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PHASE RELATIONS INVOLVING ARSENOPYRITE IN THE SYSTEM Fe-As-S AND THEIR APPLICATION[1]

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ABSTRACT

Subsolidus recrystallization experiments in the system Fe-As-S have been carried out using dry, eutectic, halide fluxes to speed reaction rates. At 300°C the composition range of arsenopyrite extends from less than 30 at. % As in equilibrium with pyrite and arsenic to approximately 33.5 at.% As in equilibrium with pyrrhotite and loellingite. At 700°C arsenopyrite contains approximately 38.5 at. % As irrespective of the assemblage in which it is synthesized. The As-content of arsenopyrite may be obtained from its d_{131} and the equation:

At. % arsenic $= 866.67\ d_{131} - 1381.12$

Microprobe analyses show that natural arsenopyrite crystals coexisting with pyrrhotite, pyrite or pyrite+pyrrhotite are commonly zoned with a S-rich center and an As-rich rim. The zoning in arsenopyrite from As-rich environments is in the opposite sense. At present, the most reasonable explanation is that the zoning reflects local disequilibrium during growth. However, the overall compositional limits of natural arsenopyrites are dependent on the coexisting Fe-As-S minerals and these limits correspond very well with compositional limits determined experimentally. Because of its refractory nature, arsenopyrite does not readily re-equilibrate on cooling and its composition reflects formation temperature provided an estimate of the sulfur activity prevailing at deposition can be made from the coexisting minerals.

The results of high-pressure experiments were not conclusive, but taken in conjunction with calculations and the composition of arsenopyrite from metamorphosed ore deposits, they suggest that the effect of confining pressure is much smaller than indicated by Clark (1960c) and that arsenopyrite is unlikely to be a useful geobarometer.

SOMMAIRE

Des expériences de recristallisation sub-solidus dans le système Fe-As-S ont été effectuées à l'aide de flux d'halogénures secs et eutectiques afin d'augmenter la vitesse des taux de réaction. A une température de 300°C, la gamme de compositions d'arsénopyrite s'étend de moins de 30% (atomique) As en équilibre avec la pyrite et l'arsenic, jusqu'à environ 33.5 at. % As en équilibre pour la pyrrhotine et la loellingite. A 700°C, l'arsénopyrite contient presque 38.5% d'atomes d'As, ceci sans dépendre de l'assemblage dans lequel elle est synthétisée. Le contenu en As de l'arsénopyrite est lié à d_{131} par l'équation:

% atomique d'arsenic $= 866.67\ d_{131} - 1381.12$

Des analyses à la microsonde électronique démontrent que les cristaux naturels d'arsénopyrite en co-existence avec la pyrrhotine, la pyrite ou la pyrite+pyrrhotine sont souvent zonés avec un centre riche en S et une bordure riche en As. C'est le contraire pour l'arsénopyrite provenant de milieux riches en As. Actuellement, la meilleure explication est que la zonation reflète un déséquilibre local pendant la croissance. Par contre, les limites de composition des arsénopyrites naturelles dépendent des minéraux Fe-As-S co-existants; ces limites correspondent très bien aux limites compositionnelles déterminées par les synthèses. L'arsénopyrite, à cause de sa nature réfractaire, ne peut atteindre l'équilibre en refroidissant, et sa composition indique la température de formation, en autant qu'une évaluation de l'activité du soufre lors de la déposition peut se faire à partir des minéraux co-existants.

Les résultats des expériences à haute pression n'ont rien apporté de définitif; cependant, s'ils sont considérés avec les calculs et la composition de l'arsénopyrite provenant de gisements de minerai métamorphosés, ils suggèrent que l'effet de la pression lithostatique est moins important que ne l'avait proposé Clark (1960c) et que l'arsénopyrite ne sera probablement pas un géobaromètre utile.

(Traduit par le journal)

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[1] Tables of data from this study pertaining to interlaboratory microprobe analyses of arsenopyrite standards; detailed microprobe analyses of arsenopyrites produced in experiments and other experimental details; microprobe analyses of loellingite, pyrite, pyrrhotite and sphalerite produced in various experiments; and microprobe analyses of natural arsenopyrites are in Kretschmar (1973), a microform copy of which can be obtained at nominal cost from Canadian Theses, National Bibliographic Division, National Library of Canada, 395 Wellington Street, Ottawa, Ontario K1A 0N4.

Analyzed arsenopyrite samples from this study are stored at the Department of Mineralogy and Geology, Royal Ontario Museum, Toronto, Ontario M5S 2C6.

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INTRODUCTION

Arsenopyrite, $FeAs_{1\pm x}S_{1\pm x}$, is the most refractory of the common sulfides which, together with its wide range in As/S ratio, makes it a potentially useful geochemical tool for deciphering conditions of its formation. In recognition of the possible usefulness of such a goethermometer–geobarometer, Clark (1960a) determined detailed phase relationships in the condensed Fe-As-S system between 400° and 750°C and also investigated the effect of pressure to 2.07 kbar. The results of his study have been applied widely for estimating temperatures and pressures of formation or metamorphism of ore deposits.

Figure 1 depicts our present knowledge of phase relationships in the Fe-As-S system over the temperature range of interest to geologists. Clark's geothermometer is based on the variation of *d* of the (131) X-ray reflection of synthetic arsenopyrite as a function of assemblage (Fig. 1) and temperature at which it is synthesized. The geobarometer stems from Clark's (1960b,c) observation that confining pressure apparently produces a more S-rich arsenopyrite for each assemblage and temperature, and raises the invariant point involving arsenopyrite +pyrite+pyrrhotite+liquid+vapor (491°C in Fig. 1) by 1.8°C/kbar.

In applying Clark's data it is usually assumed that naturally-occurring arsenopyrite lies at its S- or As-saturated compositional limit. However, Barton (1969) cautioned that this is not necessarily so. Proper application of arsenopyrite as a geochemical tool requires an estimate of sulfur activity, $a(S_2)$, during equilibration in nature. Barton (1969) made an important contribution to our further understanding and use of the Fe-As-S system by measuring, with the pyrrhotite-indicator method (Toulmin & Barton 1964), the $a(S_2)$-dependence of sulfidation reactions involving arsenopyrite (Fig. 2). The essence of the arsenopyrite geothermometer-geobarometer is to determine the composition of arsenopyrite as a function of temperature and pressure in each of the assemblages surrounding arsenopyrite in Figure 1 or, in other words, to determine how the composition of arsenopyrite varies along each segment of the buffer curves in Figure 2.

Our study is an attempt to present an internally consistent thermochemical model of arsenopyrite formation and falls into two parts. First, it is an experimental reinvestigation and extension to temperatures below 400°C of phase relations involving arsenopyrite in the system Fe-As-S. In recent years there have been substantial improvements in experimental and analytical techniques and Barton's (1969) sulfidation study has provided an important framework within which to reconsider arsenopyrite geochemistry. The general phase relations involving arsenopyrite (Fig. 1) are in agreement with the results of Clark (1960a) and Barton (1969), but there are significant differences from Clark's results in the composition of arsenopyrite from various assemblages, and his effects of confining pressure could not be reproduced. The second part of our study consists of a detailed examination of the compositional variation of arsenopyrite from a large number of occurrences in order to test whether this compositional variation is consistent with the experimental results.

Symbols and abbreviations are given in Table 1. Standard deviation of the mean of d_{131} is expressed in the same unit as the last decimal(s) quoted in the mean (e.g. $d_{131} = 1.6341 \pm 3$ means 1.6341 ± 0.0003).

EXPERIMENTAL PROCEDURES

Arsenopyrite was synthesized in different bulk compositions surrounding its stability field (Fig. 1) by combination of the elements Fe, As

TABLE 1. SYMBOLS AND ABBREVIATIONS

As_i	at. % arsenic in arsenopyrite, determined by electron microprobe
$\overline{As}_i$	average of at. % As in arsenopyrite from microprobe analyses, reported as mean ± one standard deviation of the mean
As*	at. % arsenic in arsenopyrite, calculated from its d_{131} (equation 1)
s_{est}	standard error of estimate $s_{est} = \sqrt{(As^* - \overline{As}_i)^2/(n-2)}$
N	number of individual determinations (electron probe analyses or *d* measurements of arsenopyrite)
KL	KCl - LiCl flux
NL	NH_4Cl - LiCl flux
asp	arsenopyrite
lo	loellingite
orp	orpiment
po	pyrrhotite
py	pyrite
rl	realgar
L	sulfur-arsenic liquid whose composition is reported as L_x, where x = wt. % S
V	vapor
FAS	designation for experiments conducted in the system Fe-As-S
$a(i), a_i$	activity of component i

and S (99.999% pure) or of previously synthesized binary compounds Fe_2As, FeAs, FeS, FeS_2 and S-As glasses. The identity and homogeneity of starting materials were checked optically and by X-ray diffraction. Arsenic was heated in a thermal gradient to remove surface oxidation by distillation and, following Yund's (1962) suggestion, the compositions of S-As glasses were checked by measuring their specific gravity.

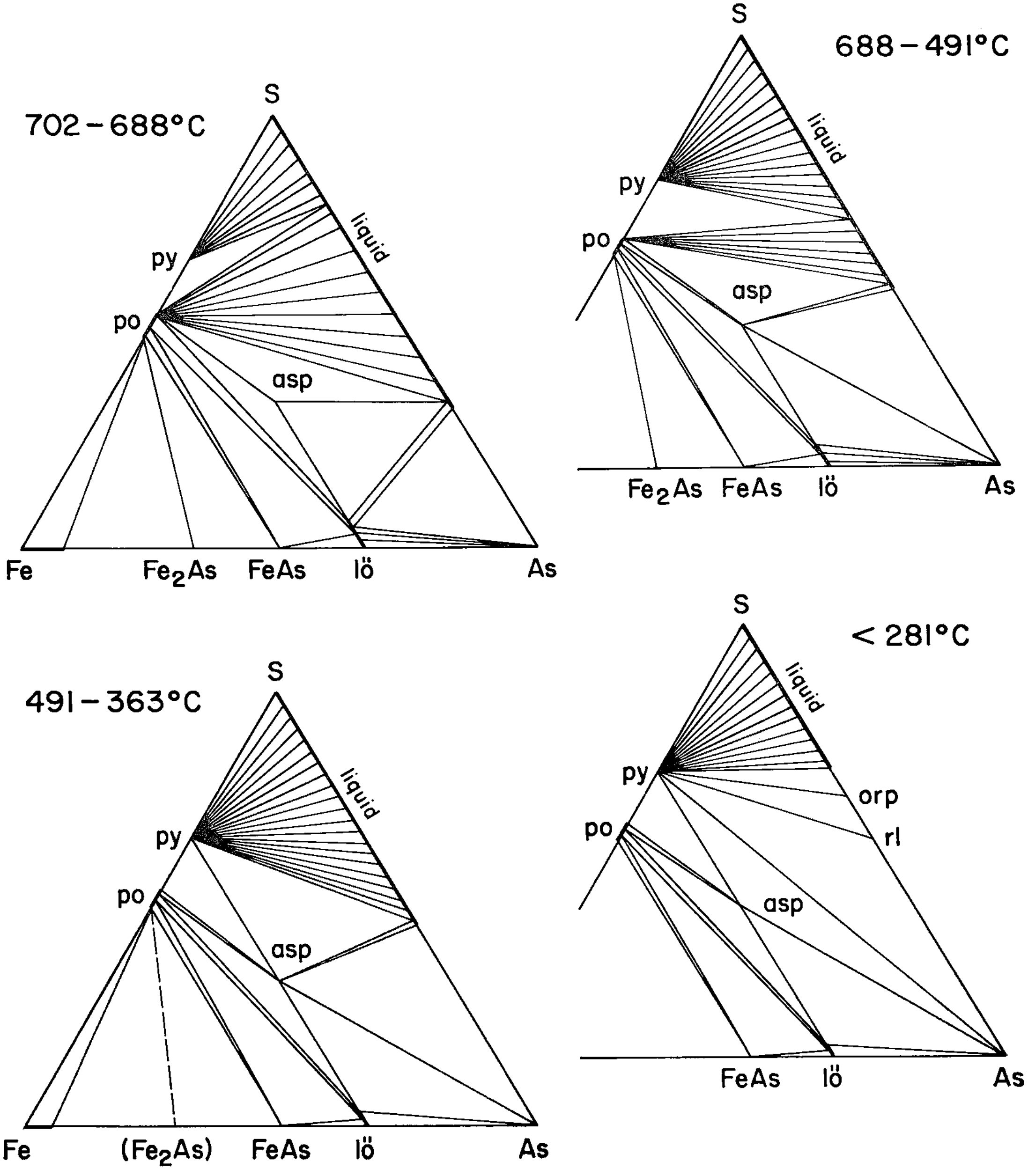

Fig. 1. Isothermal, polybaric sections through the condensed Fe-As-S system. Isotherms are drawn for the temperature midway in the ranges indicated and at 275°C (after Barton 1969). Arsenopyrite composition is shown schematically as stoichiometric FeAsS. Important invariant points involving arsenopyrite are asp=lo+po+L at 702±3°C (Clark 1960a); asp+As=lo+L at 688±3°C (Clark 1960a); asp+py=po+L at 491±12°C (Clark 1960a); py+As=asp+L at 363±50°C (Barton 1969).

