

Chemical behaviour of sphalerite and arsenopyrite in hydrothermal and metamorphic environments*

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ABSTRACT. Examples of application of equilibria in the systems Fe-Zn-S, Cu-Fe-Zn-S, Fe-As-S, and Fe-Zn-As-S are drawn from modern sulphide-forming hydrothermal vents on the East Pacific Rise, from ancient vein deposits and from metamorphosed sulphide ores. The ZnS content (1.2 and 1.3 mole %) of Cu-Fe-S intermediate solid solution (*iss*) from the sea-floor deposits gives temperatures of equilibration of 331° and 335 °C from experimental curves, in excellent agreement with the 350 °C expected from actual measurement of the hot springs. Heterogeneities in sphalerite in these deposits do not necessarily represent disequilibrium during deposition but can be explained simply by small fluctuations in a_{S_2} . Diagrams of $\log a_{S_2}$ vs. $1000/T, K$ for sphalerite and arsenopyrite are useful for estimating temperature and activity of sulphur in hydrothermal or metamorphosed deposits provided that equilibrium can be demonstrated and the systems are properly buffered.

The sphalerite geobarometer has had wide applications, some successful (mostly vein deposits) and some not (particularly metamorphosed ores in which chalcopyrite is in contact with sphalerite). Compositions of sphalerites which are totally enclosed within metablastic pyrites represent preserved high P - T equilibria which have been isolated from further reaction during subsequent retrograde conditions by the inert encapsulating pyrite and may provide more reliable estimates of pressure.

ATTEMPTS to use sulphide mineral equilibria for estimating temperature, pressure, and activities of components during ore formation or subsequent metamorphism have met with only partial success, the main problem being changes in compositions during cooling. Most sulphides easily undergo retrograde reactions and only the most refractory can provide reliable information from high P and T . Among the common sulphides, sphalerite and arsenopyrite are the best understood and most useful. Equilibrium compositions of these two minerals are usually preserved from hydrothermal vein deposits which cool relatively rapidly. However, equilibrium may not always be preserved, particularly for sphalerite, from regionally metamorphosed sulphides which can cool very slowly.

*Invited contribution.

This paper surveys recent experimental studies involving sphalerite and arsenopyrite, and gives examples of how these data may be applied for estimating temperatures, sulphur activities (a_{S_2}) and pressures. Examples are drawn from hydrothermal deposits in which quenching was relatively rapid, such as the recently discovered sulphide chimneys forming on the sea-floor of the East Pacific Rise and ancient vein deposits, as well as from metamorphosed base metal deposits where, despite slow cooling, some geobarometrically useful equilibria are preserved.

Fe-Zn-S system

Low pressure. Phase relations involving sulphides under conditions where pressure is not an important variable are most conveniently displayed on $\log a_{S_2}$ (or $\log f_{S_2}$)- $1000/T, K$ diagrams. Such a diagram for the Fe-Zn-S system is shown as fig. 1. Sphalerite has a maximum FeS content when in equilibrium with troilite (Fe-FeS buffer). The FeS content decreases gradually with increasing a_{S_2} across the pyrrhotine field until at the pyrrhotine-pyrite buffer the sphalerite contains 20.6 mole % FeS below 600 °C or slightly less FeS at higher temperatures. Within the pyrite field the decrease in FeS content of sphalerite with increasing a_{S_2} is much greater resulting in a close spacing of isopleths near the pyrite-pyrrhotine buffer and in very low FeS contents in sphalerite at high a_{S_2} . The effect of pressure on the diagram is to raise all buffer curves to higher values of a_{S_2} and all isopleths to even higher values (e.g. resulting in lower FeS content in sphalerite along the pyrite-pyrrhotine buffer). Below a kilobar these effects are very small, producing a shift of only a few hundredths of a $\log a_{S_2}$ unit per 100 bars. In a qualitative sense, it is commonly found that sphalerites formed at high a_{S_2} such as in equilibrium with bornite + pyrite + chalcopyrite (fig. 1) have a honey yellow to light brown colour consistent with their low FeS contents whereas those formed at lower a_{S_2} within the pyrite

