial temperature and $f(S_2)$ were low, the following reaction could take place:

$$2\text{FeAsS} + S_2 = 2\text{FeS}_2 + 2\text{As(S)} (6).$$

Other arsenopyrite-bearing deposits have a sulfide assemblage that is dominated by pyrite (± pyrrhotite) and contain sparse Fe as silicates or oxides. Once metamorphosed, such a deposit is likely to follow a log $(S_2)$–T path similar to that indicated by Path B on Figure 2. In this case, pyrite breakdown on the Py–Po buffer leads to high $(S_2)$ conditions that are eventually buffered beyond the stability field of arsenopyrite, leading to the following incongruent reaction of arsenopyrite melting:

$$\text{FeAsS} + \text{FeS}_2 = \text{As}–\text{S(melt)} + 2\text{Fe}_{1–x}\text{S} (7).$$

At the boundary of individual crystals of arsenopyrite, the log $(S_2)$–T path (starting from the black dot in the Py + Apy field on Fig. 2) may have a near-vertical trajectory initially, as arsenopyrite liberates sulfur during metamorphism, thereby increasing $(S_2)$. The localized log $(S_2)$–T path would thus intersect the curve for reaction (5), but instead of crossing the curve, sulfur liberation from arsenopyrite would buffer $(S_2)$ along (5), towards the invariant reaction (7), where melting would take place. The position of reaction (7) in P–T space is shown in Figure 3. In comparing the position of this reaction with the X$(\text{H}_2\text{S})$ contents of metamorphic fluids (see Fig. 5d of Connolly & Cesare 1993), one can see that hydrothermal fluids do not contain significant amounts of sulfur when the reaction occurs. Therefore, reactions (2) and (3) do not consume enough pyrite to prevent reaction (7) in pyrite-rich rocks, unless a large amount of H$_2$O is produced or introduced. Sulfdation of Fe-oxides and ferromagnesian minerals (e.g., reaction 4) may be more effective in consuming pyrite in natural rocks.

If all of the pyrite in a deposit initially containing pyrite + pyrrhotite + arsenopyrite is consumed during metamorphism before reaction (7) can take place, or if mineralization was precipitated in the stability field of arsenopyrite + pyrrhotite, another incongruent reaction of arsenopyrite melting is possible (Path C, Fig. 2):

$$\text{FeAsS} (+ \text{Fe}_{0.94}\text{S}) = \text{As}–\text{S(melt)} + \text{Fe}_{0.95}\text{S} (8).$$
FIG. 2. Log $f(S_2)$ – temperature grid showing the stability field of arsenopyrite, realgar and orpiment (grey shaded areas) and the position of the pyrite–pyrrhotite buffer (reaction 1). Original experimental work conducted by Barton (1969), 5 kbar pressure constraint determined by Sharp et al. (1985). The diagram also shows how $f(S_2)$ is buffered in various rocks, and how high $f(S_2)$ can lead to melting of arsenopyrite (explained in text). Note the position of the bold dashed curve, which divides the diagram into two fields; above this line As is only stable as a liquid (with sulfur) at moderate to high temperature, whereas below the line, it is stable as a solid.
This reaction (the stoichiometry of pyrrhotite is meant as an example only) may be a likely occurrence where arsenopyrite is hosted by massive to semimassive pyrrhotite. The liberation of S from pyrrhotite (the N$_{FeS}$ isopleths of Fig. 2 indicate that pyrrhotite loses sulfur as temperature increases), as well as the continued desulfidation of arsenopyrite with increasing temperature, are likely to maintain a steep log $f(S_2)$–T trajectory that intersects the curve for reaction (8) in pyrrhotite-rich rocks (Path C, Fig. 2), provided that an external fluid is not introduced. Depending on the composition of coexisting pyrrhotite, reaction (8) may occur at temperatures between 491° and 702°C at 1 bar, or approximately 560° and 770°C at 5 kbar (Clark 1960a, Sharp et al. 1985).

However, reaction 8 is not enough to cause melting of all arsenopyrite that might be in the rock. Figure 4A shows that arsenic–sulfur melt requires slightly less than one mole of S for every mole of As. Because all sulfur required for the reaction comes from pyrrhotite, the log $f(S_2)$–T path must be buffered along the reaction (8) curve. Calculations indicate that from the 0.94 N$_{FeS}$ isopleth to the 0.95 N$_{FeS}$ isopleth, ~92 moles of pyrrhotite are required to melt one mole of arsenopyrite on the reaction (8) curve. In some massive sulfide deposits, ratios of pyrrhotite to arsenopyrite such as this or greater do occur. In these cases, the log $f(S_2)$–T path may track along the reaction (8) curve until arsenopyrite is consumed, at which point it will deviate upward on a track subparallel to the N$_{FeS}$ isopleths again. In deposits lacking sufficient pyrrhotite, the log $f(S_2)$–T path will continue to track along the reaction (8) curve toward the invariant point at the upper stability-limit of arsenopyrite. At this point the following incongruent melting reaction occurs:

$$3\text{FeAsS} = \text{As}–\text{S(melt)} + \text{FeAs}_2 + 2\text{Fe}_{1–x}\text{S}$$

(9).