Two types of charges were prepared. In a few high-temperature runs we followed standard procedures for evacuated silica tube experiments as outlined by Kullerud (1971) and Scott (1974a). In most experiments, particularly at low temperatures where sluggish reaction rates are a severe problem, we added eutectic mixtures of binary halides which were molten at the run temperatures and served to flux the reactions. The halide mixtures which we used (with mole ratio and temperature range) were KCl–LiCl (KL, 42:58, >360°C) and NH_4Cl–LiCl (NL, 50:50, 270–350°C). Procedures for preparing and handling these fluxes are given by Moh & Taylor (1971) and by Scott (1974a).

In both types of experiments, the silica tubes were heated in furnaces controlled within ±5°C or better. Periodically, the charges were quenched in cold water and carefully reground to facilitate reaction. At the termination of an experiment, charges were quenched and then examined optically, by X-ray diffraction and by electron microprobe.

In using fluxes, it is essential that salt components do not enter the FeAsS structure and that the salt system is thermodynamically inert relative to the sulfide system. Although it is difficult to demonstrate the former satisfactorily, the following observations are an indication that the fluxes play no part in the reaction and that their role is strictly that of a catalyst.

(1) Experimental results at low temperature where fluxes were used are consistent with

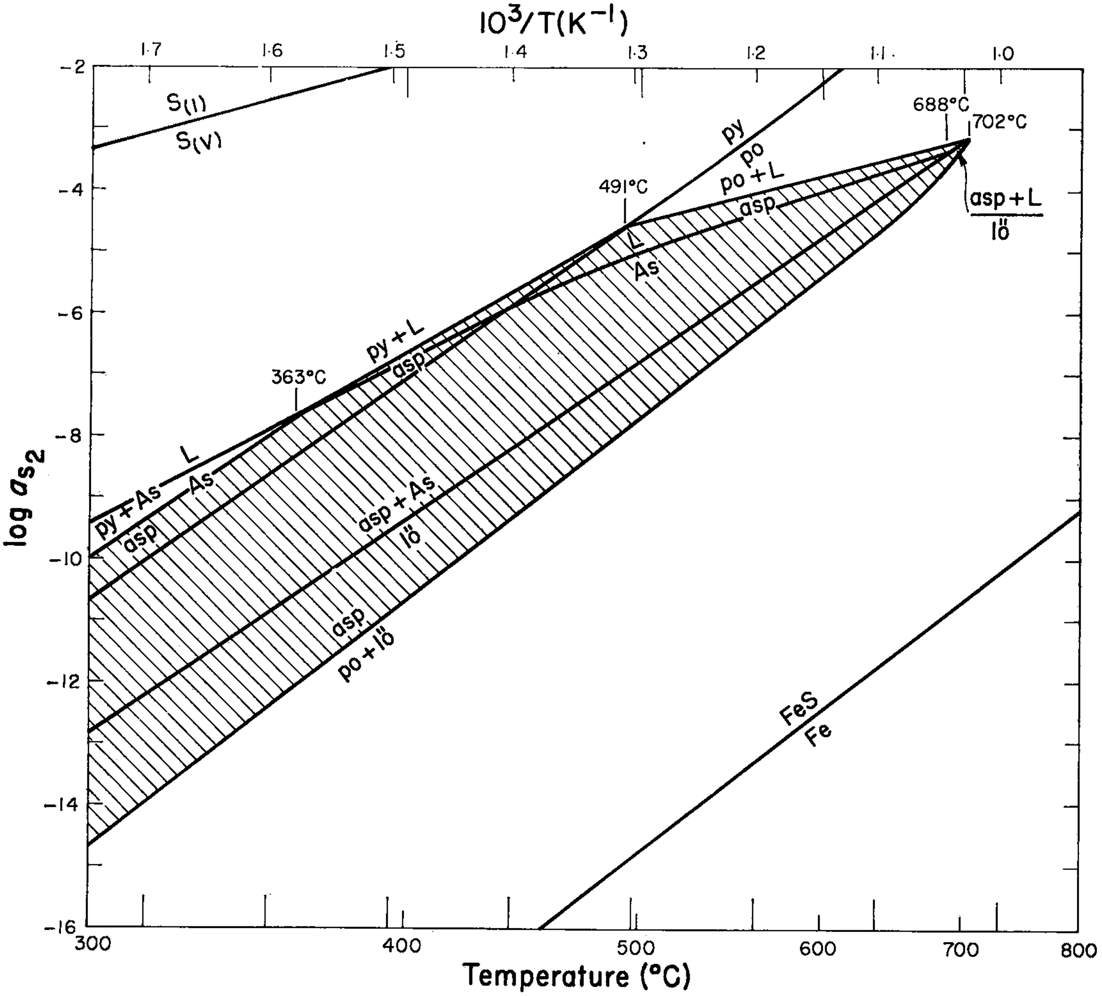

FIG. 2. Activity of S_2-temperature projection of buffered assemblages involving arsenopyrite in the Fe-As-S system (after Barton 1969). Pyrite-pyrrhotite (Scott & Barnes 1971), S_l-S_v (Braune *et al.* 1951) and Fe-FeS (Robie & Waldbaum 1968) are shown for reference. Arsenopyrite stability field is shaded.

those at high temperatures determined with and without salt fluxes.

(2) Qualitative electron microprobe analyses for Cl in selected high-temperature arsenopyrite produced in halide fluxes showed no detectable chlorine (i.e. less than about 0.1 wt. % Cl).

(3) The atomic properties of K, Li, NH_4 and Cl are not similar to those of Fe, As or S so they are not expected to substitute into the FeAsS lattice.

Both Klemm (1965) and Delarue (1960) found discoloration of the fluxes accompanied reaction between the flux and sulfide system. If the flux was clear upon termination of the annealing period, we assumed that no reaction had taken place between the flux and the charge and that the salt system had remained thermodynamically inert relative to the Fe-As-S system.

Attempts to synthesize FeAsS by hydrothermal recrystallization (Scott 1975) in NH_4Cl, NH_4I and HCl solutions met with failure. As early experiments showed that neither gold nor platinum could be used as containers because of reaction with arsenic (see also Clark, 1960a), silica tubes were used. These proved very difficult to seal especially for high-percent fill (high pressure) and many runs failed because the seal dissolved during the annealing period. Regardless of experimental conditions used, arsenopyrite dissolved nonstoichiometrically, forming large euhedral crystals of pyrite, pyrrhotite or arsenic at the cool end of the tube.

A few experiments were made at 5 kbar confining pressure in KL flux using the apparatus described by Scott (1973). Because of reaction between As and gold, the charge was contained in a silica tube, open at the top, and sealed inside a gold tube. A pin-hole in the gold allowed access of the argon pressure medium to the charge.

TABLE 2. d_{131} PEAK POSITION VS. ARSENOPYRITE COMPOSITION

Sample No.	d_{131}(Å)	N	$\overline{As_i}$ (at. %)	N	$As^{*\dagger}$	$s_{est}^{\dagger\dagger}$
Asp 2	1.6303±5	4	31.55±0.4	4	31.82	0.08
Asp 56	1.6292±6	5	30.99±0.68	3	30.86	0.04
Asp 57	1.6332±3	4	34.28		34.33	0.01
Asp 58	1.6300±4	4	31.75±0.23	4	31.55	0.07
Asp 130**	1.6353±2		36.04±0.45		36.15	0.03
Asp 135**	1.6312±2		33.2±0.45		32.85	0.10
Asp 137**	1.6340±2		34.50±0.45		35.02	0.15
Asp 138**	1.6352±2		35.98±0.8	4	36.06	0.02
Asp 200	1.6304±5	14	31.77±0.45	24	31.90	0.04
Asp 276	1.6311±4	8	32.93±0.6	3	32.49	0.13
FAS 41	1.6371±5	15	37.7±1.2	10	37.71	0.00
FAS 46C	1.6330		33.74±1.21	8	34.15	0.12
FAS 46D	1.6333±9	4	34.43±0.93	6	34.41	0.01
FAS 46E	1.6350±7	8	35.35±0.79	8	34.89	0.13

†Calculated from equation (1). $^{\dagger\dagger}n=14$ $^{**}d_{131}$ from Kelly & Turneaure (1970); $\overline{As_i}$ from at least 10 grains in grain mounts.

ANALYSES

X-ray diffraction

As Morimoto & Clark (1961) noted, changes in the position of the (131) peak of arsenopyrite are a sensitive indication of differences in arsenopyrite composition. The (131) peak has sufficiently high intensity, is well removed from most interfering peaks and, since it occurs at relatively high 2θ, may be precisely measured.

Arsenopyrite (131) spacings were determined using FeKα radiation, a single crystal monochromator (with graphite crystal) as detector and reagent-grade CaF_2 which had been annealed for 24 hours at 700°C as an internal standard. The (311) line of CaF_2 was calculated to be at 1.6470 Å from its unit cell edge of 5.4626Å* (Swanson & Tatge 1953). Arsenopyrite (131) peaks were scanned at least six times at ½° 2θ/min and a chart speed of 60 cm/hr. The sample, a glass slide smear mount, was rotated 180° about an axis normal to the slide between scanning cycles. Enough CaF_2 was added to make the intensity of the CaF_2 (311) peak roughly equal to (131) of arsenopyrite. All (131) measurements are reported as the mean and one standard deviation of the mean. The precision of at. % arsenic obtained from the (131) spacings, using a linear equation relating the two, is at least ±0.45 at. % As (one standard deviation) as discussed below.

Morimoto & Clark (1961) derived a linear equation relating d_{131} and arsenopyrite composition but according to Barton (1969) the equation is misprinted. It is also misprinted in Barton's paper and should read $d_{131} = 1.6006 + 0.00098$ at. % As. Inasmuch as this equation is based on only a few analyses, it was desirable to refine it. Only natural unzoned arsenopyrites with less than 1 wt. % combined Co, Ni and Sb and a few synthetic arsenopyrites were used to derive our X-ray determinative curve in Figure 3. An equation for this line is:

$$As^{*} = 866.67\, d_{131} - 1381.12 \qquad (1)$$

and has an estimated one standard deviation of ±0.45 in As*.

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*This value has been revised to 5.4638±0.0004Å (Robie *et al.* 1967) but the Swanson & Tatge value must be used with our calibration curve (Fig. 3).

The (131) values were obtained in the manner described above and at. % arsenic is from electron microprobe analyses. Individual data points are presented in Table 2. The line was drawn freehand to pass through Asp 200 and FAS 41 — data points for which we have the greatest number of determinations. An unweighted least-squares line (dot-dash in Fig. 3) with a correlation coefficient of 0.991 has the equation: As* = 832.08 d_{131} − 1324.70. It is nearly coincident with the line for equation (1). For a given d_{131} a much higher As value is obtained from equation 1 than from Morimoto & Clark's line (dashed in Fig. 3). Equation 1 was used throughout our study.

If either pyrite or loellingite are present in experimental reaction products in amounts greater than about 10%, it becomes impossible to determine the *d*-value of the arsenopyrite (131) line because of interference from pyrite (311) at 1.6332Å and loellingite (031) and (221) lines at 1.6401 and 1.6344Å respectively. This problem was overcome by preparing the bulk composition of the charge very close to arsenopyrite so that other phases were present in minor amounts relative to arsenopyrite.