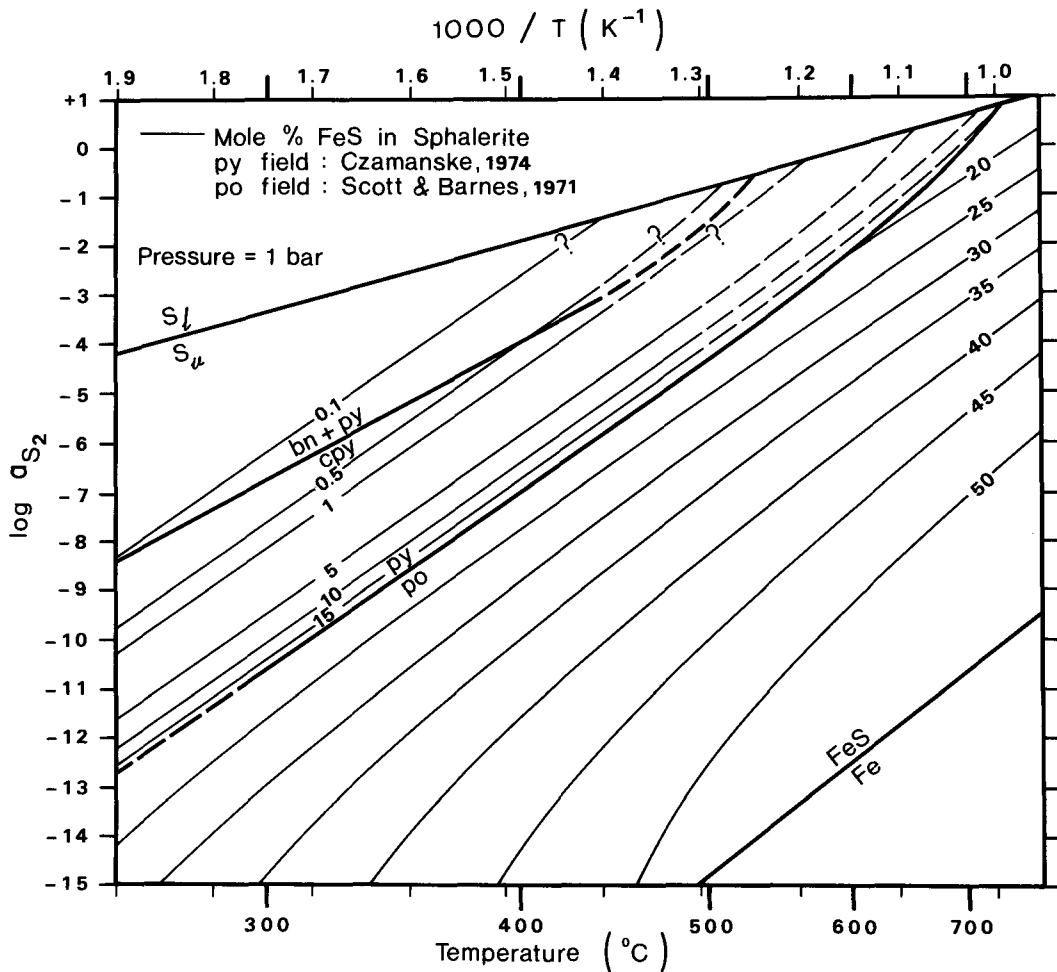


FIG. 1. Phase relationships for the Fe-Zn-S system at 1 bar compiled from Barton and Toulmin (1966), Scott and Barnes (1971) and Czamanske (1974). Isopleths are mole % FeS in sphalerite coexisting with pyrrhotine or pyrite. Abbreviations: bn, bornite; cpy, chalcopyrite (or intermediate solid solution); po, pyrrhotine; py, pyrite; S_{\downarrow} , liquid sulphur; S_{\uparrow} , sulphur vapour.

field or at any a_{S_2} within the pyrrhotine field are dark brown to black. The assemblage sphalerite + bornite + pyrite + chalcopyrite, which is not uncommon in porphyry copper ores and in some copper vein deposits, is a potential geothermometer (Czamanske, 1974). However, the shallow intersection of sphalerite isopleths with the buffer curve, coupled with the usual precision of electron microprobe analyses of only a few tenths mole % FeS precludes accurate estimation of temperature. The FeS-rich isopleths at lower a_{S_2} would be more useful for geothermometry provided an equilibrium buffer assemblage was present which cuts the isopleths at a steep angle. The pyrite-pyrrhotine assemblage is not a convenient buffer except above

600 °C because it is parallel or nearly so to the sphalerite isopleths. I will return to these geothermometric discussions below.

Fig. 1 may be more suitable for estimating a_{S_2} than temperature. Styr et al. (1981) and Hekinian et al. (1980) have reported microprobe analyses of zinc sulphide (wurtzite and sphalerite) from hydrothermal vents at 21° N. on the East Pacific Rise (water depth 2600 m, confining pressure 260 bars, maximum T of vented fluids 350 °C). Their analyses show a wide scatter but when viewed in the context of variations in sphalerite compositions with a_{S_2} , in fig. 1, the scatter is not unexpected. For example, Hekinian et al. (1980) found that most sphalerites coexisting with pyrite in inactive vents

