

GEOCHEMISTRY

Stability of Arsenopyrite at Temperatures below 300°C

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The composition and assemblage of arsenopyrite have been experimentally and theoretically studied in a temperature range of 358–700°C [1, 2]. The behavior of this mineral at a temperature below 300°C, typical of many hydrothermal deposits, has no unequivocal interpretation as yet. Arsenopyrite has not been synthesized below 358°C, and all of the physicochemical studies are limited to theoretical calculations [3], experiments on the behavior of natural arsenopyrite in solutions and air media under various physicochemical parameters [4, 5], and interpretation of formation conditions of natural assemblages [6]. Arsenopyrite is unknown in definitely low-temperature assemblages in nature. Therefore, it is reasonable to question the lower limit of its stability at a temperature of ~250°C [7]. This work is aimed at the thermodynamic calculations of arsenopyrite stability in medium- and low-temperature regions based on mineral relationships observed in nature.

The association of arsenopyrite with pyrite (\pm pyrrhotite) or löllingite (\pm pyrrhotite) is typical for natural samples. A four-phase assemblage of arsenopyrite, löllingite, pyrrhotite, and pyrite was found at the Igunenov gold-quartz deposit [8]. This assemblage is characterized by the unusual coexistence of pyrite and löllingite without obvious indications of mutual replacement. The breccia-like quartz veins, which host this assemblage, are localized in the distal exocontact zone of the Ulakhan granitoid pluton. Sulfide dissemination in quartz is composed of euhedral arsenopyrite crystals and their aggregates with abundant oblong löllingite grains in their central portions. One can also observe pyrite and löllingite aggregates with occasional arsenopyrite zone developed between them (Fig. 1). In some cases, pyrite occupies a marginal position in these aggregates and is characterized by a cubic habit and fine zonal structure. Pyrrhotite occurs as small (0.01 mm) equant inclusions within arsenopyrite and löllingite. Pyrrhotite segregations as large as 0.4 mm are localized in the outer zone of pyrite-arsenopyrite-löllingite

intergrowths and in defects of such aggregates. One can recognize at least two pyrrhotite generations: (1) syngenetic (with respect to other phases of the Fe-As-S system) generation and (2) younger generation that cements the intergrowths of these phases. Pyrite likely also crystallized in several stages.

Table 2 shows that arsenopyrite is characterized by the absence of explicit zoning and a narrow compositional range: As_{\min} 33.4, As_{\max} 37.6; As_{av} 34.8 at %, $D = 0.6$; $N = 46$. The sulfur content in löllingite varies from 2.7 to 4.6 at % ($N = 9$). The As content in pyrite ranges from 0.2 to 1.0 at % ($N = 14$). Pyrite at the contact with löllingite is depleted in As (0.4–0.5 at %) relative to the contact with arsenopyrite (0.6–1.0 at %).

The homogenization temperature of fluid inclusions in the host quartz near the sulfide aggregate is $\sim 258 \pm 5^\circ\text{C}$ ($N = 38$, $p = 0.95$ [7]). Quartz in the studied specimen is equigranular and rich in heterogeneous inclusions represented by the predominant gaseous and the subordinate gaseous-liquid, liquid, and gaseous-liquid-solid phases.

The geological setting of the four-phase assemblage suggests the following mechanisms of its formation: (1) thermal impact on the older arsenopyrite or its assemblage with pyrite; (2) spatial juxtaposition of the younger pyrite with the arsenopyrite + löllingite + pyrrhotite assemblage, and (3) equilibrium crystallization of all four phases. Let us analyze these scenarios.

Formation of the polysulfide assemblage as a result of *metamorphism of the monomineral arsenopyrite* contradicts the stable composition of the phases without reaction rims in the boundary zones (Fig. 2). The arsenopyrite zone between löllingite and pyrite may be interpreted as a reaction product only in certain cases (Fig. 1). The heating of synthetic arsenopyrite up to 692°C at 1035 bar during 6 h [1] results in the complete breakdown of arsenopyrite into löllingite + pyrrhotite + glass (As, S). Iron arsenide was formed in experiments with the reaction of arsenopyrite with CO_2 at 525–600°C in [5]. An increase in the partial pressure of As (gas) produces FeAs_2 instead of FeAs . Arsenopyrite is present in the studied sample; i.e., either the reaction was not complete or this assemblage is formed by another mechanism.