Electron microprobe

Precise and accurate determination of the composition of arsenopyrite is an integral part of this study and considerable effort was expended in selection of a suitable standard for

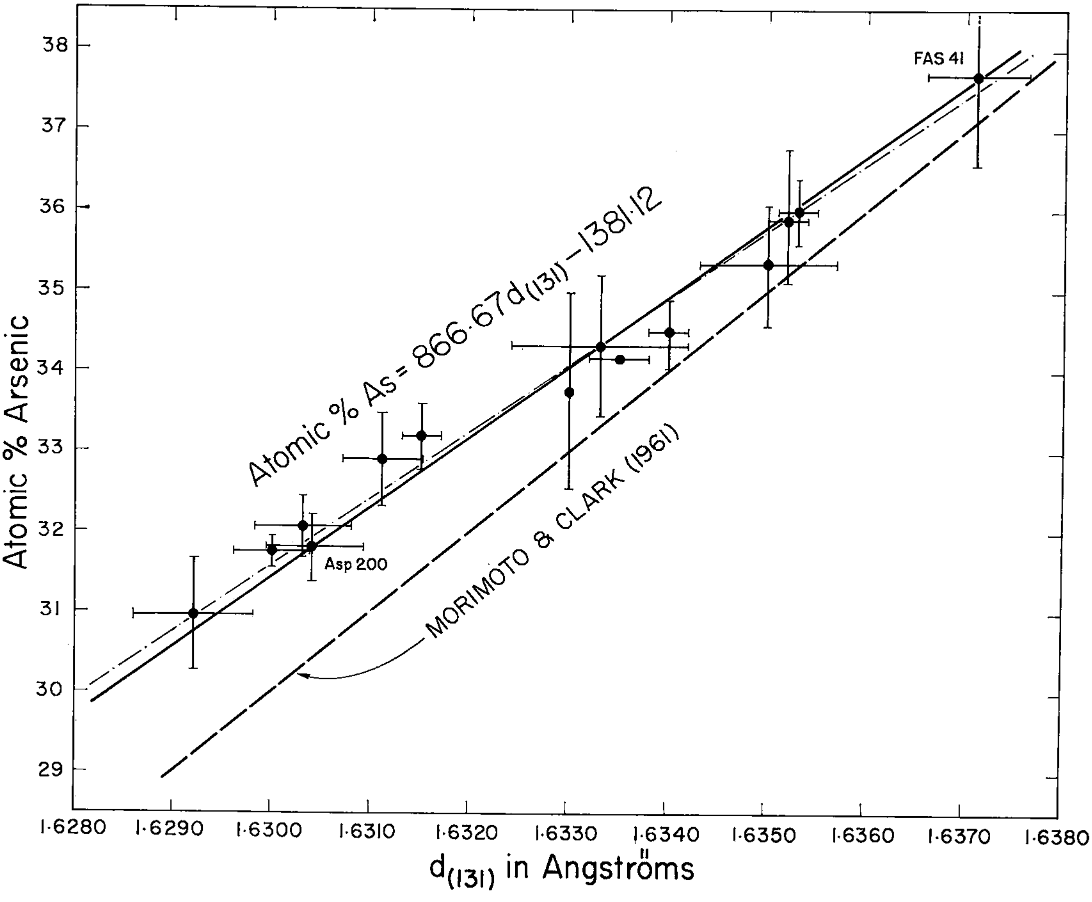

FIG. 3. Relationship between d_{131} X-ray peak position and arsenopyrite composition. Error bars represent one standard deviation of the mean for arsenic and d_{131} determinations (see Table 2). The solid line representing equation (1) was drawn to include FAS 41 and Asp 200. A least–squares line based on the same data has the equation As* = 832.08 d_{131}–1324.70 and is shown by dot-dash symbols. Arsenic values obtained using this equation are not significantly different from those obtained using equation (1) shown in the Figure. Equation (1) was used throughout this study. The curve from Morimoto & Clark (1961) has the equation $d_{131} = 1.6006 + 0.00098$ at. % As as corrected (but misprinted) in Barton (1969).

microprobe analysis. Several chemically analyzed samples that Morimoto & Clark (1961) described were available for study. Arsenopyrites were also provided by R. V. Kirkham (Kirkham 1969). These chemically analyzed arsenopyrites were checked for homogeneity and Co, Ni and Sb. Inhomogeneous arsenopyrites or those containing more than 1 wt. % combined Co, Ni and Sb were rejected. Each of the remaining suitable specimens was then used in turn as a standard to analyze the rest. Since the arsenopyrites had been chosen on the basis of superior chemical analyses, that sample which gave the closest correspondence between published chemical and microprobe analyses for the largest number of specimens was chosen as the microprobe standard. The wet chemical analysis for the sample so chosen, Asp 57, is presented in Table 3. All electron microprobe analyses of natural and synthetic arsenopyrite reported in this study were obtained using the same approximately 1 mm square area on a polished section of Asp 57 as standard.

Asp 200 is a natural, homogeneous, S-rich arsenopyrite without detectable Co or Ni (see below, however) from the Lucie pit of the Helen siderite mine near Wawa, Ontario. A 1 mm square spot on a single crystal was analyzed as an unknown at the beginning and end of each set of analyses throughout this study. Its composition, based on the first 24 such independent analyses on different days, is shown in Table 4.

The analytical procedure, data collection and correction of raw data are very similar to those described by Rucklidge *et al.* (1971) who used the same electron microprobe (ARL-EMX) and associated facilities. Data were corrected using EMPADR VII (Rucklidge & Gasparrini 1969). Analytical conditions used throughout this study are as follows: accelerating voltage = 15 kV; specimen current on Asp 57 = 0.03 microamps; beam current = 0.50 microamps; spectral lines = FeKα, AsLα, SKα, CoKα, NiKα and SbLα. Eight 10 sec. counts were collected on Asp 57 and on each spot on the unknown. The number of spots analyzed per unknown varied widely because it was not always possible to find the same number of suitable locations.

TABLE 3. WET CHEMICAL ANALYSIS OF Asp 57*

	Wt. %	At. %
Fe	33.85	33.17
As	46.94	34.28
S	19.08	32.55
Co	0.0042	
Ni	0.0011	
Bi	0.01	
Sb	0.04	
Cu	0.015	
Total	99.94	100.00

*Analysis by R.V. Kirkham; sample 65-144 of Kirkham (1969).

TABLE 4. THE COMPOSITION OF Asp 200 BASED ON 24 INDEPENDENT ELECTRON PROBE ANALYSES*

Element	Average Wt. %	At. %	One Std. Dev. (wt. %)	Range (wt. %)
Fe	34.51	33.10	0.20	33.8-35.3
As	44.44	31.77	0.45	43.7-46.1
S	21.03	35.13	0.31	19.8-21.6
Total	99.98			

*A limited number of chips from Asp 57 and Asp 200, that can be used as probe standards, are available from S.D. Scott.

Considerable difficulty was encountered during electron probe analysis of reaction products. Their fine-grained and intimately intergrown nature commonly precluded probing. Many reaction products were porous (multigrain aggregates mixed with S-As liquid) and resulted in low totals. A few zonal arrangements of reaction products persisted despite regrinding. Only analyses from well-formed grains with well-defined outlines, and which satisfied the following rigorous criteria, were used for determining arsenopyrite phase relations:

(1) The homogeneity index for all three elements, Fe, As and S must be less than 5. The EMPADR VII computer program indicates a homogeneity index for each analysis. This index is defined by Boyd *et al.* (1969) as the ratio of the observed standard deviation to the standard deviation predicted from counting statistics. Few analyses had to be rejected because the H.I. was greater than 5. In most cases it was <3 and usually <1, but in one or two instances it was necessary to accept a value of up to 5 for As.

(2) The analysis must sum to between 98.0 and 101.0 wt. %. It is possible to obtain acceptable microprobe analyses summing to less than 100.0 wt. % if the reaction products are porous. However, totals greater than 101.0 must be due to significant errors.

(3) An "analysis" must consist of at least two sets of 10 sec. counts. With very fine-grained reaction products and a very fine electron beam, some difficulty was occasionally encountered in keeping the beam on the sample.

(4) The final analysis for the elements Fe, As and S in the secondary standard Asp 200 must lie within two standard deviations of the composition accepted for Asp 200 (Table 4).

(5) If arsenopyrite contains iron in stoichio-

metric amounts (see discussion below), the at. % Fe in an analysis will give an indication of the quality of the microprobe analysis which is not apparent from the wt. % Fe since the latter may range from 30.3 to 35.5, depending on the S/As ratio of the arsenopyrite. Therefore, analyses with more than 34.3 at. % Fe were rejected (arbitrarily 1% > 33.3 at. % Fe) because they may have included pyrrhotite or unreacted FeAs or Fe_2As. Only 15 arsenopyrite analyses (approximately 10% of total number of analyses) showed Fe > 33.3 at. %; the majority tended to be slightly deficient in Fe. The existence of very fine, optically homogeneous intergrowths of arsenopyrite and pyrite, or arsenopyrite and loellingite (all of which have 33.3 at. % Fe) could not be recognized by microprobe alone, and other criteria had to be used to delineate the extremes of the S/As compositional range.

To estimate interlaboratory precision of electron microprobe analyses of arsenopyrite, pieces of the primary standard, Asp 57, and secondary standard, Asp 200, were sent to electron microprobe analytical laboratories at the Department of Energy, Mines and Resources, Ottawa (D. Owens, analyst); U.S. Geological Survey, Menlo Park (J. T. Nash, analyst) and McGill University, Montreal (W. H. MacLean, analyst). It was requested that the operators analyze these arsenopyrites using their own methods and also to use Asp 57 to analyze Asp 200. With the exception of Nash's results, if Asp 57 is used as standard, the composition of Asp 200 obtained is the same (at the two standard deviation level) as the accepted value for all three elements. When analysts used their own standards, agreement with the accepted values was much poorer.

The general consensus of the analysts was that Asp 57 appeared homogeneous on the micron scale but may be slightly inhomogeneous over large areas. Co and Ni were below the limit of detection (stated to be 0.05 wt. % Co or Ni). Small lamellar areas with high Co and Ni were reported by one analyst to be present in his piece of Asp 200.

An estimate of interlaboratory uncertainty of microprobe analysis of arsenopyrite in general may be obtained from averaging the results of analyses carried out by the three laboratories. The average and one standard deviation of the mean for 5 analyses of Fe, As and S in Asp 200 are 34.43±0.66, 43.91±1.49 and 21.24±0.43 at. %. For 4 analyses of Asp 57 the values are 33.94±0.66, 46.55±1.57 and 19.05±0.39 at % for Fe, As and S respectively.

Experimental Results and Discussion

Condensed subsolidus phase relations

All successful experiments at the vapor pressure of the system (including fluxed runs) are plotted on a *T-X* section in Figure 4 and are summarized in Table 5. For runs such as FAS 46B, 46C and 46E where there is a difference between the microprobe and X-ray diffraction analyses for As, both have been plotted.

The equilibrium boundaries in Figure 4 were drawn free-hand to fit most closely to the means for arsenopyrite composition in the various assemblages in Table 5. They are not constrained to be straight lines, but straight lines fit all data within one standard deviation of the mean. Where necessary, their relative positions are fixed within the spread of the experimental points by assuming that the arsenopyrite solid solution conforms to a regular solution model of components FeS_2 and $FeAs_2$. This is a valid assumption for many if not most sulfide solid solutions. For example, as Barton (1969) has indicated (Fig. 2), the asp+As+lo+V equilibrium must lie between asp+po+lo+V and asp+po+L+V in log $a(S_2)$-temperature space and therefore also in *T-X* space. The invariant points determined by Clark (1960a) and by Barton (1969) for the Fe-As-S system are retained in this study and have not been redetermined. Dashed lines indicate that uncertainty remains in the S-rich portion of the system below 400°C.