(CYAMEX area) contain 14–20 mole % FeS and those included within pyrite 15–25%. Inactive vent material analysed by Styrst *et al.* (1981) gave 6–21 mole % FeS. For a reasonably constant temperature of precipitation of zinc sulphide, all of Styrst *et al.*'s (1981) analyses lie within a remarkably small range of one order-of-magnitude in a_{S_2} (i.e. 10^{-10} to 10^{-11} for 300 °C) within the pyrite stability field immediately adjacent to the pyrrhotine field. The zinc sulphide compositions more FeS-rich than 21 mole % found by Hekinian *et al.* (1980) and by Styrst *et al.* (1981) (up to 33% in active vents) are probably a consequence of periodic excursions of a_{S_2} into the pyrrhotine stability field and is consistent with the observation by Haymon and Kastner (1981) that the iron sulphide precipitating in the 'black smoke' issuing from the vents is hexagonal pyrrhotine. Similar variations in composition of zinc sulphides are seen in active vents at 21° N. where temperatures of venting are accurately known. Samples of wurtzite coexisting with pyrite, barite, and anhydrite from two active vents whose temperatures were measured to be 273 and 295 °C contain 9.5–16.2 and 12.0–16.8 mole % FeS, respectively (Marjorie Styrst, pers. comm., 1981). Despite the rather wide range of FeS contents and assuming that fig. 1 applies equally well to wurtzite as to sphalerite and that the depositional temperature was the same as was measured in the vent fluids, these samples give very similar values for $\log a_{S_2}$ of 11.4 ± 0.3 and 10.5 ± 0.2 , respectively. The reason for the small variation in $\log a_{S_2}$ over a wide range of sphalerite composition coexisting with pyrite is, of course, the close spacing of the sphalerite isopleths near the pyrrhotine stability field in fig. 1. In fact, compositionally zoned sphalerites should be expected from hydrothermal ores formed under comparable conditions of a_{S_2} and temperature within the pyrite stability field because a_{S_2} is unlikely ever to be buffered so precisely to give constant compositions. Such buffering is possible, however, through long term annealing during metamorphism.

High pressure (sphalerite geobarometry). The variation of FeS content in sphalerite as a function of pressure when buffered by pyrite and hexagonal pyrrhotine is independent of temperature over a considerable range (fig. 2) and has given rise to the concept of the sphalerite geobarometer (Barton and Toulmin, 1966; Scott and Barnes, 1971; Scott, 1973, 1976; Hutchison and Scott, 1981). The geobarometer has received wide applications, some successful and some not. Most of the successes have been with hydrothermal mineralization in which cooling was reasonably fast such as skarns (e.g. Shimizu and Shimazaki, 1981) and veins (e.g. Hudson Bay Mountain area; Hutchison and Scott,

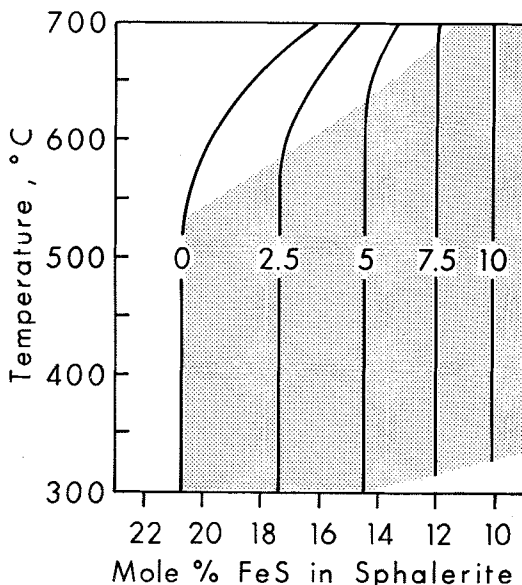


FIG. 2. Temperature-composition section along the ZnS-FeS join of the system ZnS-FeS-S of sphalerite + pyrite + hexagonal pyrrhotine equilibria as a function of pressure (in kbar). Temperature-independent portion of the isobars is shaded. Drawn from the data of Boorman (1967), Scott and Barnes (1971), Scott and Kissin (1973), Scott (1973), Lusk and Ford (1978), and Hutchison and Scott (1981). From Hutchison and Scott (1980).

1981). Metamorphosed deposits which have cooled very much more slowly, on the other hand, commonly show evidence of extensive retrograde changes in sphalerite composition, particularly in Cu-rich environments (Hutchison and Scott, 1981). The resulting sphalerites are considerably depleted in FeS relative to that expected from the high P and T of metamorphism and, indeed, are more consistent with compositions expected from a low-temperature assemblage of sphalerite + pyrite + monoclinic pyrrhotine (Scott and Kissin, 1973). In order to avoid the problems attending retrogression and the very real but not understood interference by copper, sphalerite inclusions, and particularly those with accompanying pyrrhotine as in fig. 3, that are totally encapsulated in pyrite should be sought and analysed. Presumably, such poikiloblastic inclusions were equilibrated during or near peak metamorphic conditions. They display the requisite buffer assemblage and would have been protected from hydrothermally enhanced retrogression by the inert encapsulating pyrite. Such inclusions are not uncommon in metamorphosed ores and their analysis from a wide variety of deposits is now required in order to test their usefulness for geobarometry.