The composition of the As–S melt that results from arsenopyrite melting through the various reactions is constrained by the phase relations illustrated in Figure 4A, which indicate the minimum sulfur content of the As–S melt over a range of temperatures. The melt composition is determined by the stoichiometry of the reactions. In each invariant-point melting reaction (7 and 9), the sulfur-rich pyrrhotite product requires slightly more sulfur than necessary for perfect stoichiometric ratios. Therefore, the As–S melt contains slightly less sulfur than a 1:1 sulfur to arsenic ratio. In this way, the melt composition may be buffered toward the minimum sulfur content, on the liquidus, indicated on Figure 4A.

If the original deposit contained arsenopyrite + pyrrhotite, but no pyrite, the following reaction may occur if there is insufficient pyrrhotite to buffer the sulfur fugacity to conditions required for reactions (8) and (9):

$$4\text{FeAsS} = 2\text{FeAs}_2 + 2\text{FeS} + \text{S}_2$$

(10).

Liberation of sulfur by this reaction could theoretically buffer $f(S_2)$ (Path D, Fig. 2) to high enough conditions to reach the upper stability of arsenopyrite, causing melting through reaction (9). Along Path D, reactions (2) and (3) (or equivalents thereof, considering that arsenopyrite and not pyrite is the reactant in this case) are capable of overwhelming the positive $f(S_2)$ buffering effects of reaction (10). This may prevent reaction (9) from taking place in many rocks, particularly in disseminated deposits that follow a low log $f(O_2)$ trajectory during metamorphism. In addition, it may not be possible for arsenopyrite hosted in massive pyrrhotite to generate a log $f(S_2)$–T trajectory steeper than the N$_{FeS}$ isopleths of Figure 1 through reaction (10), because the additional sulfur generated would tend to be incorporated into pyrrhotite. Melting via reaction (9) along Path D might thereby be precluded in these rocks. Melting along Path D requires a low ratio of pyrrhotite to arsenopyrite, a lack of Fe silicates or oxides, and H$_2$O-deficient conditions, a combination that is probably rare.

Arsenopyrite is commonly found in orogenic gold deposits, where gold, arsenopyrite, pyrite or pyrrhotite (or both) were precipitated from a hydrothermal fluid at moderate temperatures, typically at or below the greenschist–amphibolite facies transition (~300 ± 50°C and 1–3 kbar, Groves et al. 1998). Many of these deposits are hosted in banded iron-formation (BIF) or mafic and ultramafic units, in which case the sulfides are associated with Fe-oxides and ferromagnesian silicates. During metamorphism of such rocks, pyrite is consumed at low temperatures, and then the relative
sulfur fugacity falls owing to reactions such as (2–4). Ultimately, arsenopyrite starts to be converted to löllingite + pyrrhotite (Path E on Figure 2) through reaction (10). Note that reactions such as (2–4) are continuous along Path E, as sulfur is constantly liberated from both arsenopyrite and pyrrhotite during prograde metamorphism, leading to ongoing depletion of iron from Fe-oxides and ferromagnesian silicates. Any metamorphic fluid grows increasingly effective at incorporating sulfur. The extent to which the log $f(S_2)$–$T$ trajectory follows reaction (10) depends upon the efficiency of sulfur sequestration by these processes, which in many rocks may lead to a löllingite + pyrrhotite assemblage at moderate temperatures without melting.

The system Au–Fe–As–S

Clark (1960a) found that where gold and arsenopyrite occur together, an Au–As–S melt forms by a modification of reaction (9):

$$3\text{FeAsS} + \text{Au} = \text{FeAs}_2 + 2\text{Fe}_1-x\text{S} + \text{As–Au–S(melt)}$$

Reaction (11) occurs at slightly lower temperatures than reaction (9). The $f(S_2)$ stability limits of this reaction are unknown. Given that Roland (1968) found 2 vol.% gold in Pb–As–S melt at 549°C, it is probable that some or all of the other arsenopyrite melting reactions are capable of incorporating gold in the melt if it is present.

Effects of element substitution in arsenopyrite

Arsenopyrite in many deposits contains Co and Ni in substitution for Fe, and also Sb in substitution for As. The presence of these elements is likely to affect the stability of arsenopyrite in the various reactions described above. In the case of Co and Ni, a range of binary alloy phase-diagrams indicate that these elements have a refractory behavior similar to that of Fe (see Massalski et al. 1990), implying that like Fe, they are unlikely to contribute significantly to the melt. Therefore, incongruent melting of intermediate and end-member phases in the system arsenopyrite – cobaltite – gersdorffite (FeAsS–CoAsS–NiAsS) is likely to produce As–S melt and solid sulfide phases such as pentlandite or cobalt-pentlandite in addition to pyrrhotite. These have been no experimental studies that show how the presence of Co or Ni affects the invariant melting reactions (7 and 9).

Experiments have shown that the mineral geduminite (FeSbS), an end-member in the system FeAsS–FeSbS, is not stable beyond 280°C (Barton 1971), and breaks down at this temperature to form pyrrhotite and native antimony. Berthierite (FeSb$_2$S$_4$) starts to melt incongruently at 530°C (and it decomposes at 563°C) in the presence of pyrrhotite to form an Sb–S melt (Barton 1971). It is likely then that a small amount of Sb substituting for As in arsenopyrite is not likely to greatly offset the melting temperature, and any such offset may be toward a lower temperature.