At high temperature (above about 650°C) the difference in arsenopyrite compositions with assemblage is indeterminate, but below about 550°C, and at a given temperature, arsenopyrite displays a large compositional range depending on the assemblage in which it occurs. Arsenopyrite compositions have been determined most precisely in the assemblage asp+po+L+V and asp+po+lo+V, because well-formed, free-standing arsenopyrite crystals that were easy to analyze by microprobe were found in the run products. In the other assemblages intergrown loellingite or pyrite, or very fine-grained reaction products, or zonal arrangement of reaction products made it very difficult to find arsenopyrite grains suitable for analysis and the large standard deviation on some of the points is directly attributable to these factors. The problem of reaction rates and equilibrium is discussed in detail below. The criteria for placing the less well-defined equilibria are as follows:

(1) The position of the asp+py+L+V equilibrium is based on a few rather imprecise analyses, the invariant point at 491±12°C (Clark 1960a) and the consideration that

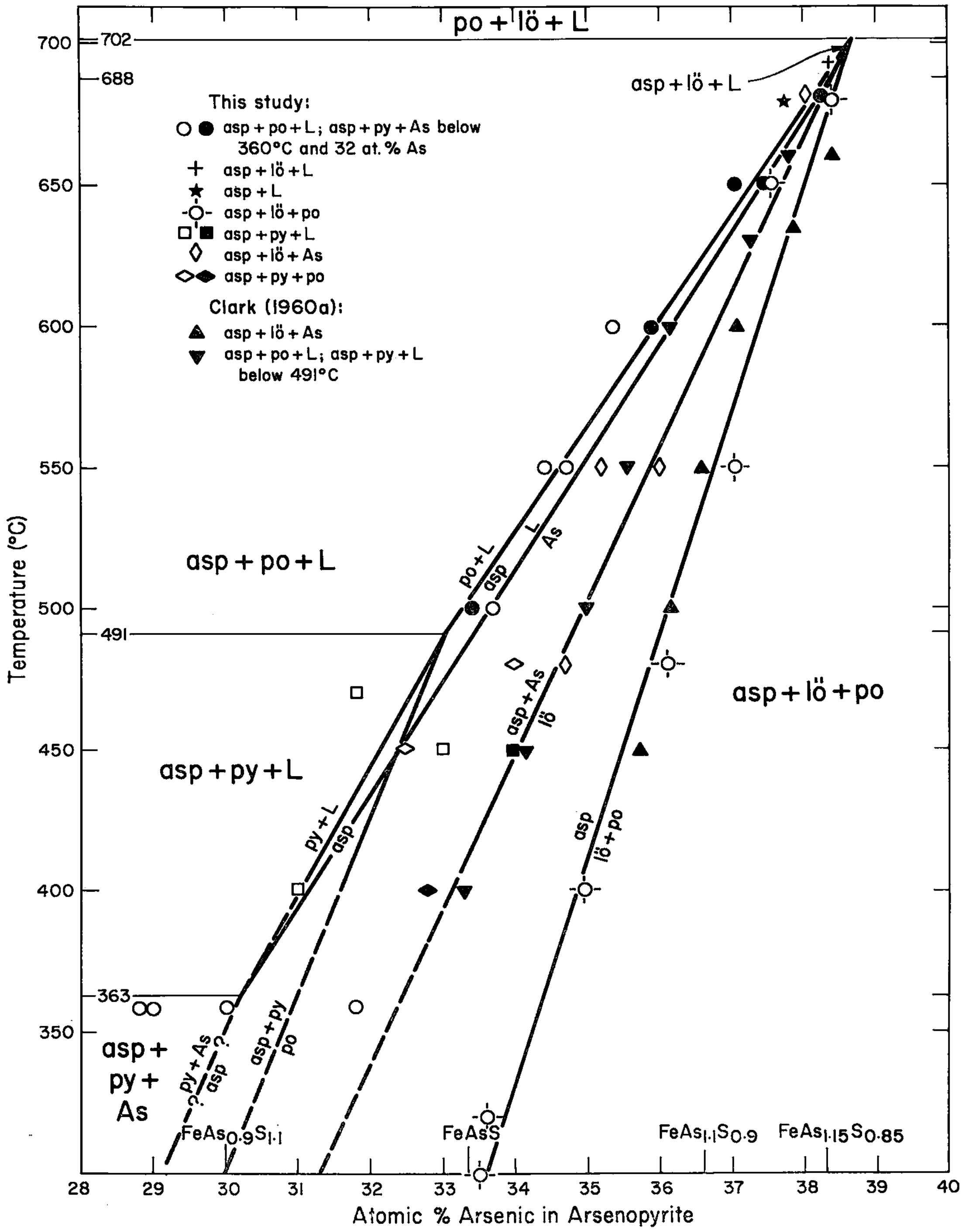

FIG. 4. Pseudobinary *T-X* section along the pyrite-loellingite join showing arsenopyrite composition as a function of temperature and bulk composition in which it was synthesized. The composition of arsenopyrite represented by solid symbols was determined by converting d_{131} measurements to at. % As using equation (1). The precision of measurements for d_{131} is ±0.0005Å which corresponds to about 0.45 at. % As. Open symbols denote arsenopyrite compositions measured by microprobe; the precision of these measurements is about ±0.45 at. % As. All assemblages include vapor. Data from Clark (1960a) are shown for comparison and were converted from his d_{131} measurements to at. % As using equation (1).

there must be a break in slope such that the high-temperature metastable extension of the asp+py+L+V curve lies outside of the stability field of arsenopyrite.

(2) The asp+lo+As+V equilibrium is well located at 550°C by bracketing runs of similar bulk composition but different reaction paths and by the single point at 480°C.

(3) Although experiments were inconclusive, geometrical restrictions require that the asp+po+py+V equilibrium line must lie between the asp+py+As+V and asp+As+lo+V lines.

(4) An unsuccessful attempt was made to de-

TABLE 5. DATA USED IN CONSTRUCTING THE ARSENOPYRITE *T-X* SECTION (FIGURE 4)

FAS No.	Temp. (°C)	Flux	Duration (days)	Starting Materials	Bulk Composition (wt. %)	$\overline{As}_i$	*N*	d_{131}	*N*	As*2
Assemblage[1]: asp+po+L+V										
91	684		19	asp 200,po	$Fe_{44.0}As_{25.0}S_{28.0}$			1.6377±11	8	38.22
34	650		38	py,lo	$Fe_{35.2}As_{42.5}S_{22.2}$			1.6368±5	5	37.45
72	650	KL	90	Fe_2As,L_{60}	$Fe_{37.0}As_{40.0}S_{23.0}$			1.6364±3	11	37.10
45E	600	KL	14	Fe_2As,L_{50}	$Fe_{32.3}As_{44.7}S_{23.0}$			1.6355±5	7	36.32
46E	600	KL	21	Fe_2As,L_{50}	$Fe_{32.3}As_{44.7}S_{23.0}$	35.4±0.7	5	1.6350±7	8	35.89
90D	550	KL	102	po, L_{23}	$Fe_{44.0}As_{23.0}S_{33.0}$	34.7±0.5	2			-
46D	550	KL	56	Fe_2As,L_{50}	$Fe_{32.3}As_{44.7}S_{23.0}$	34.4±0.9	6	1.6333±9	14	34.41
46C	550	KL	21	Fe_2As,L_{50}	$Fe_{32.3}As_{44.7}S_{23.0}$	33.7±1.2	8	1.6321±4	8	33.41
Assemblage: py+asp+L+V										
46H	470	KL	26	Fe_2As,L_{50}	$Fe_{32.3}As_{44.7}S_{23.0}$	31.8±1.2	9			
46B	450	KL	67	Fe_2As,L_{50}	$Fe_{32.3}As_{44.7}S_{23.0}$	33.0±1.3	12	1.6329±2	12	34.07
46A	400	KL	172	Fe_2As,L_{50}	$Fe_{32.3}As_{44.7}S_{23.0}$	31.0	1			
Assemblage: py+po+asp+V										
90C	480	KL	187	po,L_{23}	$Fe_{44.0}As_{23.0}S_{33.0}$	34.0	1			
90E	450	KL	68	po,L_{23}	$Fe_{44.0}As_{23.0}S_{33.0}$	32.5±1.8	5			
90A	400	KL	68	po,L_{23}	$Fe_{44.0}As_{23.0}S_{33.0}$			1.6314±12	5	32.78
Assemblage: py+asp+As+V[3]										
101B	358	KL	102	Fe_2As,L_{50}	$Fe_{30.0}As_{45.0}S_{25.0}$	29.0±0.3	3			
97A	358	KL	102	po,L_{23}	$Fe_{31.7}As_{38.0}S_{30.3}$	30.0±0.5	3			
97B	358	KL	179	po,L_{23}	$Fe_{31.7}As_{38.0}S_{30.3}$	31.8±1.4	8			
98B	358	KL	102	FeAs,S	$Fe_{31.9}As_{42.8}S_{25.3}$	28.9	1			
Assemblage: As+asp+lo+V										
96A	684		30	FeAs,L_{40}	$Fe_{28.7}As_{58.5}S_{12.8}$	38.0	1			
96C	550	KL	96	FeAs,L_{40}	$Fe_{28.7}As_{58.5}S_{12.8}$	35.2±1.1	8			
86	550	KL	25	Asp 200,lo,As	∿1: 1: 1	36.0±0.9	4			
96D	480	KL	174	FeAs,L_{40}	$Fe_{28.7}As_{58.5}S_{12.8}$	34.7±1.0	2			
Assemblage: As+asp+L+V										
41	680		103	lo,L_{23}	$Fe_{13.6}As_{74.9}S_{11.5}$	37.7±1.2	10	1.6371±5	15	37.71
Assemblage: asp+lo+L+V										
82	692		35	lo,L_{23}	$Fe_{14.9}As_{74.7}S_{10.4}$	38.3±1.0	3			
Assemblage: asp+po+lo+V										
71	680	KL	35	Fe_2As,L_{50}	$Fe_{37.0}As_{44.0}S_{19.0}$	38.4±0.45	3			
93	650	KL	4	Asp 200	$Fe_{34.5}As_{44.4}S_{21.0}$	37.5±0.87	9			
73A	550	KL	20	py,lo	$Fe_{32.5}As_{52.8}S_{14.7}$	37.1±0.65	8			
71C	480	KL	159	Fe_2As,L_{50}	$Fe_{37.0}As_{44.0}S_{19.0}$	36.1±0.51	8			
53E	400	KL	130	FeAs,L_{50}	$Fe_{32.6}As_{55.7}S_{11.7}$	34.9±0.69	12			
53D	320	NL	130	FeAs,L_{50}	$Fe_{32.6}As_{55.7}S_{11.7}$	33.6±0.17	3			
53C	300	NL	175	FeAs,L_{50}	$Fe_{32.6}As_{55.7}S_{11.7}$	33.5	1			

[1] Assemblage at equilibrium for bulk composition and temperature.

[2] The uncertainty associated with this value (one standard deviation of the mean) is at least ±0.45 at. % As (see text).

[3] Arsenic can be distinguished from S-As liquid only with difficulty and experiments to determine the asp+py+As+L+V invariant, which was predicted from thermodynamic data by Barton (1969), were unsuccessful. See further discussion in text.

termine the asp+py+As+L+V invariant, calculated to be at 363±50°C by Barton (1969). After 102 days at 358°C, no reaction had taken place between pyrite and arsenic. For different reaction paths and reaction times up to 179 days, pyrite and arsenopyrite formed but arsenic was not present. Therefore, the position of the asp+py+As +V equilibrium line is based on acceptance of the invariant temperature of 363±50°C (Barton 1969), a few imprecise and widely scattered electron probe analyses and the requirement that there be a break in slope between contiguous curves.

Agreement with the results of Clark (1960a) is good at high temperatures, but below about 550°C arsenopyrite in all assemblages is more S-rich than he indicated and the difference is not accounted for by our respective X-ray de-