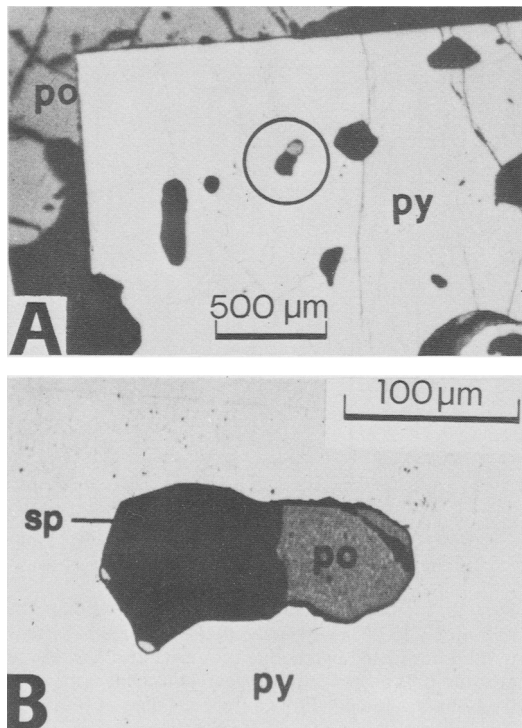


FIG. 3. (A) Poikiloblastic pyrite from the Ducktown Cu-Zn metamorphosed massive sulphide deposit, Tennessee. One inclusion containing both sphalerite and pyrrhotite (circled) and suitable for sphalerite geobarometry is enlarged in (B). Some inclusions in (A) are transected by fractures so may have been accessed by fluids during retrograde metamorphism and are unsuitable for geobarometry.

Cu-Fe-Zn-S system

A texture commonly seen in hydrothermal Cu-Zn sulphide ores is an emulsion of tiny (1 to 20 μm) chalcopyrite inclusions in sphalerite. The texture has been named 'chalcopyrite disease' by Barton (1970, 1978) who has described examples from vein deposits at Creede, Colorado and from the Kuroko massive sulphide deposits (fig. 4). Chalcopyrite disease is also found in zinc sulphides from hydrothermal vents of the East Pacific Rise at 21° N. (Oudin, 1981; Février, 1981) and of Guaymas Basin in the Gulf of California (Scott *et al.*, 1983). Traditionally, the texture has been described as an exsolution of chalcopyrite from sphalerite. However, Barton (1970, 1978) and Kalogeropoulos (1982) have convincing evidence that 'chalcopyrite disease' is a 'cancerous' replacement produced by Cu in aqueous solution reacting with FeS in sphalerite. Their arguments are borne out by the experimental

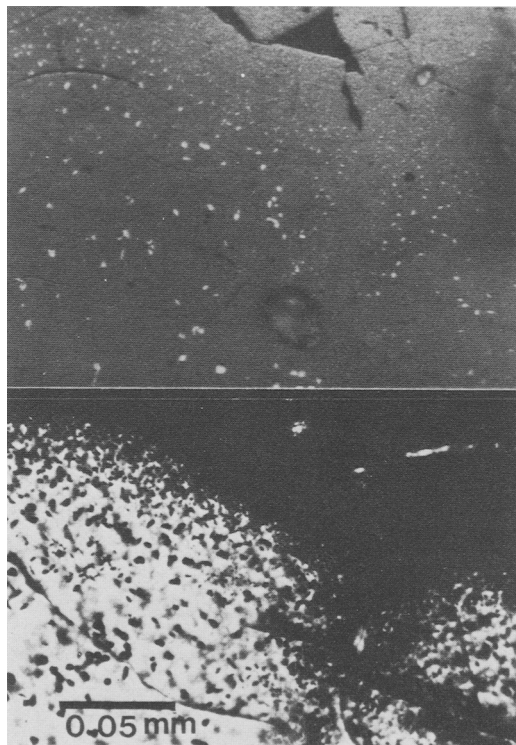


FIG. 4. Small blebs of chalcopyrite in sphalerite ('chalcopyrite disease') from the Uwamuki no. 2 Kuroko deposit, Kosaka mine, Japan. (Upper) reflected light; (lower) transmitted light. The concentration of chalcopyrite at the top of each photomicrograph is so high as to render the normally translucent sphalerite opaque in transmitted light. From Farr (1980).

data of Hutchison and Scott (1981) who have shown that at high a_{S_2} , such as those encountered in the above examples, the solubility of CuS in sphalerite is very low, less than 1 mole % below 600 °C. The cited examples formed at far below 600 °C (200–400 °C) where the equilibrium solubility of Cu in sphalerite must be in the range of tens or hundreds of ppm which, together with the fact that the samples from the East Pacific Rise were quenched rapidly in ambient 3 °C seawater, rules out the possibility of exsolution being an explanation for 'chalcopyrite disease'. Nevertheless, this texture can easily be confused with exsolution and it is not difficult to envisage how such chalcopyrite might be redistributed during recrystallization to produce a texture which would be indistinguishable from true exsolution.