Summary

It is important to understand the above processes in order to interpret the behavior of arsenopyrite in natural occurrences. Within any one mineral deposit, arsenopyrite may undergo a range of different reactions during metamorphism depending on the local abundance and type of accompanying sulfide, silicate and oxide minerals. Although it may undergo melting in some areas, in others it may be preserved or undergo subsolidus metamorphism to löllingite + pyrrhotite.

RECOGNITION OF TEXTURES INDICATIVE OF AS–S MELT

Arsenopyrite melting should be considered as a possibility in any sulfide deposit that has been metamorphosed above the mid-amphibolite facies (>520°C, 2 kbar). Most rocks that have experienced this degree of metamorphism show signs of pervasive ductile deformation. Under these conditions, sulfide melts are highly mobile (Tomkins et al. 2004), so the ideal sites to investigate for evidence of As-bearing melts are structurally dilatant regions (such as boudin necks, extensional fractures, fold hinges and fault jogs) where mobile materials accumulate. Because As-bearing melts may persist to very low temperatures (Tomkins et al. 2004), even dilational structures that formed well after the peak of metamorphism may be sites of accumulation.

In studies of sulfide melts in igneous rocks, the occurrence of rounded nodules of sulfides (typically pyrrhotite, pentlandite and chalcopyrite) within mafic to ultramafic igneous rocks has been noted at many localities (Lightfoot et al. 1984, Naldrett 1984, Czamanske et al. 1992, Pritchard et al. 2004). These globular inclusions of sulfide are thought to form through immiscibility between silicate melt and sulfide melt. This is a very different physical environment to a much lower-temperature deforming solid metamorphic rock that contains a small amount of highly non-viscous sulfide melt. In the metamorphic environment, we do not expect to see large rounded nodular accumulations of sulfides. Instead, we expect that sulfide melts would mimic the shape of any dilational structural site (boudin necks, dilatational fractures, etc.) because the tendency of the silicates, and particularly the melt, to deform under high strain would override the relatively minor surface-tension requirements of the molten sulfide to form a sphere. The best textural evidence that an assemblage was molten is that it occurs at a structurally dilatant site that formed at or near peak conditions of metamorphism (see Tomkins et al. 2004), though clearly this alone is not enough. Textural evidence of mobilization must be
FIG. 4. Phase relations amongst As-bearing sulfosalts. (A) The system As–S (modified from Massalski et al. 1990). (B) The system As$_2$S$_3$–PbS (modified from Kutolglu 1969). Here it is instructive to consider the effect of melting of a small proportion of arsenopyrite (to produce As–S melt) in the presence of galena. Symbols: Srt: sartorite, Bmh: baumhauerite, Rth: rathite, Duf: dufrenoysite, Jrd: jordanite. (C) The system As–Pb–S at 550°C [constructed from information in Roland (1968) and Massalski et al. (1990)]. (D) The system As$_2$S$_3$–PbS–Bi$_2$S$_3$ (after Walia & Chang 1973). (E) The system Cu–As–S (modified from Maske & Skinner 1971), showing the distribution of mineral phases and melt at 300°C, and the distribution of melt at 500°C, 600°C and 665.5°C. Symbols: Cv: covellite, En: enargite, A: unnamed compound, S: sinnerite, Lt: lautite, Dom: domeykite, fcc: face-centered cubic, hcp: hexagonal-closest packed. (F) The system As$_2$S$_3$–Sb$_2$S$_3$–Tl$_2$S (modified from Sobott 1984) showing phase distribution at 315°C (at 1 bar). The lightly shaded region represents the extent of the liquid field at 275°C.
coupled with experimental evidence that the mobilized assemblage would have been molten.

Arsenic–sulfur melts have the potential to cause significant melting of other sulfide and sulfosalts phases because they lower the melting temperature of a variety of these minerals, such that a range of elements can be incorporated in the melt at amphibolite-facies conditions (Fig. 4). Although they do not match exactly, As$_2$S$_3$ is considered a reasonable proxy for the actual composition of the As–S melt (see above) produced through arsenopyrite melting in these diagrams (e.g., on Fig. 4C, one can see that a pseudobinary join drawn between the approximate As–S melt composition and PbS would produce almost the same topology as between As$_2$S$_3$ and PbS, which is shown in Fig. 4B; in the former, slightly more PbS would contribute to the melt). As has been shown at the Hemlo and Challenger gold deposits (Tomkins & Mavrogenes 2002, Tomkins et al. 2004), As-bearing melts readily incorporate and therefore mobilize gold. This is important because a high proportion of gold deposits contain appreciable disseminated arsenopyrite and pyrite. The high ratio of arsenopyrite to gold in these deposits implies that if an As–S melt is produced during metamorphism, it will melt much of the gold with which it comes in contact (if not all of it; see Roland 1968).

The presence of realgar or orpiment in and around dilatational structures that formed approximately synchro-

coupled with experimental evidence that the mobilized assemblage would have been molten.

