

## 'Derived' and Observed Sulphosalt-Sulphide Phase Assemblages Compared – A Case Study from Rajpura-Dariba, India

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**Abstract.** Log  $a_{S_2}$ -T diagrams for several sulphosalts (and sulphides) are constructed from published thermochemical data. Additionally, extension of published data on the Cu-S system (Barton, 1973) to the univariant phase equilibria involving fahlore and 'high-chalcocite' in the Cu-Sb-As-S system (Luce et al., 1977) permits construction of approximate As-isopleths for fahlore in log  $a_{S_2}$ -T space. Phase relationships thus derived are compared with the sulphosalt-sulphide assemblages present in the bi-phase, polymetallic mineralization at Rajpura-Dariba where geology, genesis and mineral-chemistry are well documented. A gratifying correspondence between the two is observed. Biphasic origin of the orebody, inferred from geological data, is confirmed, and rigorous narrow limits of variation of  $a_{S_2}$  and T could be set for some assemblages belonging to the second phase of mineralization. The phase diagrams also indicate that the observed pyrrhotite-proustite textural relation and the decomposition fabric of some fahlores, independently, point to an intermittent increase in the activities of  $S_2$  and As during the second phase mineralization.

### Introduction

Thermochemical studies pertaining to sulphosalts are rare in mineralogical literature due, primarily, to paucity of experimental works on relevant mineral systems. The first attempt was that of Craig and Barton (1973) who approximated the free energy changes ( $\Delta G^f$ ) associated with sulphidation reactions leading to formation of sulphosalts in appropriate systems. Two assumptions are implicit in such approximations: the sulphosalts are *stable* intermediate phases on metal sulphide – semimetal sulphide joins, and the mixing is *ideal*. The attempt is noteworthy because it provides a basis for further work even on systems for which thermodynamic data are scanty or non-existent.

Objectives of the present work are: (a) preparation of log  $a_{S_2}$ -T diagrams for several sulphosalts, based mainly on the data of Craig and Barton (1973), (b) enhancing the usefulness of the diagrams by constructing approximate isopleths of fahlore composition (in terms of atomic fraction of As), from a few available microprobe data of pertinent univariant assemblages in the Cu-Sb-As-S system (Luce et al. 1977) and indirect utilization of data from

thermochemical studies in the Cu-S system (Barton, 1973), and (c) checking the validity of the 'derived' phase relations against a natural ore assemblage (at Rajpura-Dariba, Rajasthan, India) where textural equilibrium among relevant phases are displayed. Microprobe data of fahlore and arsenopyrite of the deposit are utilized for such cross-checks.

### Method of Calculation

For the purpose of thermochemical calculation Craig and Barton's (1973) data on  $\Delta G^f$  for different sulphidation reactions (for formation of sulphosalts) are used. It must be emphasized here that these equations (for  $\Delta G^f$ ) represent thermochemical approximations and the resulting sulphidation curves are also inherently first approximations for delineating the stability fields of sulphides and sulphosalts in log  $a_{S_2}$ -T space.

The sulphidation curve of Barton and Skinner (1979) for pyrrhotite-pyrite is plotted as a reference line. Stability relation of an intermetallic compound approximated as  $Ag_{0.82}Au_{0.18}$  is extrapolated from Barton and Toulmin (1964) with a view to matching against an actual assemblage discussed later. Sulphidation curves for owoyheite and minerals of the ramdohrite group are terminated at  $\approx 300^\circ C$ , in consonance with experimental data (Hoda and Chang, 1975) on the upper limits of thermal stability of these minerals.

First,  $\Delta G^f$  for several sulphidation reactions at different temperatures are calculated (col. 6, Table 1). Activity of sulphur (in terms of log  $a_{S_2}$ ) at different temperatures is calculated from these data by the simple relation  $\log a_{S_2} = \Delta G^f / 2.303 RT$  (where R is the gas constant and T is the temperature in  $^\circ K$ ) and is incorporated in col. 7, Table 1. The univariant lines representing sulphidation reactions are plotted in log  $a_{S_2}$ - $10^3 \times T^{-1}$  diagrams (Figs. 1 and 2).