ZnS solubility in Cu-Fe sulphide intermediate solid solution (*iss*) is another possible geothermometer (fig. 5) although its use is restricted to

those rare natural occurrences where *iss* has been preserved and has not inverted to other Cu-Fe sulphide phases. The composition of *iss* which coexists with sphalerite + pyrite + pyrrhotine is near CuFe_2S_3 (Hutchison and Scott, 1981). Fortunately, this is the portion of the extensive *iss* field which can be quenched and *iss* is found in samples from

Fe-As-S system

The Fe-As-S system (figs. 6 and 7) determined by Kretschmar and Scott (1976) has had modest success in estimating a_{S_2} during tin mineralization at Renison Bell, Tasmania (Patterson *et al.*, 1981) and as a geothermometer in metamorphosed massive sulphide deposits of the Skellefte district in Sweden (Berglund and Ekstrom, 1978), an Archaean banded iron formation from Western Australia (Gole, 1980), a silver vein deposit from Nevada, USA (Vikre, 1981), and topaz greisen veins in Missouri (Lowell and Gasparini, 1982). However, as presently constituted, the arsenopyrite geothermometer is useful only when the univariant buffer assemblages in figs. 6 and 7 are operative. Arsenopyrite may be a common mineral in ores but the buffering phases löllingite, arsenic, and As-S liquid (solidified to orpiment and realgar) are not. In order to make full use of the arsenopyrite isopleths of fig. 6 an appropriate a_{S_2} sliding scale buffer is required which occurs commonly with arsenopyrite, does not form a solid solution with arsenopyrite and whose isopleths cut those of arsenopyrite at a steep angle. Sphalerite coexisting with pyrite or pyrrhotine (or both) meets these criteria.

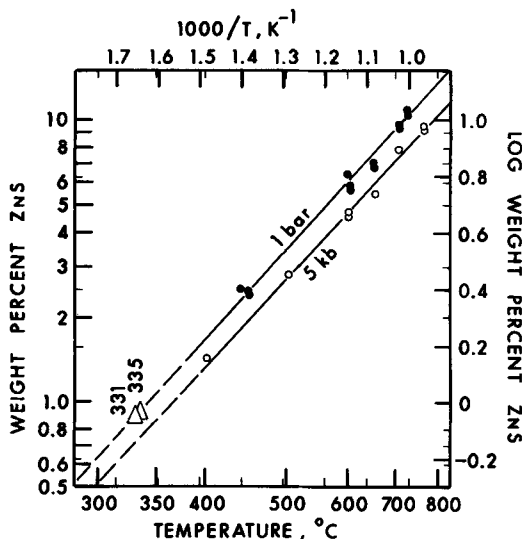


FIG. 5. Solubility of ZnS in intermediate solid solution (*iss*) coexisting with pyrite and pyrrhotine in the Cu-Fe-Zn-S system as a function of temperature and pressure (1 bar, 5 kbar). Experimental data are from Hutchison and Scott (1981). Triangles are analyses of ZnS in *iss* by Oudin (1981) from sulphide chimneys at 21° N. of the East Pacific Rise. Confining pressure here is about 260 bars.

hydrothermal vents at 21° N. (Styrt *et al.*, 1981; Haymon and Kastner, 1981; Oudin, 1981; Février 1981) and Guaymas Basin (Scott, unpubl.). Two *iss* samples analysed by Oudin (1981) contain 1.2 and 1.3 mole % ZnS from which fig. 5 provides estimated temperatures of equilibration of 331 and 335 °C, respectively. These are very close to the 350 °C maximum temperature of the 21° N. vents and suggest that equilibrium may have prevailed. Analyses by A. J. Brackmann (unpubl.) give a range of 1.4 to 3.2 mole % ZnS in *iss* corresponding to 343 to 440 °C. In making these temperature estimates from *iss* analyses I have assumed that the experimentally determined curves of Hutchison and Scott (1981) in fig. 5 can be reasonably linearly extrapolated to lower temperatures and that the small increase in a_{S_2} above the pyrite + pyrrhotine solvus as was deduced from fig. 1 is unimportant.

Fe-Zn-As-S system

Phase relations for the Fe-Zn-As-S system (fig. 8) were obtained by simply combining figs. 1 and 6. (See also Barton, 1970, Fig. 8). Secondary reactions which may occur between sphalerite and As phases have been ignored and are assumed to be unimportant because Zn-As-S minerals are not found in ores, whereas coexisting sphalerite and arsenopyrite are ubiquitous under a wide range of pressure and temperature conditions. The isopleths for sphalerite and arsenopyrite in an assemblage with pyrite and/or pyrrhotine intersect at sufficiently large angles in fig. 8 to constitute a useful geothermometer. Furthermore, because each isopleth is univariant at fixed pressure, their intersections are invariant and define a unique a_{S_2} as well as temperature.

The area of superposition of arsenopyrite and sphalerite compositions covers that in which many ore deposits are formed or metamorphosed. However, the diagram is rather cluttered and awkward to use. For geothermometric purposes, the same data are better displayed on temperature-composition axes (fig. 9). This diagram is drawn for 1 kbar pressure, which is appropriate for many hydrothermal veins, by applying the pressure corrections for Zn-Fe-S equilibria determined experimentally by Scott (1973) and Hutchison and