Arsenic–sulfur melts have the potential to cause significant melting of other sulfide and sulfosalts phases because they lower the melting temperature of a variety of these minerals, such that a range of elements can be incorporated in the melt at amphibolite-facies conditions (Fig. 4). Although they do not match exactly, As$_2$S$_3$ is considered a reasonable proxy for the actual composition of the As–S melt (see above) produced through arsenopyrite melting in these diagrams (e.g., on Fig. 4C, one can see that a pseudobinary join drawn between the approximate As–S melt composition and PbS would produce almost the same topology as between As$_2$S$_3$ and PbS, which is shown in Fig. 4B; in the former, slightly more PbS would contribute to the melt). As has been shown at the Hemlo and Challenger gold deposits (Tomkins & Mavrogenes 2002, Tomkins et al. 2004), As-bearing melts readily incorporate and therefore mobilize gold. This is important because a high proportion of gold deposits contain appreciable disseminated arsenopyrite and pyrite. The high ratio of arsenopyrite to gold in these deposits implies that if an As–S melt is produced during metamorphism, it will melt much of the gold with which it comes in contact (if not all of it; see Roland 1968).

The presence of realgar or orpiment in and around dilatational structures that formed approximately synchro-

TABLE 1. MELTING TEMPERATURE OF ARSENIC-BEARING SULFOSALTS

<table>
<thead>
<tr>
<th>Mineral Association</th>
<th>Formula</th>
<th>Melting temperature °C at 1 bar</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Sartorite</td>
<td>PbAsS$_3$</td>
<td>305</td>
<td>Knutiglo (1969)</td>
</tr>
<tr>
<td>Orpiment</td>
<td>As$_2$S$_3$</td>
<td>310</td>
<td>Masaishi _et al. _ (1990)</td>
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<tr>
<td>Realgar</td>
<td>AsS</td>
<td>321</td>
<td>Masaishi _et al. _ (1990)</td>
</tr>
<tr>
<td>Baumhauerite</td>
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<td>458</td>
<td>Knutiglo (1969)</td>
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<tr>
<td>Rutilite</td>
<td>(Pb,Tl)$_2$As$_2$S$_6$</td>
<td>474</td>
<td>Knutiglo (1969)</td>
</tr>
<tr>
<td>Jordanite – Geoschorite</td>
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<td>549</td>
<td>Roland (1969)</td>
</tr>
<tr>
<td>Dobrinczite</td>
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<td>-600</td>
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<tr>
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<td>670</td>
<td>Clark (1960a)</td>
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<tr>
<td>Gersdorffite</td>
<td>NiAsS</td>
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<td>Cobaltite</td>
<td>CoAsS</td>
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<td>&lt;275</td>
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<td>Tomkins _et al. _ (2004)</td>
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<td>&lt;310</td>
<td>Wals &amp; Chang (1973)</td>
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<td>0.09</td>
<td>0.28</td>
<td>-</td>
<td>0.00</td>
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<td>Total</td>
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<td>100.82</td>
<td>99.35</td>
<td>82.03</td>
<td>99.15</td>
<td>100.03</td>
<td>99.96</td>
<td>97.47</td>
<td>95.48</td>
<td>97.33</td>
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| S at. % | 34.82 | 59.33 | 66.22 | 44.14 | 31.72 | - | 53.23 | 3.35 | 35.08 | 49.85 | 0.76 | 54.26 |
| As | 30.22 | 1.62 | 0.03 | 55.10 | 34.91 | - | 0.01 | 0.00 | 30.72 | 0.00 | 0.00 | 0.00 |
| Sb | 0.01 | 38.48 | 0.00 | 0.43 | - | - | - | - | 22.61 | 0.04 | 1.02 | 0.75 | 23.73 |
| Pb | 0.00 | 0.00 | 0.00 | 0.00 | - | - | - | - | 0.00 | 0.00 | 48.57 | 0.00 | 16.59 |
| Cu | 0.01 | 0.02 | 0.00 | 0.00 | - | 0.18 | 0.00 | 0.05 | 0.00 | 0.04 | 0.00 | 0.20 |
| Ag | 0.00 | 0.00 | 0.01 | 0.04 | - | 3.06 | - | 64.98 | 0.02 | 51.55 | 19.45 | 5.16 |
| Au | 0.00 | 0.00 | 0.00 | 0.00 | - | 96.76 | - | 8.98 | 0.00 | 0.00 | 43.30 | 0.00 |
| Fe | 34.91 | 0.30 | 33.46 | 0.00 | 31.35 | - | 46.41 | 0.04 | 34.14 | 0.01 | - | 0.05 |
| Co | - | - | - | - | - | 0.00 | - | - | - | - | - | - |
| Ni | - | - | - | - | - | 0.84 | - | - | - | - | - | - |
| Bi | 0.00 | 0.00 | 0.00 | 0.00 | - | - | - | - | - | - | - | - |
| Zn | 0.00 | 0.06 | 0.02 | 0.00 | - | 0.19 | - | - | - | - | - | - |
| Hg | 0.01 | 0.09 | 0.02 | 0.10 | - | 0.00 | - | - | - | - | - | - |
| Total | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

example, in the sample from Hemlo (Fig. 5B), arsenopyrite is associated with stibnite + realgar (+ several other rarer sulfosalts), a combination that melts well below the 600–650°C of peak metamorphism at Hemlo (Powell et al. 1999, Tomkins et al. 2004). Confidence that a sulfosalt–arsenopyrite association formed through crystallization of a metal–As–S melt may be strengthened where sulfosalts containing low-melting-point chalcophile elements (LMCE: Sb, Bi, Tl, Sn, Cd, Hg, Au and Ag; Frost et al. 2002a) are significantly more abundant than elsewhere (as is the case in Fig. 5F).