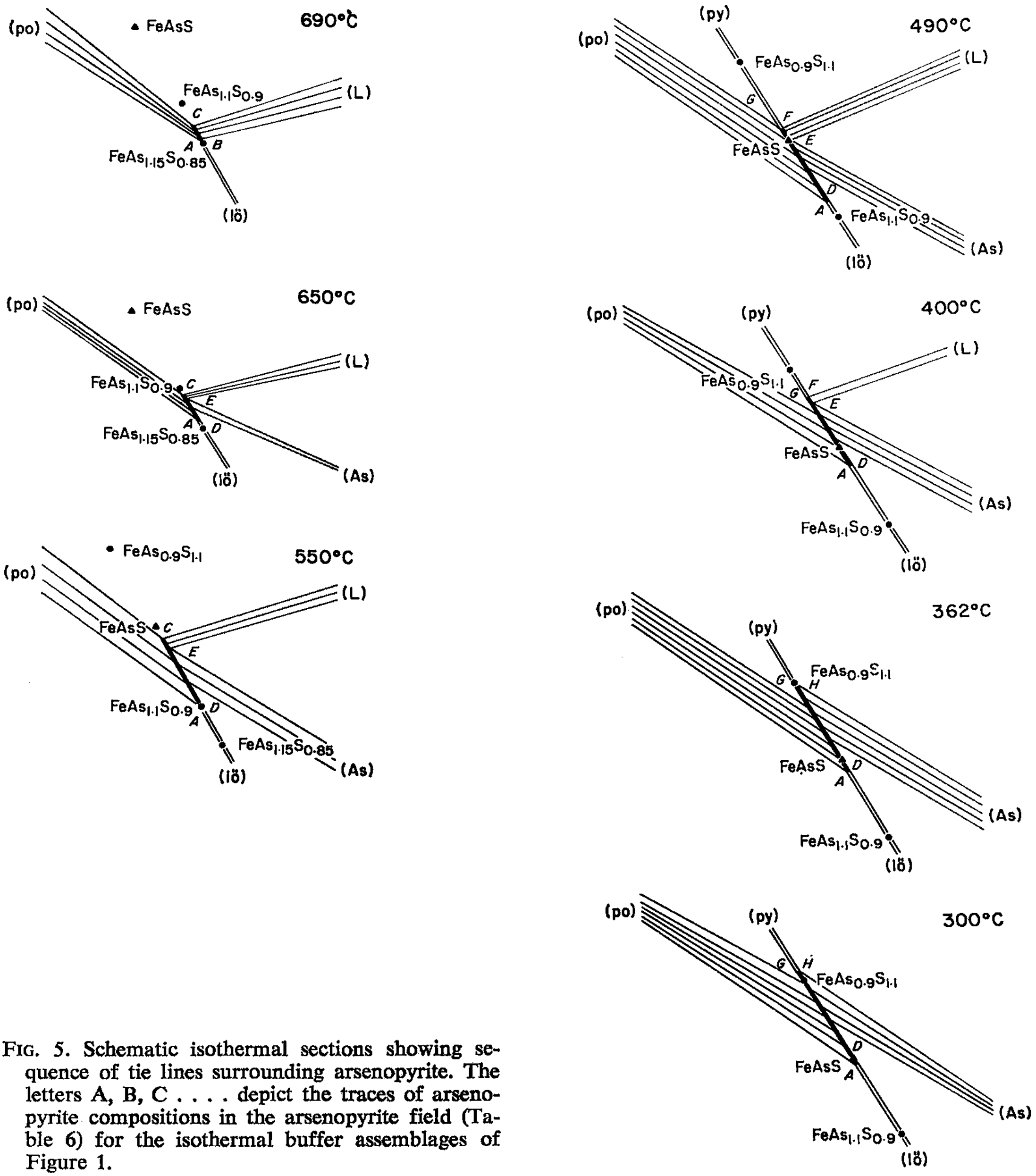

FIG. 5. Schematic isothermal sections showing sequence of tie lines surrounding arsenopyrite. The letters A, B, C . . . . depict the traces of arsenopyrite compositions in the arsenopyrite field (Table 6) for the isothermal buffer assemblages of Figure 1.

terminative curves. Above 500°C in the assemblage asp+po+L+V there is a maximum 0.9 at. % difference between the two sets of results. Since uncertainty in arsenic determinations is at least 0.45 at. % (one standard deviation), the results are compatible. As Clark (1960a) stated, failure of pyrite to nucleate in his 450 and 400°C runs may render his d_{131} measurements questionable. Clark's work shows that the single remaining point, at 500°C, is 1.5 at. % more As-rich than was found in our study. There is no ready explanation other than the failure of Clark's arsenopyrite to attain equilibrium even after 86 days. For the assemblage asp+lo+As+V there is again quite good agreement above 500°C between the two sets of data. Below 500°C the discrepancies may be explained by postulating interference from loellingite during measurement of the arsenopyrite (131)-spacing as is discussed below.

Isothermal sections

Schematic isothermal sections showing the configuration of tie-lies surrounding the arsenopyrite field are depicted in Figure 5 and may be derived directly from the *T-X* section of Figure 4. Table 6 lists arsenopyrite composition as a function of phase assemblage at various temperatures. The letters A, B, C . . . depict the trace of arsenopyrite compositions in the arsenopyrite field for the various isothermal buffer assemblages.

At 690°C, arsenopyrite has essentially constant composition (about 38.4 at. % As or $FeAs_{1.15}S_{0.85}$) regardless of the phase assemblage in which it is synthesized and contains only very slightly less than the maximum amount of arsenic possible (about 38.7 at. % As or $FeAs_{1.16}S_{0.84}$ at 702°C).

The univariant reaction describing the upper stability limit of crystalline arsenic is represented by the line labelled As-L on Figures 2 and 4. A portion of this line lying within the arsenopyrite stability field originates at 688°C and meets the asp+py+As+L+V invariant at 363°C. Although formation and decomposition of arsenopyrite in this assemblage (asp+As+L+V) cannot be described as a simple sulfidation reaction, it is compositions along this line that are represented by point E. At all temperatures, this line is close to the S-rich limit of the arsenopyrite stability field and one would therefore expect arsenopyrite to have a composition very similar to that in the assemblage asp+po+L+V (point C) and asp+py+L+V (point F). If, as an approximation, one assumes regular

TABLE 6. ARSENIC CONTENT OF ARSENOPYRITE IN ATOMIC % AS A FUNCTION OF TEMPERATURE AND ASSEMBLAGE

	Phase Assemblage*							
Temp. (°C)	po+lo A	lo+L B	po+L C	As+lo D	As+L E	py+L F	po+py G	py+As H
702	38.7	38.7	38.7	-	-	-	-	-
688	38.6	38.4	38.3	38.4	38.4	-	-	-
650	38.1	-	37.2	37.7	37.5	-	-	-
600	37.5	-	35.9	36.8	36.2	-	-	-
550	36.8	-	34.6	35.9	34.9	-	-	-
491	36.0	-	33.0	35.0	33.4	33.0	33.0	-
450	35.5	-	-	34.0	32.4	32.1	32.4	-
400	34.9	-	-	33.1	31.2	31.0	31.6	-
363	34.4	-	-	(32.4)	(30.2)	(30.2)	(30.9)	(30.2)
300	33.6	-	-	(31.3)	-	-	(30.0)	(<30)

*All assemblages include asp+V. Letters correspond to similarly labelled points in Fig. 5.

TABLE 7. ATTEMPTS TO REVERSE ARSENOPYRITE COMPOSITION

FAS No.	Temp. (°C)	Flux	Duration (days)	Starting Materials	Bulk Composition (wt.)	Product Arsenopyrite Composition ($\overline{As}_i$ or As*)	*N*
88	550	KL	30	FAS 41[1], po	1:1[2]	As*=38.0 d_{131}=1.6374±4	6
89	480	KL	166	FAS 41, po, py asp 200 nucleus	1:1:1	$\overline{As}_i$=38.3±1.0	4
72A	480	KL	91	FAS 72[3]	$Fe_{37.0}As_{40.0}S_{23.0}$	$\overline{As}_i$=35.7±1.6	12
72B	450	KL	104	FAS 72	$Fe_{37.0}As_{40.0}S_{23.0}$	$\overline{As}_i$=36.4±1.7	4
99B	600	KL	4	asp 200[4], As	1:1	$\overline{As}_i$=31.7±0.8	4
92	680	--	30	asp 200	$Fe_{34.5}As_{44.4}S_{21.0}$	$\overline{As}_i$=36.9±0.4	2
86	550	KL	25	asp 200, As, lo	1:1:1	$\overline{As}_i$=36.0±0.5	4
91	684	--	19	asp 200, po	1:1	As*=38.2 d_{131}=1.6377±11	8
102B	686	--	31	asp 200 crystal	$Fe_{34.5}As_{44.4}S_{21.0}$	$\overline{As}_i$=32.9±0.5	3
102C	680	KL	19	asp 200 crystal	$Fe_{34.5}As_{44.4}S_{21.0}$	$\overline{As}_i$=32.8±0.3	4

1. For arsenopyrite FAS 41, d_{131}=1.6371±5, *N*=14; As*=37.7.
2. Indicates approximate ratio of starting materials.
3. For arsenopyrite FAS 72, d_{131}=1.6364±3, *N*=11; As*=37.1.
4. For asp 200 $\overline{As}_i$=31.8±0.4, *N*=24; d_{131}=1.6304±5, *N*=14.

solution behavior, arsenopyrite composition should be proportional to $a(S_2)$ at a given temperature. At 400°C the difference in log $a(S_2)$ units between the assemblages asp+po+L+V and As+L+V is 1.0, which is the maximum difference in $a(S_2)$ between these two equilibria. A difference of 1.0 log $a(S_2)$ units corresponds to 0.8 at. % As in arsenopyrite. Because the precision of As determinations by microprobe is ±0.45 at. % As, the difference in arsenopyrite composition among the assemblages represented by points C, E and F is experimentally indeterminate at all temperatures. An experiment at 515°C to check this prediction failed due to incomplete equilibration.

At 650°C the arsenopyrite field lies entirely between the compositions $FeAs_{1.1}S_{0.9}$ and $FeAs_{1.15}S_{0.85}$. At 550°C the configuration of tie lines is essentially the same as at 650°C but the arsenopyrite solid-solution field now lies between the limits FeAsS and $FeAs_{1.1}S_{0.9}$.

With the establishment of the py-asp tie line at 491°C, points F and G attain the same composition. At 400°C, the entire stability field of arsenopyrite has shifted to more S-rich compositions and except for arsenopyrite from the assemblage asp+po+lo+V (point A), arsenopyrite is more S-rich than 33.3 at. % As in all equilibrium assemblages.

The isothermal section for 300°C is a distant extrapolation from higher temperature. The greatest uncertainty is associated with the position of point H.

Reaction rates and attainment of equilibrium

The greatest single experimental problem in this study of the subsolidus phase relations of arsenopyrite was the extremely slow reaction rate. Neither Clark (1960a) nor Barton (1969) were satisfied that equilibrium had been attained much below 500°C and Clark attaches an uncertainty of ±12°C to the asp+po+py+L+V equilibrium at 491°C because sluggish reactions prohibit bracketing in runs lasting several tens of days.

In the present study, the following precautions were taken to maximize the probability that equilibrium arsenopyrite compositions were attained: (1) starting materials were finely ground (<300 mesh); (2) fluxes were used; (3) charges were reground about every 4 weeks; and (4) where possible, S-rich and As-rich starting materials were used in order to vary the path of the reaction and attempt to approach equilibrium from different directions.

The extent of reaction was judged by optical examination of the reaction products to assure textural equilibrium, changes in the X-ray pattern as a function of time, and by quantitative electron microprobe analysis of reaction products.

Experiments designed to reverse arsenopyrite-forming reactions were only partly successful (Table 7). In experiments FAS 88 and 89, the high-temperature arsenopyrite (680°C) from experiment FAS 41 (assemblage asp+As+L+V) did not change composition even after 166 days at 480°C and the Asp 200 nucleus in FAS 89 did not change weight. Similarly, arsenopyrite in experiments 72A and B did not change composition (*t* statistic at the 95% level of confidence).

S-rich arsenopyrite seems to react more readily. After 4 days, using KL flux (FAS 99B), Asp 200 did not change composition at 600°C; however, at 680°C for 30 days (FAS 92), its composition changed to 36.9 at. % As. Since only two suitable grains could be found for electron microprobe analysis, this value is not plotted on Figure 4, although it is in good agreement with FAS 91. In the assemblage asp+As+lo+V at 550°C, Asp 200 changed composition to 36.0 at. % As after 25 days at 550°C (FAS 86) in agreement with the accepted equilibrium value of 35.9 at. % As. Experiments demonstrating that S-rich arsenopyrite becomes more As-rich by exsolution of pyrrhotite and a S-As liquid (in agreement with relations in Fig. 5) are presented by Kretschmar (1973).

Attempts to bracket equilibria and vary reaction paths were made by using S-rich and As-rich starting materials (Table 5). The difference in composition of arsenopyrite in experiments 46D and 90D at 550°C in the assemblage asp+po+L+V is statistically indeterminate at the 95% level of confidence. In the assemblage asp+As+lo+V at 550°C, arsenopyrite synthesized from Asp 200 appears to be more As-rich (36.0±0.9 at. % As, FAS 96C) than the arsenopyrite synthesized in the same assemblage using FeAs as starting material (35.2±1.1 at. % As, FAS 86). However, the measurements are imprecise and are not statistically different at the 95% level of confidence.