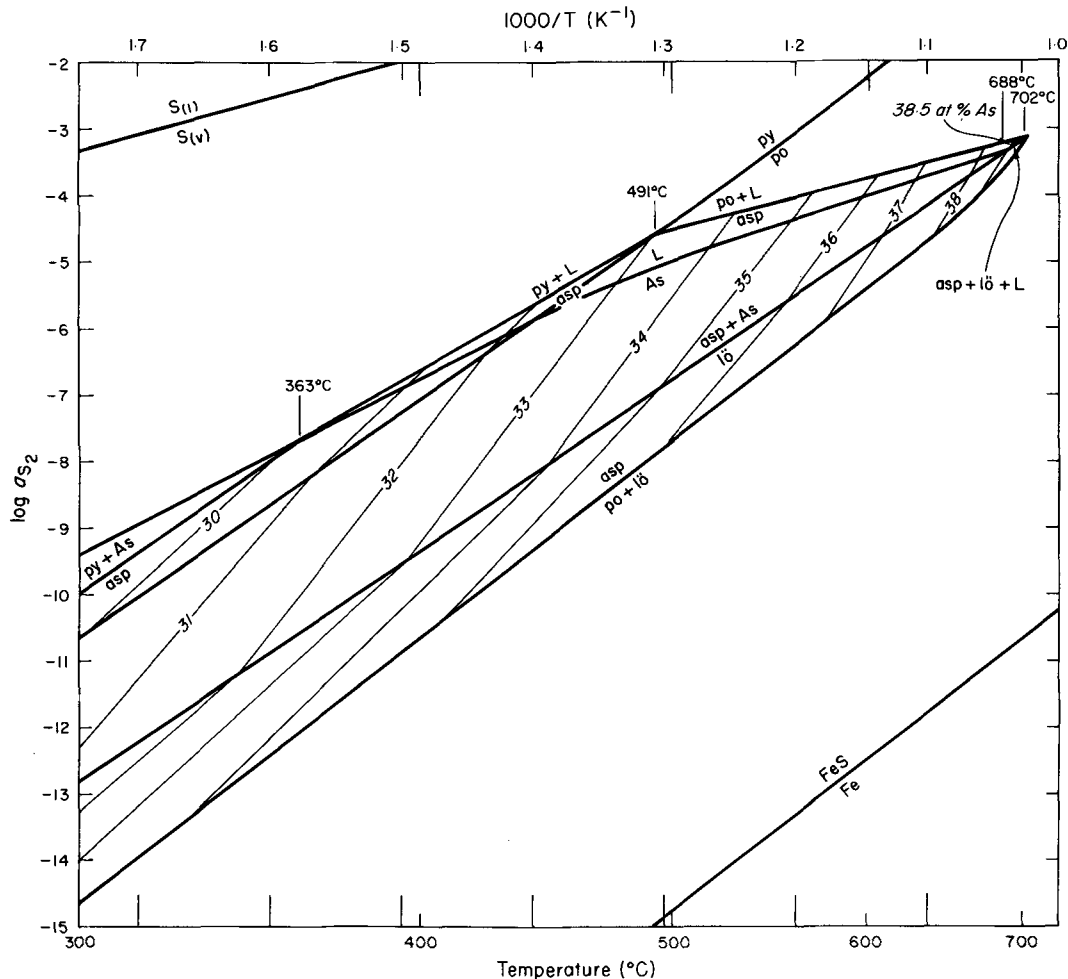


FIG. 6. Phase relations for the Fe-As-S system in equilibrium with vapour. Isopleths are atomic % As in arsenopyrite. Abbreviations as in fig. 1 plus the following: asp, arsenopyrite; L, As-S, liquid; l6, löllingite. From Kretschmar and Scott (1976).

Scott (1981) and assuming no effect by pressure on Fe-As-S equilibria as concluded by Kretschmar and Scott (1976). The effects of confining pressure on estimated temperature for an arsenopyrite-sphalerite pair is very small, approximately 4 °/kbar at 1 kbar.

As an example of an application of fig. 9, Kirkham (1969) and Kretschmar (1973) have analysed two coexisting sphalerites and arsenopyrites occurring with pyrite in base metal veins surrounding the cogenetic Hudson Bay Mountain porphyry molybdenum deposit in British Columbia. Sphalerite geobarometry (fig. 2) indicates a confining pressure of 1.5 ± 0.5 kbar (Hutchison and Scott, 1981) so fig. 9 is applicable. The coexisting arseno-

pyrite and sphalerite compositions (31 atomic % As and 20 mole % FeS; 31.8 atomic % As and 18 mole % FeS) give estimated temperatures of 360 and 425 °C, respectively. Liquid+vapour fluid inclusions analysed by Bloom (1981) from the central molybdenite deposit homogenize over a temperature range of 300–440 °C but their relationship to the surrounding base metal veins is not known.