**AN EXAMPLE OF MELTING AT HIGH SULFUR FUGACITY: PATH A: THE HEMLO GOLD DEPOSIT**

**Background**

The Hemlo deposit, in central Ontario, Canada, is one of the world’s largest gold deposits and has an enigmatic mineral assemblage analogous with both epithermal- and porphyry-style mineralization; it has thus far evaded widely accepted categorization (e.g., Muir 2002). Most recent authors (see Tomkins et al. 2004) consider it to be a premetamorphic gold deposit that was metamorphosed at 600–650°C and 6–7 kbar (Powell et al. 1999). The deposit contains abundant evidence for the existence of an Sb–As–rich melt during peak metamorphism (Tomkins et al. 2004). The As component of this melt could theoretically have come from breakdown of realgar or orpiment (or both) if mineralization was originally introduced at low temperatures (<~318°C, depending on pressure). However, disseminated arsenopyrite is preserved in strained wallrocks at Hemlo (Harris 1989), suggesting that the premetamorphic conditions of mineralization (Fig. 2) were beyond the stability of realgar and orpiment (melted realgar or orpiment would have been mobilized from such rocks). Thus, arsenopyrite is the most likely As-bearing reactant phase for generation of the As-rich melt within the orobesity.

The following observations of the Hemlo mineralization serve as the basis for our discussion. (1) The majority of host rocks are pyrite-rich and poor in Fe silicates and oxides. Only a minor biotite-rich metabasic rock contains an appreciable amount of Fe in silicates and oxides. (2) Arsenopyrite is relatively common in the hanging-wall rocks, where it is the principal mineral of arsenic, yet it is rare within the ore zones (Harris 1989). Where it does occur in the ore zones, it is more prevalent in biotite-rich zones (Harris 1989). Within the felsic and pelitic units (i.e., units poor in Fe oxides and ferromagnesian silicates), we have observed arsenopyrite only in dilational structural domains, where polymetallic melts accumulated, and where it is intimately associated with pyrite and sulfosalts (Fig. 5B). (3) The sulfur-bearing mineral assemblage throughout the deposit is dominated by pyrite, barite and molybdenite (Harris 1989), to the extent that these are the only sulfur-bearing minerals that are abundant and widespread throughout the deposit. Pyrrhotite and magnetite are rare within the ore zones, occurring mainly in biotite-rich rocks, whereas in the hanging-wall rocks, they are comparatively common (Harris 1989). (4) Barian K-feldspar and barian mica are widely distributed throughout the deposit (Harris 1989). Most barian K-feldspar grains show consistent concentric zoning, with wide zones of low-Ba core and high-Ba margin (Fig. 4C in Tomkins et al. 2004). These typically display a granoblastic texture with ~120° triple-junctions, and intervening material is commonly restricted to triple junctions. Grain boundaries of barian silicates and small fractures therein have anomalous Ba contents.

**Factors controlling arsenopyrite melting at Hemlo**

The fact that large amounts of pyrite are preserved within the Hemlo deposit indicates that high $f(S_2)$ conditions must have prevailed during peak metamorphism. The highlighted region on the pyrite–pyrrhotite buffer curve (Fig. 2) represents the actual $f(S_2)$ conditions in rocks containing pyrrhotite + pyrite, and the minimum $f(S_2)$ conditions in rocks lacking pyrrhotite. Although there are a number of other desulfidation reactions that buffer $f(S_2)$ (e.g., Seal et al. 1990), many of these are likely to have been localized and short-lived at Hemlo because most of the minerals involved are relatively uncommon. Conversely, because pyrite, barite and molybdenite dominate the sulfur-bearing mineral assemblage at Hemlo, reactions involving these minerals are expected to have had the most widespread influence on $f(S_2)$.

In the absence of significant Fe silicates and oxides, reaction (1) is capable of raising $f(S_2)$ beyond the stability of arsenopyrite, leading to melting through reaction (7). However, both reactions (1) and (7) produce pyrrhotite, of which there is a distinct lack in many parts of the deposit, suggesting that arsenopyrite did not melt on the Py–Po buffer. Alternative explanations of arsenopyrite melting require the consumption of a widespread S-bearing mineral within the stability field of pyrite and at sulfur fugacities above the pyrite–pyrrhotite buffer (i.e., reaction 5). The assemblage molybdenite + pyrite is stable up to ~750°C (Grover et al. 1975), so the only abundant mineral capable of keeping the system at high $f(S_2)$, off the Py–Po buffer, is barite. The observations listed above support the notion of barite instability during metamorphism, particularly the ~120° triple-junctions among zoned barian K-feldspar grains. Furthermore, the anomalously high Ba contents along microfractures within barian K-feldspar indicate continued late mobility of barium.