Where loellingite is one of the starting materials, it is significantly more difficult to attain equilibrium, as run 73A demonstrates. Also, after 30 days at 515°C, arsenopyrite synthesized from py+lo in KL flux contained 37.2 at. % As (d_{131} = 1.6365±3Å, N=12) which is far removed from expected values. In general, there is a tendency for reaction rates to decrease the more As-rich a phase on the Fe-As join is used as starting material (i.e. formation

TABLE 8. ELECTRON MICROPROBE ANALYSES OF SYNTHESIZED ARSENOPYRITES

FAS. No.	Arsenopyrite Composition Atomic %			N	Temp. (°C)	Duration (days)	Assemblage†	Starting Materials	Flux
	Fe	As	S						
41	33.2±0.29	37.7±1.21	29.2±0.67	27	680	103	As,L	lo,L_{23}	-
71	32.92±0.29	38.38±0.45	28.88±0.78	6	680	35	lo,po	Fe_2As,L_{50}	-
93	32.7±0.22	37.5±0.87	29.9±1.01	9	650	4	lo,po	asp 200	KL
53E	33.17±0.15	34.86±0.69	32.14±0.84	12	400	130	lo,po	FeAs,L_{50}	KL
101B	32.93±0.45	28.96±0.35	38.40±0.58	3	358	102	py,As	Fe_2As,L_{50}	KL
97B	32.30±0.27	31.77±1.64	36.05±1.57	8	358	179	py,As	po,L_{23}	KL
46D	32.73±0.21	34.43±0.93	33.03±0.84	6	550	58	po,L	Fe_2As,L_{50}	KL
90D	32.46±0.20	34.72±0.54	32.80±0.74	2	550	102	po,L	po,L_{23}	KL
46B	32.32±0.30	33.04±1.26	34.64±1.05	12	450	67	py,L	Fe_2As,L_{50}	KL
45C††	32.68±0.43	34.41±0.96	32.90±0.78	3	500	28	py,L	Fe_2As,L_{50}	KL
45B††	31.44±0.11	35.12±1.39	33.17±0.92	4	450	28	py,L	Fe_2As,L_{50}	KL
45A††	31.73±0.44	33.96±0.75	34.29±0.86	5	400	28	py,L	Fe_2As,L_{50}	KL
46A	31.59±0.22	35.26±0.86	33.22±0.66	7	400	172	py,L	Fe_2As,L_{50}	KL

†All include asp+V. ††These runs did not reach equilibrium.

of arsenopyrite is significantly slower if $FeAs_2$ rather than Fe_2As is used).

Our observations on equilibrium agree with those of Clark, who found that arsenopyrite, once synthesized, will not change composition even after 304 days at 550°C (Clark 1960a). It is also clear from our results that using fluxes and grinding starting materials very finely increases reaction rates significantly and permits reversals of runs.

Stoichiometry of arsenopyrite

A compilation of selected wet-chemical analyses of natural arsenopyrite made by Klemm (1965) indicates that the mineral may be Fe-deficient. Natural arsenopyrites examined in our study exhibit a similar trend.

Table 8 shows electron microprobe analyses of arsenopyrite from various phase assemblages synthesized at different temperatures along the S-rich and As-rich limit of the arsenopyrite stability field. Included in this table are analyses of arsenopyrite from runs that clearly had not reached equilibrium (e.g. 45A, B and C), as well as those that do represent equilibrium and were used to plot Figure 4. None of these latter experiments produced arsenopyrite with less than 32.2 at. % Fe. Nevertheless, the mean Fe-content for arsenopyrite in all assemblages is less than 33.3 at. % and there are very few individual arsenopyrite analyses of greater than 33.3 at. % Fe. Micro-inclusions of S-As liquid in synthetic arsenopyrite could explain some, but not all, of the apparent nonstoichiometry in Table 8. However, for the assemblages not including S-As liquid, the Fe-deficiency is not likely a function of the analytical method because repeated microprobe analysis of loellingite and pyrite, which are known to be stoichiometric (Rosenthal 1972; Kullerud & Yoder 1959), consistently gave 33.3 at. % Fe.

The apparent Fe-deficiency is an additional source of uncertainty which affects the *T-X* section (Fig. 4), since this is drawn on the assumption that arsenopyrite is stoichiometric. For example, if an arsenopyrite has a 1.0 at. % Fe-deficiency, it will plot at 0.5 at. % more S-rich composition on the *T-X* section after recalculation onto the FeS_2–$FeAs_2$ join.

Theoretical considerations dictate that, since the arsenopyrite stability field has a finite thickness (Fig. 5), arsenopyrite must be slightly nonstoichiometric. However, the Fe-deficiency is less than 1 at. % and, in agreement with Morimoto & Clark (1961), arsenopyrite is probably stoichiometric to ±0.7 at. %, the precision of Fe determination from the interlaboratory comparison of arsenopyrite analyses.

ACTIVITY OF FEASS IN ARSENOPYRITE

In his derivation of univariant curves for sulfidation reactions in the Fe-As-S system, Barton (1969) noticed slight discrepancies for alternative calculation paths which he attributed to "small, but apparently significant, variations in activities of components within phases". Because the S/As ratio varies considerably in arsenopyrite, *a*(FeAsS) is expected to vary also.

In is convenient to define the mole fraction of FeAsS in arsenopyrite in terms of the components FeAsS and FeS_2 in order to take maximum advantage of thermodynamic data for the Fe-S system. Defined in this way, the mole fraction of FeAsS in arsenopyrite, $N^{asp}_{FeS_2}$ is 1.0 for 33.3 atomic % As, is positive for values less than 33.3 at. % As and is greater than unity for values greater than 33.3 at. % As, in which case $N^{asp}_{FeS_2}$ is negative.

TABLE 9. CALCULATED ACTIVITY OF FeAsS IN ARSENOPYRITE AT 500°C

Assem-blage	At. % As	N^{asp}_{FeAsS}	log a_{S_2}	a_{FeS}	a_{FeS_2}	$N^{asp}_{FeS_2}$	a^{asp}_{FeAsS}
asp+po+L+V	33.3	1.000	-4.5	0.51	0.725	0	1.000
	33.6	1.008	-5.0	0.56	0.448	-0.008	0.999
asp+L+V	33.7	1.011	-5.2	0.58	0.368	-0.011	0.998
	33.9	1.017	-5.3	0.59	0.334	-0.017	0.998
	34.4	1.032	-5.9	0.62	0.176	-0.032	0.991
	34.7	1.041	-6.2	0.65	0.131	-0.041	0.987
asp+As+lo+V	35.2	1.056	-6.7	0.69	0.0779	-0.056	0.977
	35.4	1.062	-6.9	0.71	0.0637	-0.062	0.972
	35.8	1.074	-7.4	0.74	0.0373	-0.074	0.956
asp+po+lo+V	36.2	1.086	-7.6	0.76	0.0304	-0.086	0.949

Activities of FeAsS were calculated from the Gibbs-Duhem equation:

$$\sum_i n_i \, d\mu_i = 0 \ldots\ldots\ldots\ldots \quad (2)$$

where $d\mu_i = 2.303\, RT\, d \log a_i$.
For the binary system FeAsS-FeS$_2$:

$$N^{asp}_{FeAsS}\, d \log a^{asp}_{FeAsS} + N^{asp}_{FeS_2}\, d \log a^{asp}_{FeS_2} = 0. \quad (3)$$

and

$$d \log a_{FeAsS} = - N^{asp}_{FeS_2} / N^{asp}_{FeAsS}\, d \log a_{FeS_2} \ldots \quad (4)$$

Equation (4) was integrated for the range of arsenopyrite compositions across the stability field at 500°C. For a given ratio of $N^{asp}_{FeS_2}/N^{asp}_{FeAsS}$, log a(FeAsS) is given by the area under the curve in a plot of N/N vs. $-$ log a(FeS$_2$). The a(FeS$_2$) in equation (4) was calculated from the relationship

$$2FeS + S_2 = 2FeS_2 \ldots\ldots\ldots\ldots \quad (5)$$

for which

$$a(FeS_2) = a(FeS) \cdot a(S_2)^{\frac{1}{2}} \cdot K^{\frac{1}{2}} \ldots\ldots \quad (6)$$

The equilibrium constant, K, was calculated from the free energy of reaction for equation (5) using the data of Barton & Skinner (1967), corrected for the improved ΔG°_f for pyrite given by Scott & Barnes (1971). Values of a(FeS) and a(S$_2$) within the arsenopyrite stability field are from Toulmin & Barton (1964).

Results in Table 9 show that at 500°C the activity of FeAsS in stoichiometric arsenopyrite is, by definition, 1.0 in the most S-rich assemblage, asp+po+L+V, and only slightly lower (0.949) in the most As-rich assemblage, asp+po+lo+V. This small departure from unit activity of FeAsS is sufficient to cause the discrepancies noted by Barton. Such small variation in a(FeAsS) may be important for precise thermochemical calculations (see Barton 1969), but they are insignificant for interpretation of natural arsenopyrite compositions and we have not evaluated them further.

EFFECT OF CONFINING PRESSURE ON ARSENOPYRITE COMPOSITION

Clark (1960c) found that arsenopyrite synthesized at 1 or 2 kbar confining pressure is more S-rich than arsenopyrite synthesized at the same temperature under the vapor pressure of the system, regardless of the assemblage. The crystallographic data of Morimoto & Clark (1961) shows that S-rich arsenopyrite has a lower molar volume than As-rich arsenopyrite so is, indeed, the favored composition at high pressure. However, relative molar volumes do not give the magnitude of the pressure effect.

We have attempted to check Clark's (1960c) results by synthesizing arsenopyrite at 500°C under 5 kbar confining pressure in the assemblage asp+po+L using KL flux. The vapor from the charges in these experiments was in contact with the walls of the pressure vessel so the results (Table 10) must be treated with caution. In summary, our experiments indicate that high-temperature arsenopyrite used as starting material became only slightly more

TABLE 10. ATTEMPTS TO SYNTHESIZE ARSENOPYRITE AT 5 kb AND 500°C*

FAS No.	Starting Materials	Duration (days)	Products	Comments
5P3	FAS 41 asp,po,py	6	asp,po,py	-pyrite asspears to be breaking down -initial asp composition (FAS 41): As_i= 37.7±1.2 -product asp d_{131} = 1.6350±4, N=10; As* = 35.90±0.4
5P4	po,L_{20}	6	asp,po,py	-product asp d_{131} = 1.6340±13, N=11, As* = 35.0±1.1 -product pyrrhotite composition, N_{FeS} = 0.934 -initial pyrrhotite composition, N_{FeS} = 0.9579
5P5	po,L_{20}	99	asp,po,L	-$\overline{As}_i$ = 33.3±0.2, N=5. Not enough left to X-ray. This value may be as much as 0.6 at. % As high due to analytical difficulties.
5P6	FAS 41,asp,po	99	asp,po, FeAs, Fe$_2$As (disequilibrium assemblage)	-flux disappeared, severe vapor loss, po grew on spacing rod.

*Vapor from charges in contact with and may have reacted with walls of the pressure vessel.

S-rich (5P3), but is clearly not in equilibrium with py+po or po+L at any pressure. Arsenopyrite grown from pyrrhotite and a sulfur-arsenic liquid (5P4) was much less S-rich than expected from Clark's results. In a longer experiment (5P5), arsenopyrite was up to 0.6 at. % more S-rich than 33.3 at. % As (the equilibrium As-content at 500°C in the assemblage asp+po+L+V, from Fig. 4) but far less S-rich than expected from Clark's data. In trying to explain this discrepancy between our results and Clark's it must be kept in mind that (1) Clark carried out his high-pressure experiments in gold tubes whereas our experiments were in glass-lined gold tubes and (2) he was unable to determine the upper stability limit of arsenopyrite at high pressure (702°C at <1 bar) because of reaction between gold and arsenic (Clark 1960c). We sealed arsenopyrite with KL flux in both Pt and Au tubes. After only 2 days at 500°C, the containers had melted almost completely because the flux accelerated the reaction between Au and As. Clark states that there is very low solubility of Au in arsenopyrite since d_{131} value of arsenopyrite, reacted for 19 days at 600°C with Au in silica tubes, was unchanged. There is, however, no assurance that this is true at higher pressures. Moreover, any reaction between Au and As will lower the activity of As [raise $a(S_2)$] and, in response, arsenopyrite should become more S-rich. Therefore, the apparent effect of pressure on arsenopyrite composition observed by Clark for the assemblage asp+po+L may possibly represent As-Au interaction.

For the assemblage asp+lo+As, there is a similar discrepancy which may be explained by analytical interference of loellingite. The (221) X-ray line of loellingite is at 1.6344Å (PDF Card No. 11-699), approximately in the middle of the commonly observed range of arsenopyrite d_{131} values. If this line is mistaken for (131) of arsenopyrite, one obtains 35.4 at. % As from equation (1). Four out of five of Clark's 2 kbar data points lie within 0.2 at. % of 35.4, which suggests that it may have been the loellingite d_{221} that he measured and not arsenopyrite (131). However, Clark (written communication 1976) was well aware of this possibility and attempted to minimize it.