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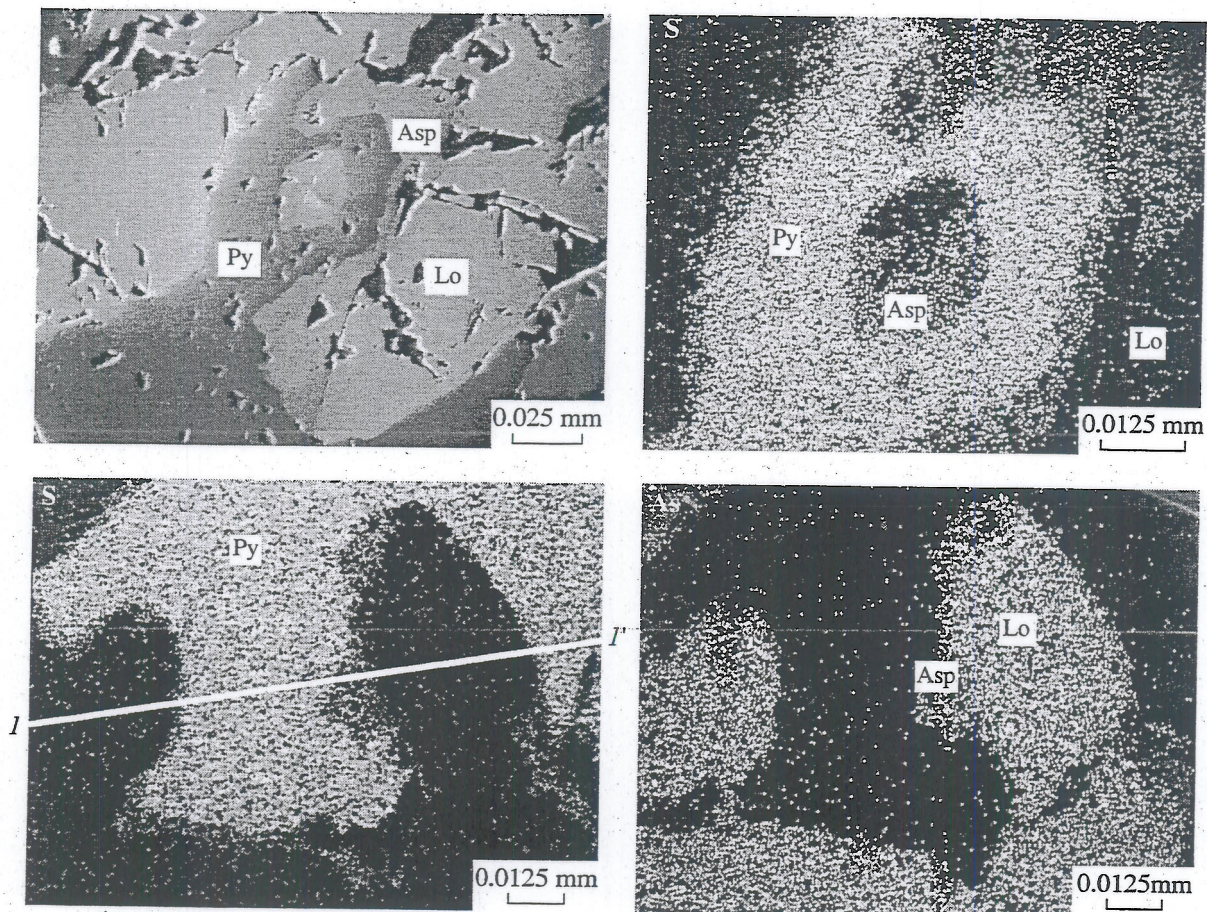


Fig. 1. Relationships between pyrite, arsenopyrite and löllingite in a sample from the Igumenov deposit. BSE and characteristic X-ray (S and As) images of two areas of a polished sample. (I-I') Scanning profile shown in Fig. 2.

Metamorphism of the *pyrite-arsenopyrite assemblage* is also hardly probable. As has been shown in experiments with the heating of the pyrite-arsenopyrite assemblage above 491°C [1], these minerals never come into physical contact in decomposition products and they are always divided by a pyrrhotite layer. The composition of arsenopyrite in the previously studied, definitely metamorphosed natural assemblage with pyrite at the Degdekan deposit varies in a wide range ($As_{min} = 26.3$, $As_{max} = 40.1$, $As_{av} = 34.5$ at %; $D = 4.1$; $N = 142$) and löllingite does not come in contact with pyrite [9]. Arsenopyrite in the above assemblage has a stable composition (Table 1) and all phases come in contact with one another.