These observations suggest a variable stability of barite with increasing temperature, and not simply instability of barite during the hydrothermal reaction(s) that introduced mineralization. An example of how barite might be consumed during progressive metamorphism...
Fig. 5. Examples of textures and mineral associations that may indicate that an As-bearing melt was generated during metamorphism (if considered together with metamorphic grade and timing of mineralization). Symbols: Apy: arsenopyrite, Py: pyrite, Po: pyrrhotite, Gn: galena, Ste: stibnite, Rlg: realgar, Dys: dyscrasite, Td: tetrahedrite, Ccp: chalcopyrite. (A) Photograph of part of a boudinaged quartz vein from the Hemlo gold deposit, interpreted to have been deformed approximately synchronously with peak metamorphism, involving temperatures of 600–650°C (Tomkins et al. 2004). Brightness and contrast have been enhanced to highlight the realgar (AsS), which appears orange and red. Realgar (T_m = 318°C; Massalski et al. 1990), together with stibnite and many other sulfosalts, were concentrated in dilational structures in and around many similar features at Hemlo (Tomkins et al. 2004). (B) BSE image of an intergrowth of arsenopyrite and pyrite within a boudinaged feldspar vein from Hemlo. This may represent the reversal of reaction (5), as there is no pyrrhotite in most rocks at Hemlo.
to produce Ba-enriched K-feldspar is given by the following reaction:

\[
3\text{BaSO}_4 + 6\text{KAI}_2\text{Si}_2\text{O}_8 + 2\text{H}_2\text{O} = 3\text{BaAl}_2\text{Si}_2\text{O}_8 + 18\text{SiO}_2 + 2\text{H}_2\text{S} + 1/2 \text{S}_2 + \text{O}_2 + 6\text{K}^+
\]

(12).

Other reactions are possible, depending on assumptions about element mobility. Note that this reaction is both an oxidizing and a desulfidation reaction. Through this and similar mechanisms of barite consumption, we anticipate conditions of increasing \(f(S_2)\) during progressive metamorphism, favoring conditions within the stability field of pyrite throughout much of the Hemlo deposit (Fig. 2). In a study on barite-rich rocks 21 km to the west of Hemlo, Pan & Fleet (1991) similarly suggested that barium in muscovite and feldspars came from the adjacent barite-rich units during peak metamorphism.

In the biotite-rich metamafic rock, reactions similar to reaction (4) are expected to have maintained conditions of lower \(f(S_2)\), thus ensuring the persistence of arsenopyrite. Similarly, in the hanging wall, where pyrrhotite and magnetite are more abundant, the diminished amount of pyrite (the pyrite present now may be retrograde) is expected to have led to lower \(f(S_2)\) conditions during peak metamorphism, allowing preservation of arsenopyrite.

Also present is stibnite with abundant exsolution-induced blebs of realgar (\(T_m < 556^\circ\text{C}\); Tomkins et al. 2004). (C) Photomicrograph of an arsenopyrite–gold inclusion from the Challenger gold deposit. An experiment on an offcut of this rock showed that similar arsenopyrite–gold inclusions melted at \(P\text{–}T\) conditions below those estimated at Challenger (\(T_{\text{metam}} = 800–850^\circ\text{C}\); Tomkins & Mavrogenes 2002). (D) BSE image showing an association between arsenopyrite and galena from the Montauban Zn–Pb–Au deposit (\(T_{\text{metam}} = -650^\circ\text{C}\); Jourdain 1993). Also present are Au-bearing dyscrasite (Ag 3SbS 3; \(T_m = 558^\circ\text{C}\); Hanson & Anderko 1958), Au–Ag alloy and fizeulyte (\(\text{Pb}_4\text{Ag}_2\text{Sb}_2\text{S}_4\text{S}_6; T_m = \text{unknown}\)), and linking many similar associations are veinlets of pyargyrite (Ag 3SbS 3; \(T_m = 485^\circ\text{C}\); Blythia & Kleppa 1985). (E) BSE image showing an association between arsenopyrite, pyrite and pyrrhotite (minor galena) from the same sample as (D), which we consider likely to represent the reversal of reaction (7). (F) Element–distribution maps of Bi, Pb, As and Sb, showing an association between arsenopyrite, galena and Bi-rich owyheeite [\(\text{PbAg}_x(\text{Sb},\text{Bi})_y\text{S}_z; T_m = \text{unknown}\)] from the Geco Zn–Cu deposit (600° < \(T_{\text{metam}} < 700^\circ\text{C}\); Peterson & Zaleski 1999). Also present are minor amounts of Ag-rich tetrahedrite [(Ag,Cu)_x(Fe,Ce,Zn)_y(\text{Sb,As})_zS_4; \(T_m = 485^\circ\text{C}\); Blythia & Kleppa 1985], native Bi (\(T_m = 271^\circ\text{C}\); e.g., Massalski et al. 1990) and chalcopyrite. Mineral compositions confirmed using WDS analysis on the JEOL JXA8200 electron microprobe at the University of Calgary (Table 2) and reflected light microscopy.

EXAMPLES OF ARSENOPYRITE MELTING ON THE PY–PO BUFFER: PATH B: CANADIAN VMS DEPOSITS

To study arsenopyrite melting on the Py–Po buffer (reaction 7), we investigated several Canadian massive Pb–Zn sulfide deposits that were metamorphosed at conditions of the middle to upper amphibolite facies. The Geco deposit in central Ontario was metamorphosed at 600–700°C and 3–6 kbar (Peterson & Zaleski 1999), the Montauban deposit in central Quebec, at ~650°C and 5 kbar (Jourdain 1993), and the Osborne Lake deposit in western Manitoba, at ~700°C and 6 kbar (cf. Bristol & Froese 1989, Kraus & Menard 1997). These are all considered to be volcanogenic massive sulfide (VMS) deposits, and arsenopyrite melting at Osborne Lake has already been postulated by Frost et al. (2002b).