In trying to deduce from all available data what effect confining pressure will have on arsenopyrite compositions, it should be noted that natural arsenopyrites from highly metamorphosed ore deposits are not as S-rich as they should be if confining pressure has a drastic effect. We will return to this point later.

A permissible, albeit tenuous, conclusion from the foregoing is that confining pressure does cause arsenopyrite to become more S-rich, but the magnitude of the change is not known and may be much smaller than indicated by Clark (1960c).

THE COMPOSITION OF NATURAL ARSENOPYRITE

To what extent are the phase relations applicable to natural occurrences? A noteworthy preliminary observation, which suggests that arsenopyrite does attain "equilibrium" composition in nature, is in the listing of arsenopyrite-bearing assemblages by Ramdohr (1969) which shows only 5 of 98 arsenopyrite occurrences to be "non-equilibrium" (i.e. the assemblages of ore minerals belonging to the Fe-As-S system are not compatible at any temperature).

Two recent investigations have dealt with natural arsenopyrite. Klemm (1965) compiled what in his estimation were superior analyses determined by wet-chemical methods. He found that arsenopyrite composition varies approximately between the limits $FeAs_{1.2}S_{0.8}$ and $FeAs_{0.9}S_{1.1}$, and more than two thirds were sulfur-rich. The maximum deviation of Fe in arsenopyrite was approximately 1 at. %. Rosner (1969) analyzed arsenopyrite from 25 localities by electron microprobe. He found no optical or compositional zonation and no elements other than Fe, As, S, Co and Ni in concentrations exceeding 1 wt. %. The majority of natural arsenopyrites contained less than 1 wt. % Co and/or Ni and the maximum deviation of Fe from FeAsS was approximately 1 wt. %. The compositional limits he found were $Fe_{0.99}As_{1.06}S_{0.94}$ and $FeAs_{0.89}S_{1.11}$.

We have examined arsenopyrite-bearing ores from a wide variety of localities. Each was classified into assemblages on the basis of Fe-As-S minerals coexisting in the same polished section. After preliminary microprobe analyses, 54 arsenopyrites with less than 1 wt. % combined Co, Ni and Sb (with a few exceptions) were accepted for detailed study. On average, three separate spots on three different arsenopyrite grains were analyzed in each of these polished sections. Preference was given to those grains which were enclosed in or were touching other Fe-As-S minerals. Each such spot is plotted as a single analysis. Analyses from several assemblages are shown in Figure 6. The lines in Figure 6 indicate the permissible compositional range of arsenopyrite in each assemblage (Fig. 4) and are drawn at a constant Fe content of 33.3 at. %. *With a few exceptions, the compositions of natural arsenopyrites, including*

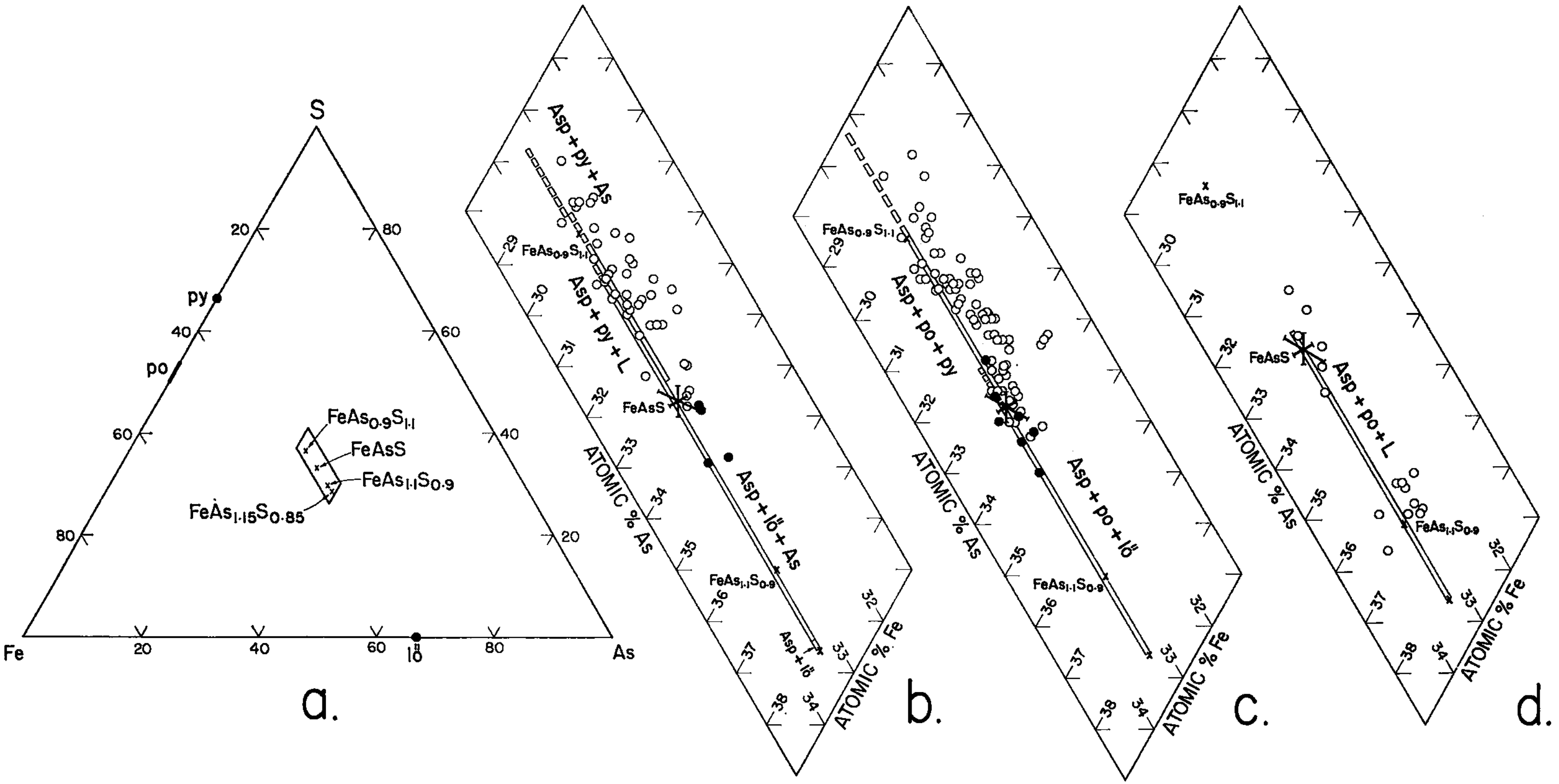

FIG. 6. Electron microprobe analyses of natural arsenopyrites. Figure 6a locates the analyses along the FeS_2-$FeAs_2$ join within the central portion of the Fe-As-S system. Lines in b, c and d show the compositional ranges from Figure 4 of arsenopyrites synthesized in various assemblages as labelled (all include vapor). One standard deviation of the mean for microprobe analyses of the elements Fe, As and S is shown at the composition $Fe_{1.0}As_{1.0}S_{1.0}$ in b, c and d.

Symbols — 6b: open circles=arsenopyrite coexisting with pyrite; closed circles=arsenopyrite coexisting with loellingite+arsenic. 6c: open circles=arsenopyrite coexisting with pyrite+pyrrhotite; closed circles=arsenopyrite coexisting with pyrrhotite+loellingite. 6d: open circles=arsenopyrite coexisting with pyrrhotite.

those from highly metamorphosed ores, fall within these permissible ranges. The As-rich limit of the arsenopyrite solid solution is taken to be $FeAs_{1.15}S_{0.85}$.

The observation that arsenopyrite is commonly zoned is discussed in detail below. All analyses have been plotted, regardless of which portion of the crystal was analyzed. This introduces a certain amount of bias because random analyses are less likely to include the exact center of a zoned grain. Most centers are S-rich and therefore there is a slight bias towards As-rich analyses in the plots.

The most common association of arsenopyrite in nature is with pyrite (Fig. 6b). It is noteworthy that there are no arsenopyrites in association with pyrite that contain more than about 33.3 at. % As. This value is in excellent agreement with equilibrium value of 33.0 at. % As for the asp+py+po+L+V invariant. The lowest As content encountered in this study is 29.1 at. % in arsenopyrite from the Caribou massive sulfide deposit (Roscoe 1971). This value is slightly less As-rich than that found for arsenopyrite at the asp+py+As+L+V invariant.

The association arsenopyrite-pyrite-arsenic is exceedingly rare in nature and only one published description was found (Pimm 1967). Our examination of ores from this location failed to reveal arsenopyrite. On the other hand, A. H. Clark (written communication 1972) has found arsenopyrite, pyrite and arsenic in contact within veins of Mina Alacrán, Chile. The arsenopyrite is not zoned and contains 0.2 wt. % Sb, no detectable Bi or Co, and has d_{131} of 1.6305±3Å. His estimates of formation temperature and maximum confining pressure are 275±50°C and 500 bars. This d_{131} value represents 32.0 at. % As, which is about 2 at. % As higher than is permissible from Figure 4. A possible explanation is that arsenopyrite formed in equilibrium with pyrite at temperatures above the asp+py+As+L+V invariant point and failed to re-equilibrate at lower temperature as arsenic crystallized. Considerable uncertainty is associated with this invariant point and many arsenopyrites from this assemblage must be studied before such data can be used to refine the invariant temperature and arsenopyrite composition. It can be predicted, however, that arsenopyrite from this assemblage should be very sulfur-rich if it formed at equilibrium.

Arsenopyrite from the assemblage arsenopyrite-loellingite has not been found and, should it exist, will be recognized only by its high As-content (>38.5 at. % As). There are descriptions of arsenopyrite rimmed by loellingite and loellingite rimmed by arsenopyrite (Ramdohr 1969) but there are no data on these occurrences from which deposition temperatures can be estimated.

Arsenopyrite and loellingite were found as tiny crystals in minute quantities in botryoidal arsenic from gold-quartz vein deposits in British Columbia. The crystals were very difficult to analyze since they are so small. Also, there is some Sb in the native arsenic and the arsenopyrite. Only the best analyses are plotted in Figure 6b.

The association arsenopyrite-pyrrhotite-pyrite is quite common in nature and our analyses (Fig. 6c) represent formation in many geological environments. About 25% of the arsenopyrites contain more than 33.0 at. % As but very few contain more than 33.4 at. % As, which is within one standard deviation of the asp+py+po+L+V invariant composition (33.0 at %). The remainder of the "anomalous" analyses are from specimens in which pyrite is clearly secondary after pyrrhotite and the arsenopyrite almost certainly formed above 491°C in equilibrium with pyrrhotite.

The association arsenopyrite-loellingite-pyrrhotite is not common and only samples from Moreton's Harbour, Newfoundland and Contwoyto Lake, N.W.T. were studied. One of the best known occurrences is Broken Hill, Australia, but preliminary analyses showed these arsenopyrites contained more than 2 wt. % combined Co, Ni and Sb so they were not examined further.

Of those specimens examined from the assemblage arsenopyrite-pyrrhotite (Fig. 6d) only two have less than 33.0 at. % As. One is from the Fox Lake mine, Manitoba; all other sections from this deposit also contain pyrite so the sample is probably misclassified. A sample from Umuzig, Hungary was placed in the asp-po assemblage because it contains tiny concentrically arranged pyrrhotite inclusions. The one crystal analyzed from this occurrence is strongly zoned from a S-rich core (30.5 at. % As) to an As-rich rim (32.3 at. % As). Only the rim composition is plotted in Figure 6d. The apparently "disequilibrium" S-rich composition of the core might represent composite analysis of arsenopyrite and tiny pyrrhotite inclusions. Most of the remaining samples of this assemblage are from the tin-tungsten deposits of Bolivia (Kelly & Turneaure 1970). The indicated formation temperatures are around 625°C, only slightly higher than Kelly & Turneaure obtained from several lines of evidence for the initial high-temperature stage of vein formation (approximately 587-602°C).

Figure 6b,c,d shows that many arsenopyrites coexisting with pyrite and/or pyrrhotite apparently have a slight iron deficiency, similar to those grown synthetically.

Zoning in arsenopyrite

Many, if not all, natural arsenopyrites are compositionally zoned. The zoning is almost impossible to detect optically without etching and optically zoned arsenopyrites are not necessarily compositionally zoned. In many cases optical inhomogeneities are due to twinning, which is almost universal in natural arsenopyrite (Morimoto & Clark 1961). Because it is a large-scale feature, the zoning is not readily detectable by back-scatter electron or X-ray scan photos on the microprobe.