Fig. 9 can also be used to detect obvious disequilibria between sphalerite and arsenopyrite. For example, sphalerite coexisting with arsenopyrite and pyrite must contain about 10 or more mole % FeS. Sphalerites in this assemblage from the Rosebery massive sulphide deposit in Tasmania

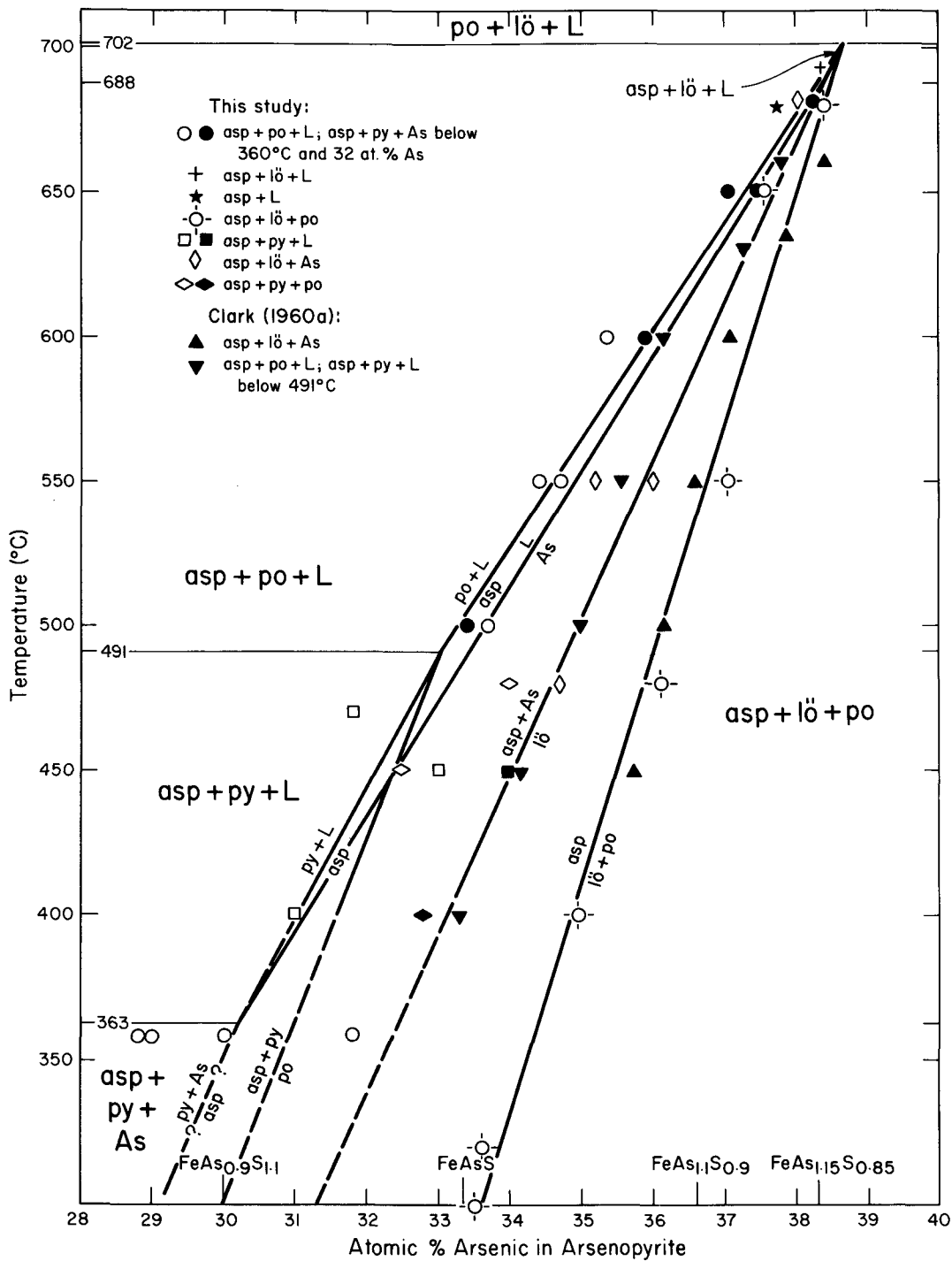


FIG. 7. Pseudo-binary condensed T-X section along the pyrite-löllingite join of the Fe-As-S system (from Kretschmar and Scott, 1976). Abbreviations are as in fig. 6.