A few available microprobe data of univariant assemblages involving fahlore and 'high-chalcocite' in the Cu-Sb-As-S-system (Luce et al., 1977) are utilized for plotting the fahlore composition as a function of  $a_{S_2}$  and T. 'High-chalcocite' is equivalent to high digenite (Barton, 1973) above  $\approx 435^\circ C$  (Morimoto and Kullerud, 1963; Roseboom, 1966). But the inversion temperature is not well-defined, due to hysteresis arising from shifting of S-atoms from hexagonal to cubic – closest packing on heating (Barton, 1973). Luce et al. (1977) obtained a high

**Table 1.** Free energy of formation (for the reaction indicated) and activity of sulphur for selected sulphosalts at different temperatures

Mineral/ Composition	References on relevant systems	Sulphidation reaction	$\Delta G^\ddagger$	Temperature		
				range in (°C)	$\Delta G^\ddagger$ at diff. temp. (Cal/formula unit)	log $a_{S_2}$ at diff. temp.
(1)	(2)	(3)	(4)	(5)	(6)	(7)
Pyrargyrite $Ag_3SbS_3$	1,2	$2/3Ag_3Sb + S_2$ $= 2/3Ag_3SbS_3$	$-47,450 + 26.6T$	25 – 486	200 °C = -34,868.20 300 °C = -32,208.20 400 °C = -29,548.20 475 °C = -27,553.20	200 °C = -16.11 300 °C = -12.28 400 °C = -9.59 475 °C = -8.05
Proustite $Ag_3AsS_3$	3,4	$2Ag_2S + 4/3As + S_2$ $= 4/3Ag_3AsS_3$	$-46,000 + 33.13T$ $-48,820 + 38.71T$	25 – 176 176 – 496	200 °C = -30,510.17 300 °C = -26,639.17 400 °C = -22,768.17 490 °C = -19,284.27	200 °C = -14.09 300 °C = -10.16 400 °C = -7.39 490 °C = -5.52
Boulangerite $Pb_5Sb_4S_{11}$	5	$5/3PbS + 4/3Sb + S_2$ $= 1/3Pb_5Sb_4S_{11}$	$-55,430 + 36.71T$	25 – 610	200 °C = -38,066.17 300 °C = -34,395.17 400 °C = -30,724.17 500 °C = -27,053.17	200 °C = -17.59 300 °C = -13.12 400 °C = -9.98 500 °C = -7.65
Tetrahedrite $Cu_{12}Sb_4S_{13}$	6	$8Cu_3SbS_3 + S_2$ $= 2Cu_{12}Sb_4S_{13}$	$-41,572 + 34.84T$	25 – 540	200 °C = -25,092.68 300 °C = -21,608.68 400 °C = -18,124.68 500 °C = -14,640.68	200 °C = -11.59 300 °C = -8.24 400 °C = -5.88 500 °C = -4.14
Enargite $Cu_3AsS_4$	7,8	$2/3Cu_{12}As_4S_{13} + S_2$ $= 8/3Cu_3AsS_4$	$-41,576 + 34.91T$	25 – 500	200 °C = -25,063.57 300 °C = -21,572.57 400 °C = -18,081.57 500 °C = -14,590.57	200 °C = -11.58 300 °C = -8.23 400 °C = -5.87 500 °C = -4.12
Famatinite $Cu_3SbS_4$	6	$2/3Cu_{12}Sb_4S_{13} + S_2$ $= 8/3Cu_3SbS_4$	$-41,577 + 39.85T^a$	25 – 540	200 °C = -22,727.95 300 °C = -18,742.95 400 °C = -14,757.95 500 °C = -10,772.95	200 °C = -10.50 300 °C = -7.15 400 °C = -4.80 500 °C = -3.04
Bournonite $CuPbSbS_3$	9	$2/3Cu_2S + 4/3PbS$ $+ 4/3Sb + S_2 =$ $CuPbSbS_3$	$-55,684 + 32.96T$	104 – 435	104 °C = -43,258.08 200 °C = -40,093.92 300 °C = -36,797.92 400 °C = -33,501.92	104 °C = -25.07 200 °C = -18.52 300 °C = -14.03 400 °C = -10.88
Seligmannite $CuPbAsS_3$	10	$2/3CuS + 4/3PbS +$ $4/3As + S_2 = CuPbAsS_3$	$-46,213 + 32.59T$	104 – 435	104 °C = -33,926.57 200 °C = -30,797.93 300 °C = -27,538.93 400 °C = -24,279.93	104 °C = -19.66 200 °C = -14.23 300 °C = -10.50 400 °C = -7.88
Meneghinite $CuPb_{13}Sb_7S_{24}$	11	$2/21Cu_2S + 51/21Pb$ $+ 4/3Sb + S_2 =$ $CuPb_{13}Sb_7S_{24}$	$-55,518 + 31.89T$	104 – 435	104 °C = -43,495.47 200 °C = -40,434.03 300 °C = -37,245.03 400 °C = -34,056.03	104 °C = -25.21 200 °C = -18.68 300 °C = -14.20 400 °C = -11.06
Owyhecite $Ag_2Pb_5Sb_6S_{15}$	11,12	$2/9Ag_2S + 10/9PbS$ $+ 4/3Sb + S_2 =$ $Ag_2Pb_5Sb_6S_{15}$	$-60,407 + 34.76T$ $-61,721 + 36.38T$	25 – 176 176 – ?	100 °C = -47,441.52 200 °C = -44,513.26 300 °C = -40,875.26	100 °C = -27.80 200 °C = -20.56 300 °C = -15.59
Andorite $AgPbSb_3S_6$	12	$2/9Ag_2S + 4/9PbS$ $+ 4/3Sb + S_2$ $= 4/9AgPbSb_3S_6$	$-55,430 + 35.52T$ $-55,744 + 36.14T$	25 – 176 176 – ?	100 °C = -42,181.04 200 °C = -38,649.78 300 °C = -35,035.78	100 °C = -24.71 200 °C = -17.86 300 °C = -13.36
Fizelyite $Ag_2Pb_5Sb_8S_{18}$	12	$1/6Ag_2S + 5/6PbS$ $+ 4/3Sb + S_2$ $= Ag_2Pb_5Sb_8S_{18}$	$-55,430 + 34.47T$ $-55,665 + 34.99T$	25 – 176 176 – ?	100 °C = -42,572.69 200 °C = -39,114.73 300 °C = -35,615.73	100 °C = -24.94 200 °C = -18.07 300 °C = -13.58