The existence of the early *arsenopyrite-löllingite assemblage* is indicated by the high As content in arsenopyrite. The extremely high stability of arsenopyrite during retrograde alterations would not have allowed a rapid reequilibration of the already crystallized mineral with the host medium under new lower temperature conditions. At the same time, the relatively coarse-grained pyrite-löllingite intergrowths in the four-phase assemblage lack any evidence of diachronous crystallization.

The simultaneous crystallization of arsenopyrite, pyrite, and löllingite is possible only in the case of the existence of a lower temperature limit of arsenopyrite stability [7]. This statement could be confirmed by the finding of native arsenic-pyrrhotite or pyrite-löllingite assemblage (Fig. 3). However, we were able to find reliable data on the existence of such natural assemblages in the literature. Barton [10] pointed out that "pyrrhotite is incompatible with crystalline arsenic," but he did not specify the temperature range. The pyrite-löllingite assemblage is often considered to be forbidden, because pyrite and native arsenic are formed during the replacement of arsenopyrite in acid solutions, while löllingite replaces arsenopyrite in an alkaline environment [4]. At the same time, both pyrite and löllingite associate with native arsenic at the late stages of various deposits [4] indicating in favor of possible existence of the pyrite-löllingite assemblage.

Thus, calculations of theoretical possibility of the löllingite-pyrite assemblage formation become an important argument for interpretation of natural assemblages. The inferred invariant (pyrite + arsenopyrite + löllingite) point in the binary pyrite-löllingite system can be calculated in different ways.

Table 1. Chemical composition of coexisting phases along scanning profiles

Point	Mineral	Wt %				At %		
		Fe	As	S	Total	Fe	As	S
Scanning profile 1-1'								
1	Lo	27.9	72.7	1.3	101.9	33.08	64.24	2.68
2	Asp	33.6	47.2	18.4	99.2	33.32	34.89	31.78
3	Lo	27.9	72.4	1.6	101.9	32.96	63.75	3.29
4	Py	46.3	0.5	52.4	99.1	33.57	0.27	66.16
4	Py	45.8	0.5	52.7	99	33.20	0.27	66.53
4	Py	45.9	0.4	52.3	98.6	33.43	0.22	66.35
4	Py	46.3	0.4	52.1	98.8	33.71	0.22	66.07
5	Py	45.9	1.2	53	100.1	33.00	0.64	66.36
5	Py	46.4	1.3	52.5	100.2	33.43	0.70	65.87
5	Py	45.9	1.2	53	100.1	33.00	0.64	66.36
Scanning profile 2-2'								
1	Asp	34.2	47.2	18.2	99.6	33.83	34.80	31.36
1	Asp	33.6	48.4	18.1	100.1	33.20	35.65	31.15
1	Asp	34	47.7	18.1	99.8	33.64	35.17	31.19
1	Asp	34.1	47.8	18	99.9	33.74	35.25	31.02
1	Asp	33.7	48.2	18.5	100.4	33.09	35.27	31.64
2	Asp	33.8	48.1	18	99.9	33.46	35.49	31.04
2	Asp	33.7	48.4	18.3	100.4	33.15	35.49	31.36
2	Asp	34.2	48.3	18.1	100.6	33.62	35.39	30.99
2	Asp	33.9	48.2	17.3	99.4	33.91	35.94	30.15
3	Lo	28.1	70.1	1.9	100.1	33.59	62.45	3.96
3	Lo	28.5	70.7	2	101.2	33.66	62.23	4.11
3	Lo	27.2	69.9	2.2	99.3	32.72	62.67	4.61
4	Lo	28	71.4	1.9	101.3	33.13	62.96	3.92
4	Lo	27.7	71.2	1.9	100.8	32.95	63.12	3.94
4	Lo	27.1	71.1	1.7	99.9	32.63	63.81	3.57
4	Lo	27.7	71.1	1.6	100.5	33.18	63.48	3.34
5*	Py	45.7	0.9	52.6	99.2	33.12	0.49	66.39
5*	Py	46	0.7	52.4	99.1	33.38	0.38	66.24
6**	Py	46	1.9	51.8	99.7	33.42	1.03	65.55
6**	Py	46.3	1.6	51.8	99.7	33.62	0.87	65.51
6**	Py	46	1.2	52.8	100.1	33.13	0.64	66.23
6**	Py	45.9	1.4	52.8	100.2	33.04	0.75	66.21
6**	Py	45.6	1.4	51.8	98.8	33.32	0.76	65.92