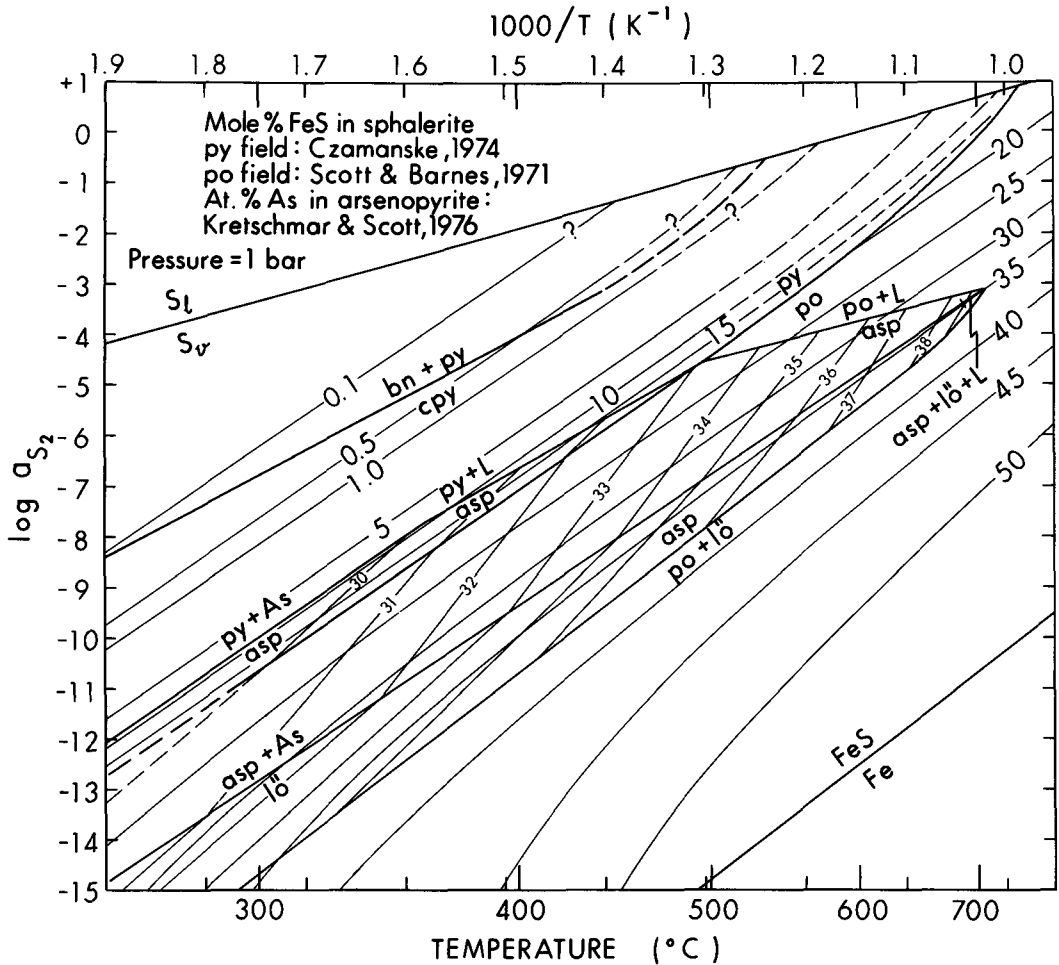


FIG. 8. Compositions of coexisting sphalerite and arsenopyrite at low pressure for the Fe–Zn–As–S system obtained by superimposing figs. 1 and 6. The small difference in pressure between the two figures (1 bar *vs.* vapour pressure) is insignificant. Isoleths are in mole % FeS for sphalerite and atomic % As for arsenopyrite.

contain less than 5 mole % FeS and Green *et al.* (1981) correctly concluded that the minerals were not in equilibrium.

Conclusions

Diagrams of $\log a_{S_2}$ *vs.* $1000/T, K$ for sphalerite and arsenopyrite can provide reliable estimates of temperature and a_{S_2} during ore formation provided the samples are cooled sufficiently rapidly to avoid retrograde reactions. Many hydrothermal vein deposits and, particularly, the mineral mounds and chimneys presently forming from hot springs on the deep ocean floor at various sites along the East Pacific Rise satisfy this constraint. Heterogeneities in sphalerite compositions from the sea-floor

deposits are readily explained by surprisingly small fluctuations in a_{S_2} , and is the preferred explanation for compositionally zoned sphalerites from ancient vein deposits as well. Emulsions of chalcopyrite inclusions in sphalerite seen both in sea-floor and vein deposits can be explained only by replacement in the light of textural observations and experimental data on the solubility of Cu in sphalerite.

Arsenopyrite, which is even more refractory than sphalerite, has been applied successfully for estimations of either a_{S_2} or temperature. However, with the exception of pyrite + pyrrhotine, the essential buffered assemblages are uncommon. By combining sphalerite solid-solution equilibria with arsenopyrite compositions in the presence of pyrite

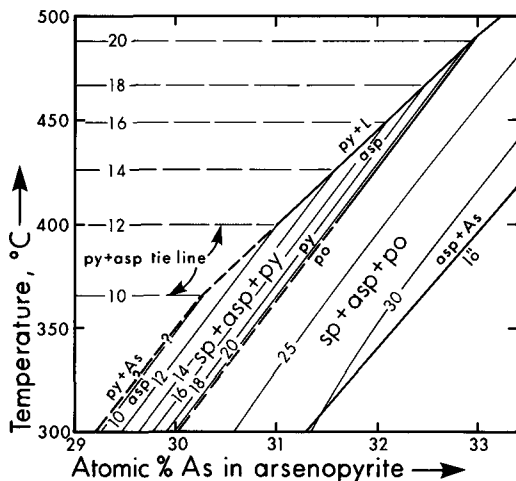


FIG. 9 Compositions of sphalerite and arsenopyrite coexisting together with pyrite and/or pyrrhotite at 1 kbar confining pressure. Contours are mole% FeS in sphalerite.

or pyrrhotite, unique values of both a_{S_2} and temperature can be obtained.

The pressure dependence of sphalerite composition in the Fe-Zn-S system is reasonably well known for all a_{S_2} -buffered assemblages. However, further experimental work is needed to elucidate the effect of pressure on arsenopyrite equilibria so that diagrams for combined sphalerite and arsenopyrite systems can be prepared over a range of pressures pertinent to all ore-forming and metamorphic conditions.

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