Although each deposit is characterized by massive sulfides, there are significant differences among them. At Geco, the massive sulfide assemblage is dominated by pyrite, pyrrhotite, sphalerite and chalcopyrite, and there is typically <1% galena in the ore (Friesen et al. 1982) and only sparse arsenopyrite. Montauban is characterized by massive sphalerite, galena, chalcopyrite, pyrite and pyrrhotite, and has marginal disseminated gold-rich sulfide mineralization (Stamatelopoulos–Seymour & MacLean 1984, Bernier et al. 1987); again, arsenopyrite is only sparsely distributed. Osborne Lake, conversely, contains relatively common arsenopyrite amongst massive pyrrhotite, pyrite (euhedral crystals locally exceeding 10 cm), sphalerite and chalcopyrite; galena is rare (Bristol & Froese 1989).

Each deposit contains both pyrite and pyrrhotite, and the pyrite is commonly euhedral, which suggests some retrograde growth on the Py–Po buffer, as is typical of highly metamorphosed massive sulfides (Craig & Vokes 1993). There is also evidence that pyrite persisted through peak metamorphism in that old cores, some with Co zonation and some without, are commonly found within euhedral pyrite [Fig. 6A; see Craig & Vokes (1993), for a discussion of similar cores]. The cores with oscillatory Co zoning are interpreted to represent remnants of the original hydrothermal mineralization event, with the alternating zones possibly representing fluctuations in fluid chemistry; these are less likely to be mimicked by slow metamorphic growth (e.g., Shore & Fowler 1996). If so, pyrite was stable throughout the history of the deposits, and \(f(S_2)\) conditions were on the Py–Po buffer during peak metamorphism in many parts of the deposits. Given that the peak conditions of metamorphism estimated for each deposit are beyond the temperature required for reaction (7), arsenopyrite probably melted, if it was present in these high-\(f(S_2)\) regions. In combination with the phase relations, the textures depicted in samples from Montauban, Geco and Osborne Lake suggest that arsenopyrite melting may have occurred at each deposit (Figs. 5, 6).
Figures 5D and E from Montauban are from the same sample; it contains numerous similar sulfide–sulfosalts aggregations, as well as microveinlets of pyrargyrite linking many of them, within a thin layer in a quartzfeldspathic rock. Many of the sulfosalts that coexist with arsenopyrite in this sample melt at temperatures (Tm) well below the peak temperature of metamorphism at Montauban, for example pyrargyrite (Tm = 485°C, Bryndzia & Kleppa 1988) and dyscrasite (Tm = ~558°C, Hanson & Anderko 1958). Others, particularly galena, are sulfides that are known to melt in the presence of As–S melts (Fig. 4B). The sulfide–sulfosalt aggregations are also highly enriched in Sb, Ag and Au relative to all other rocks in the deposit, all of which partition strongly into sulfide melts (Mavrogenes et al. 2001, Tomkins et al. 2004). There is also a lack of sphalerite, which is abundant in the massive sulfides, but which is known to be a refractory sulfide that does not contribute strongly to sulfide melts (Mavrogenes et al. 2001, Tomkins et al. 2004). These observations suggest that the sulfide–sulfosalt aggregations in this sample represent a mobilized As-bearing polymetallic melt, which was probably derived in part through melting of arsenopyrite via reaction (7).

Figure 5F, from the Geco deposit, is a good example of the problematics in establishing whether an observed assemblage was molten. The sulfide–sulfosalts material in this example occurs within a fracture in granitic wallrock adjacent to massive sulfides, and there is a moderate amount of alteration to muscovite associated with it. The muscovite might suggest that the assemblage formed as a consequence of hydrothermal mobilization from the massive sulfides. However, there are indications the assemblage was molten, and because hydrothermal fluids and sulfide melts migrate into the same structurally dilatant sites during deformation, it is possible that the alteration and mineralization are unrelated. The main observation that suggests sulfide melt mobilization rather than hydrothermal mobilization is that the mineral assemblage in question contains S, Pb, As, Bi, Cu, Sb and Ag, but little Fe and no Zn. The assemblage is strongly enriched in LMCE and depleted in Fe and Zn relative to the massive sulfides, a feature characteristic of sulfide melt extracted from...
its residue. Neither hydrothermal nor solid-state mobilization produces this characteristic fractionation, so sulfide melt mobilization is the favored explanation. It is difficult to rule out the alternative possibility that the observed assemblage was hydrothermally introduced from an external source and completely unrelated to the adjacent massive sulfides.

Figures 6B and 6C are examples from Osborne Lake. These figures show textural relationships among arsenopyrite, sulfides and sulfosalts within a fracture cutting a fragment of a quartz vein. This quartz vein fragment is presumed to be premetamorphic because ductile deformation of massive sulfides typically breaks up and mills any enclosed competent lithologies during prograde or peak deformation. There were no clearly postmetamorphic quartz veins at Osborne Lake. The fragmented vein was sampled specifically because (1) dilational microfractures commonly develop in competent lithologies during deformation into which mobile components (such as melt) migrate, and (2) the separation of any melt accumulations from large quantities of galena eliminates an exsolution origin for the sulfosalts. Figure 6B shows arsenopyrite + pyrite overgrowing pyrrhotite; this is an unstable assemblage at peak conditions of metamorphism. This texture is consistent with reaction between As–S melt and pyrrhotite (reversal of reaction 7) during cooling. Figure 6C shows a similar intergrowth involving pyrite, chalcopyrite and several As-bearing minerals including arsenopyrite, tennantite and seligmanite (PbCuAsS₃), again within a fracture transecting a quartz vein. The tennantite contains appreciable Sb and Ag, which, as indicated above, tend to be concentrated in sulfide melts. In addition to arsenopyrite, tennantite (T_m = 665°C at 1 bar, Fig. 4E) and possibly seligmanite (T_m is unknown) may also be unstable at the peak conditions of metamorphism, in which case this texture may represent a cooling reaction between an As–Cu–Pb–Sb–Ag–S melt and pyrrhotite.