Note: (Py) pyrite; (Lo) löllingite; (Asp) arsenopyrite; (*) contact with löllingite; (**) contact with arsenopyrite. Scanning profile 1-1' is shown in Fig. 1; profile 2-2' is beyond the photomicrograph boundary. Camebax microprobe, Northeastern Complex Research Institute, Magadan (V. Ya Borkhodoev, analyst). Analytical conditions: $U = 20$ keV; beam current 50 nA; specimen current 30 nA; beam diameter 2-5 μ m; counting time 5 s. Analytic lines for all elements are K_{α} . Standards (element contents are given in wt %): arsenopyrite standard Asp200—As (43.49), S (21.54), Fe (34.77); pyrite standard—Fe (46.55), S (53.45).

Calculation based on the minimization of Gibbs free energy. The equilibrium state of an isomorphous mixture is determined by tending of its free energy ΔG to a minimum. The behavior of an isomorphous mixture contain-

ing x_1 mole fractions of the first component and x_2 mole fractions of the second component is controlled by thermodynamic functions of mixing, i.e., differences of thermodynamic functions of the solid solution and

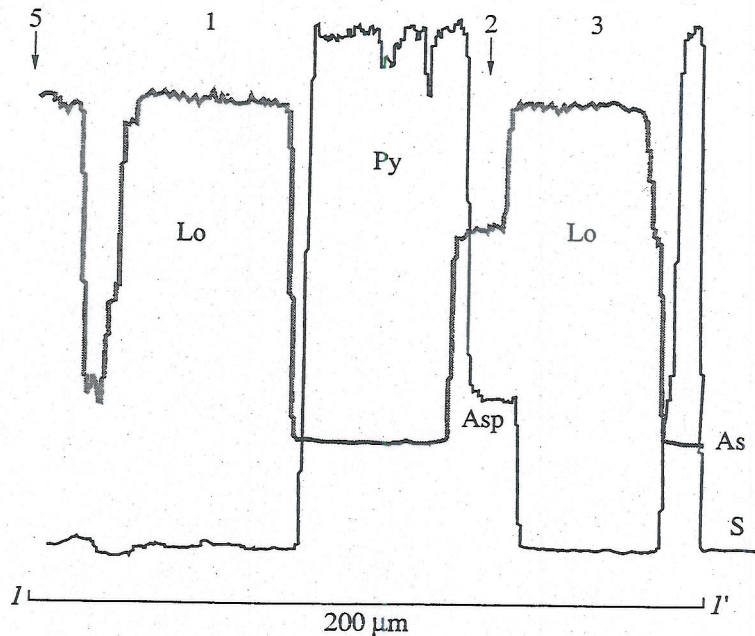


Fig. 2. Scanning profile I-I' (see Fig. 1). Numerals are analyzed points (see Table 1).

mechanical mixture of components having the same composition:

$$\Delta G_{\text{mix}}(x_1, x_2) = \Delta G_{\text{ss}}(x_1, x_2) - x_1 \Delta G_1 - x_2 \Delta G_2 \quad (1)$$

(ΔG of components of reaction $\text{FeAs}_2 + \text{FeS}_2 = 2\text{FeAsS}$ is given in Table 2). Substituting values (1), (2), and (3) from Table 2 into Eq. (1), we obtain $T_{\text{crit}} = 158 \text{ K} (-115^\circ\text{C})$. If we use the ΔG_{AsP} values from [12], i.e., (4), (2), and (3) from Table 2, then $T_{\text{crit}} = 411 \text{ K} (138^\circ\text{C})$. If the data reported by Pokrovski *et al.* [12] are supplemented with the point established by Barton [10] (ΔG_{AsP} for 298 K), then ΔG_{AsP} takes form (5) in Table 2, and $T_{\text{crit}} = 637 \text{ K} (364^\circ\text{C})$. Thus, the minimum temperature of the stability of FeAsS solid solution calculated on the basis of different constants varies from -115 to 138 and 364°C.