The zoning appears to be concentric; the compositional change is stepped and irregular with no reversals. The difference in composition between center and rim of some single arsenopyrite crystals is shown in Table 11. A limitation of the data is that we are dealing with point analyses only; nevertheless, the following generalizations apply regarding the zoning, and exceptions are explained by changes in assemblage with time:

(1) In S-rich assemblages (asp-po, asp-po-py and asp-py), centers of arsenopyrite crystals are S-rich relative to the rims.

(2) Zoning in arsenopyrite from As-rich assemblages is much less common which, in part, is a reflection of the rarity of such arsenopyrites. Nevertheless, zoning does appear to be the reverse of that shown by arsenopyrite from the S-rich assemblages, i.e. with the centers As-rich relative to the rims.

(3) The lower the indicated formation temperature, the greater is the extent of zoning in arsenopyrite from the S-rich assemblages.

(4) Both center and rim compositions of zoned arsenopyrite crystals lie within the permissible equilibrium range for each assemblage.

The existence of such marked zoning as shown in Table 11 reflects changing conditions during formation of arsenopyrite and attests to the strong resistance of arsenopyrite to internal homogenization. If arsenopyrite started to form at high temperature and continued to grow as temperature dropped, the outer zones should be progressively more S-rich than the center if buffering occurred during its growth (Fig. 4). This is indeed what we see in As-rich assemblages. However, the zoning is in the *opposite sense* in S-rich assemblages, so a different explanation must be sought.

If the effect of confining pressure is to make arsenopyrite more S-rich, the observed sequence of zones for S-rich (but not As-rich) assemblages reflects growth during gradual, nearly isothermal release of pressure attending retrograde metamorphism. This may happen in some instances but it is a highly unlikely explanation for the diagenetic low-temperature arsenopyrite from Ovens, N.S. (Asp 43 in Table 11). Reversals in slopes of the univariant curves below the temperatures at which we investigated them could explain some of the zonal patterns, but not those from high-temperature ores.

The conclusion that we are forced to accept at present is that most of the zoning is a non-equilibrium feature reflecting the kinetics of arsenopyrite growth and local fluctuations in the $a(S_2)/a(As_2)$ ratio. Generally, however, the compositional range of zoned arsenopyrite lies within the equilibrium range for each assemblage, so we suggest that zoning reflects only minor and transitory conditions of non-equilibrium during growth.

TABLE 11. MICROPROBE ANALYSES OF ZONING IN NATURAL ARSENOPYRITE

Asp No.	Fe-As-S Assemblage	Atomic % As		Locality
		Center	Rim	
288	asp only	33.7	33.3	Moreton's Harbour, Newfoundland
298	asp only	33.9	33.2	Cobalt, Ontario
67	asp only	32.8	31.3	Cobalt, Ontario
		33.3	32.3	
20	asp only	35.6	33.3	Cschlova, Barrat, Hungary
13	asp only	29.5	31.6	Trepca, Yugoslavia
42	po,asp	30.5	32.3	Umuzig, Hungary
27	py,asp	30.0	31.5	Mühlbach, Austria
16	py,asp	30.0	31.0	Stall Lake mine, Manitoba
243B	py,asp	30.5	31.0	Stall Lake mine, Manitoba
43	py,asp	29.7	31.7	Ovens, Nova Scotia
69	py,asp	30.5	32.2	Noche Buena, Mexico
54B	po,py,asp	36.7	33.4	Madeleine mine, Quebec
228	po,py,asp	31.4	30.4	Fox Lake mine, Manitoba
230	po,py,asp	29.8	31.5	Fox Lake mine, Manitoba
231	po,py,asp	30.8	31.5	Fox Lake mine, Manitoba
		30.6	30.0	Fox Lake mine, Manitoba
246	po,py,asp	30.0	32.3	Osborne Lake mine, Manitoba
247	po,py,asp	32.6	33.4	Osborne Lake mine, Manitoba
270	po,py,asp	33.0	31.3	Mattabi mine, Ontario
280	po,py,asp	33.8	35.3	Homestake mine, South Dakota

CONCLUSIONS: THE ARSENOPYRITE GEOTHERMOMETER

The excellent correspondence between the composition of natural arsenopyrite and our experimentally-determined limits suggest that, despite the zoning, arsenopyrite compositions frequently indicate initial formation temperatures. We are not convinced of the magnitude of the effect of confining pressure as measured by Clark (1960c). If, as we suspect, the pressure effect is negligible, arsenopyrite may indeed be used as a sliding-scale geothermometer. As such, and because of its refractory nature, arsenopyrite should be a good indicator of temperature and sulfur activity during ore formation but, because it is usually a minor phase in ore deposits, it is unlikely to buffer the ore-forming environment. The stability field of arsenopyrite effectively straddles the range of temperatures and sulfur activities outlining the "main-line" ore-forming environment of Barton (1970) and Holland (1965), so this geothermometer should find widespread application.

It is essential that the sulfur activity be known for proper use of the arsenopyrite geothermometer. In most cases other Fe-As-S phases will provide this information and Figure 4 can be used directly, but the presence of these phases is not essential. Any $a(S_2)$–dependent assemblage coexisting with arsenopyrite can be used, at least theoretically. For example, the assemblage bismuth+bismuthinite+sphalerite+arsenopyrite occurs in veins of the Mount Pleasant tin deposit (Petruk 1964). There are no Fe-S minerals but the univariant $a(S_2)$–T relationship may be estimated from the Bi-Bi_2S_3 assemblage which lies within the stability field of arsenopyrite.

It is with such applications in mind that we have constructed Figure 7, which is a log $a(S_2)$-temperature diagram on which arsenopyrite isopleths are contoured in at. % As. In using Figures 4 and 7 for geothermometry the following precautions should be taken:

(1) Arsenopyrite should be chosen with care from equilibrium, $a(S_2)$-buffered assemblages. Equilibrium is difficult, if not impossible, to

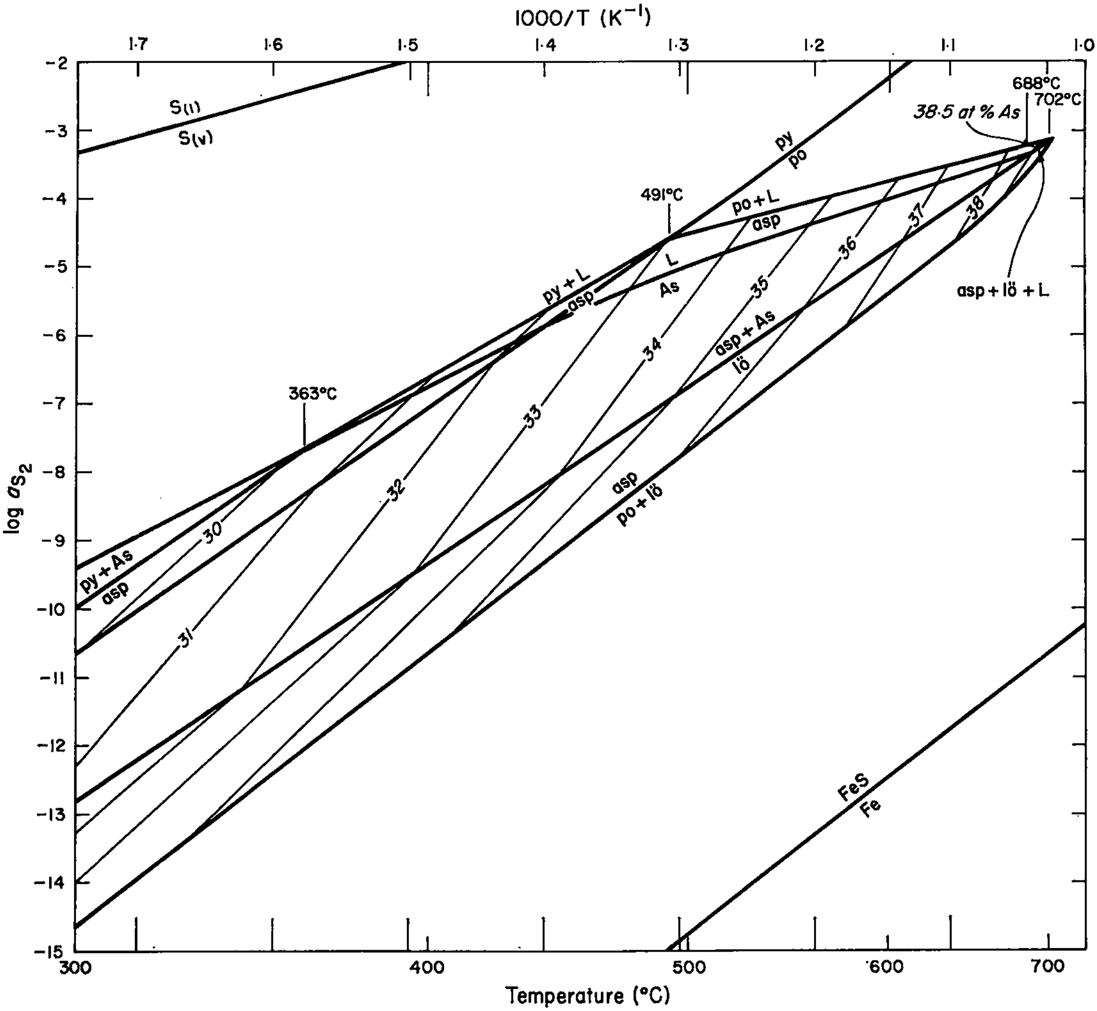

FIG. 7. Activity of S_2–temperature projection of the stability field of arsenopyrite, contoured in atomic % arsenic from the data in Figure 4. All assemblages include vapor.

prove in ores and is usually decided on paragenetic and textural grounds (Barton *et al.* 1963). In vein deposits, arsenopyrite can be presumed to be in equilibrium with other simultaneously deposited minerals, surface equilibrium among the minerals being readily achieved through the fluid phase. However, once deposited, the refractory arsenopyrite is unlikely to change its composition in response to changing conditions in the vein. Rather, it is expected to be epitaxially overgrown by younger arsenopyrites of different composition as was found, for example, by Clark (1965) in the Ylöjärvi copper-tungsten deposit where S-rich low-temperature arsenopyrite rims As-rich high-temperature arsenopyrite.

Equilibrium is easier to reconcile in metamorphosed ores by the fact that the coexisting minerals have annealed together for a long period of time, although compositional zoning which persists in some arsenopyrite from highly metamorphosed ores may preclude complete equilibration. Experience gained in using sphalerite, a less refractory mineral than arsenopyrite, as a geobarometer in metamorphosed ores (Scott 1973, 1976) emphasizes that the arsenopyrite must touch the coexisting phases constituting the buffered assemblage and preferably in triple junctions (DeWitt & Essene 1974).

(2) The combined minor-element content of the arsenopyrite should be <1 wt. %. Commonly, Co and Ni substitute for Fe. We are uncertain of their effect on As/S ratio in arsenopyrite but, more importantly, if arsenopyrite compositions are determined by X-ray diffraction their effect is to increase d_{131} (Morimoto & Clark 1961; Gammon 1966).

(3) The d_{131} value should be determined with annealed CaF_2 as a standard and using $a=$ 5.4626Å to be consistent with our determinative curve in Figure 3.

(4) If arsenopyrite is analyzed by microprobe, an arsenopyrite standard of proven homogeneity and carefully determined composition should be used. Arsenic determined using $FeAs_2$ or As as standards will be high because the As is bonded differently than in arsenopyrite.

There are still several important unresolved problems in the determination and application of phase relations of the Fe-As-S system. Chief among these is to determine the effect of pressure on arsenopyrite composition. Second, our experimental results below 450°C in the S-rich portion of the system are not entirely satisfactory. The asp+py+po+V assemblage is particularly problematical in this respect. It is a most useful assemblage for geothermometry of metamorphosed sulfide ores and yet we were not able to bracket it closely. Finally, we have not been able to resolve the cause of compositional zoning of arsenopyrite. One of its implications is that temperature estimates based on careful electron microprobe analyses will appear to be less precise because of the large range of As-contents. However, if the zoning turns out to be an equilibrium phenomenon, such estimates may eventually be more precise because the zoning will then be an additional factor for evaluating the thermal history of arsenopyrite-bearing rocks.

In conclusion, despite the several remaining uncertainties, we believe that arsenopyrite is a viable geothermometer. Nevertheless, ore-forming environments can be effectively estimated only if *all* available data are used. The information that arsenopyrite provides must not be abstracted but must be used in conjunction with silicate petrology and, above all, the geology of the deposits.

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