Although these textures suggest that some arsenopyrite at the Osborne Lake mine melted during peak metamorphism, there are also examples throughout the deposit which suggest that arsenopyrite survived peak metamorphism in some localities, such as very coarse euhedral crystals of arsenopyrite in textural equilibrium with pyrrhotite in the absence of pyrite. Although this texture could simply reflect a reversal of reaction (8), these arsenopyrite crystals do not appear to be concentrated in dilational structures and do not have rare sulfosalts associated with them.

**Arsenopyrite Stability-Relations in Low-Sulfur Environments: Path E: Metamorphosed Iron Formations**

In addition, we have shown that arsenopyrite stability is governed by pyrite-breakdown reactions in most rocks, so we can examine the fate of pyrite in metamorphosed iron-formations to gauge whether arsenopyrite would melt or be preserved.

In BIF-hosted gold deposits in Archean greenstone belts around the world, mineralization is generally thought to have been introduced during or slightly after peak metamorphism. The gold is typically associated with disseminated pyrrhotite and arsenopyrite, with pyrite usually absent or rare (see e.g., Phillips et al. 1984, Smith 1996, Mueller 1997, Neumayr et al. 1998), although there are examples with significant pyrite (e.g., Vearncombe 1986). If such a deposit becomes metamorphosed, for example during a second cycle of orogenesis, melting of arsenopyrite is unlikely to occur for several reasons. Where pyrite is absent, two mechanisms are capable of raising sulfur fugacity.

One involves liberation of small amounts of sulfur from disseminated pyrrhotite as temperature increases (Fig. 2). A second involves consumption of arsenopyrite (which is typically only a minor component) through reaction (10), leaving less of it to melt if high enough f(S₂) conditions are reached. The abundant Fe oxides and silicates in iron formations are likely to inhibit rising sulfur fugacity through reactions similar to reaction (4), especially as temperatures rise toward the >700°C necessary for arsenopyrite melting through reaction (9). Even in deposits that do contain pyrite prior to metamorphism, reactions similar to reaction (4) are likely to sufficiently suppress rising f(S₂), such that neither of reactions (7), (8) or (9) can proceed.

The Geco deposit (discussed above) and Calumet deposit (Quebec, Canada) provide useful natural laboratories with which to compare the extent of pyrite consumption during metamorphism of iron formation versus massive sulfide. Like Geco, Calumet is thought to be a VMS deposit that was metamorphosed at 650–700°C and 4–6 kbar (Williams 1990). At Geco, massive sulfides are part of a stratigraphic sequence that includes sulfidic iron formation, and at Calumet sulfidic magnetite-rich layers also are preserved. At both areas, each of these units likely contained pyrite as part of the initial assemblage deposited in a subaqueous environment. Whereas the massive sulfide bodies at both mines preserve a significant proportion of pyrite as well as pyrrhotite (Fig. 7A), the magnetite-rich layers now contain abundant pyrrhotite and some sphalerite, but only sparse retrograde pyrite (Fig. 7B). Within the massive sulfides, sulfur fugacity was driven up along the pyrite–pyrrhotite buffer as metamorphism progressed because there were no competing reactions that consumed sulfur. In these areas, arsenopyrite melting might be expected given the high peak temperature (Fig. 5F shows assemblages that support arsenopyrite melting at Geco; no arsenic minerals were found at Calumet). In contrast, all pyrite in the iron formation was consumed during metamorphism, and high f(S₂) conditions were
never reached. In these regions, arsenopyrite (if it ever existed) would be expected to be either preserved or converted to pyrrhotite + löllingite (reaction 10).

**CONCLUSIONS**

Although melting of arsenopyrite may play a role in the melting of ore deposits during metamorphism, the tendency for arsenopyrite to melt is dependent on reactions in the surrounding rock and the evolution of sulfur fugacity. In most mineral deposits, the likelihood that it will melt, or instead be transformed into löllingite + pyrrhotite, depends upon the durability of pyrite. Where pyrite remains within the rock beyond ~560°C (at 5 kbar; 491°C at 1 bar), \( f(S_2) \) is buffered to high levels, and arsenopyrite will melt by reaction (7). In deposits with disseminated sulfides and moderately abundant Fe-bearing silicates and oxides, arsenopyrite is unlikely to melt because pyrite is more easily converted to pyrrhotite at relatively low temperatures in such rocks, precluding buffering of \( f(S_2) \) to the level required for reaction (7). Arsenopyrite that occurs in pyrrhotite-rich massive sulfides may melt by reactions (8) and (9), provided that the system remains closed to external fluids during progressive metamorphism. In summary, arsenopyrite-bearing massive Pb–Zn deposits and some disseminated gold deposits may be the most likely to experience arsenopyrite melting and generation of a multi-element sulfide melt capable of segregating ore metals, particularly gold and silver, through deformation-induced mobilization.

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