Calculation based on the energy theory of heterovalent replacements. The method proposed by Urusov [13] is based on a crystallochemical model of thermodynamic functions of mixing. The critical temperature T_{crit} determined by Becker in 1937 in terms of the theory of regular solutions [13] has the following relationship with the energy of mixing Q :

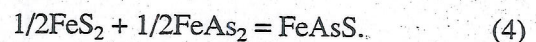
$$T_{\text{cr}} = Q/2kN \text{ or } T_{\text{cr}} = Q/4, \quad (2)$$

where Q is given in cal/mole. If Q is known, the region of immiscibility can be predicted at this approximation for any binary system. The energy of mixing or the heat of mixing ΔH_{mix} ($Q = \Delta H_{\text{mix}}$) for FeAsS (in our case, for the heterovalent isomorphism of S^{2-} and As^{3-}) will be determined by the formula [13]

$$\Delta H_{\text{mix}} = 2x_1x_2(x_1z_2^2 + x_2z_1^2)cnm(\Delta R/R)^2, \quad (3)$$

where x_1 and x_2 are mole fractions of components in the compound; z_1 , and z_2 are absolute values of charges of ions replacing each other; R_1 , R_2 , and R_3 are interatomic distances for Fe-S, Fe-As, and As-S, respectively; $R = x_1R_1 + x_2R_2 + R_3$; $\Delta R = R_2 - R_1$; m is the number of atoms in the compound; n is the coordination number, and c is the constant characterizing a degree of covalence of the compound.

We consider formation of one arsenopyrite molecule from 0.5 mole fraction of pyrite and 0.5 mole fraction of löllingite:



Substituting $z_1 = 2$; $z_2 = 3$; $R_1 = 2.25 \text{ \AA}$; $R_2 = 2.35 \text{ \AA}$; $R_3 = 2.33 \text{ \AA}$; $\Delta R = 0.10 \text{ \AA}$; $m = 3$; $n = 6$ [14]; $c = 40 \text{ kcal}$ (for disulfides with pyrite-type structure containing $[\text{S}_2]^{2-}$ anion [13, p. 64]); $R = 1/2 \cdot 2.25 + 1/2 \cdot 2.35 + 2.33 = 4.63 \text{ \AA}$ and $(\Delta R/R)^2 = 0.000484$ into formula (3),

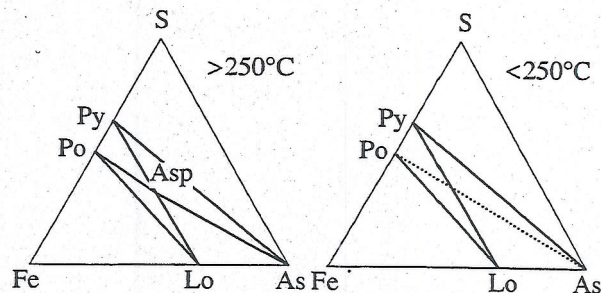


Fig. 3. Variants of phase relations in the Fe-As-S system: above 250°C (arsenopyrite-pyrite and arsenopyrite-löllingite tie-lines) and below 250°C (pyrite-löllingite and pyrrhotite-native arsenic tie-lines).

Table 2. ΔG variation for phases in the Fe-As-S system, J/mol, K

ΔG_{Asp}	ΔG_{Lo}	ΔG_{Py}	Source
$-169452 + 68.199T$ (1)	$-43304.4 - 29.706T$ (2)	—	[10]
—	—	$-300494.88 + 196.983T$ (3)	[11]
$-71661 - 160.4T$ (4)	—	—	This work*
$-55248 - 185.4T$ (5)	—	—	This work**

Note: Equations were calculated with the least squares method. (*) Data from [12]; (**) data from [10, 12].

we obtain $\Delta H_{\text{mix}} = 2.265$ kcal/mol and in compliance with formula (2)

$$T_{\text{crit}} = 566.2 \text{ K (293.2}^\circ\text{C)}.$$

If we assume that $n = 4$ (according to [15]), then formula (2) yields

$$T_{\text{crit}} = 377.5 \text{ K (104.5}^\circ\text{C)}.$$

The calculation of $(\Delta R/R)^2$ based on the unit cell volume yields an absurd value of $T_{\text{crit}} = 9672^\circ\text{C}$.

Thus, results of the calculation of an inferred invariant (pyrite + arsenopyrite + löllingite) point by several methods are poorly consistent with one another due to a low accuracy of the available thermodynamic constants for arsenopyrite at a temperature below 300°C . Nevertheless, the values of 138, 364, 293.2, and 104.5°C are rather close to the estimate of the lower temperature limit of arsenopyrite formation in natural samples based on the homogenization temperature of fluid inclusions in the host quartz ($\sim 250^\circ\text{C}$) [7]. Taking into account the absence of reliable findings of low-temperature (below 200°C) arsenopyrite in nature, this result confirms the possibility of the existence of an invariant point in the Fe-As-S system in the low-temperature region.

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