1. Chang (1963)

2. Keighin and Honea (1969)

3. Hall (1966)

4. Roland (1970)

5. Craig, Chang and Lees (1973)

6. Skinner, Luce and Makovicky (1972)

\* Data from Barton and Skinner (1979)

7. Wernick and Benson (1957)

8. Maske and Skinner (1971)

9. Frumer, Kala and Horak (1973)

10. Wernick, Geller and Benson (1958)

11. Craig and Barton (1973)

12. Hoda and Chang (1975)

temperature, cation-disordered, copper sulphide phase (at 425 and 500 °C), which they call 'fcc. phase'. Since the inversion temperature of chalcocite is not properly defined, it is assumed that the 'fcc. phase' of Luce et al. (1977) may be considered as 'high digenite'.

The isopleths of fahlore are constructed as follows. First, from the microprobe data of Luce et al. (1977), three fahlore compositions are recalculated to 13 sulphur atoms for formula unit (col. 3, Table 2). The composition of the 'fcc. phase' (=high digenite) in stable equilibrium with each of these fahlores (from Luce et al. 1977, Table 4) is represented in terms of S<sub>2</sub> and Cu<sub>2</sub>S (col. 4, Table 2) and the S<sub>2</sub>/Cu<sub>2</sub>S ratios are tabulated (col. 5, Table 2). Barton (1973) plotted isopleths of high digenite in the log a<sub>S<sub>2</sub></sub>-T space, in which a particular S<sub>2</sub>/Cu<sub>2</sub>S ratio in high digenite (=fcc) at a specific temperature represents a fixed value of log a<sub>S<sub>2</sub></sub>. For the S<sub>2</sub>/Cu<sub>2</sub>S ratios of 'fcc' from Luce et al. (1977) at corresponding temperatures the values of log a<sub>S<sub>2</sub></sub> are noted from Barton's Figure 2, and tabulated (col. 6, Table 2). Since the 'fcc' and fahlore represents stable equilibrium, the log a<sub>S<sub>2</sub></sub> values obtained from 'fcc' composition correspond to a fixed fahlore composition at a particular temperature. Two values of log a<sub>S<sub>2</sub></sub> corresponding to 425° and 500 °C for practically the same fahlore composition (f.c. of As=2.60, calculated from Table 4 of Luce et al. 1977) are plotted and the line (AB) is drawn in the log a<sub>S<sub>2</sub></sub>-T space to represent the As<sub>2.60</sub>-isopleth of the fahlore (Fig. 3). A similar line (CD) drawn parallel to the former through the other data point provides the As<sub>2.89</sub>-isopleth. Other parallel lines at equal spacings are drawn which represent isopleths of As<sub>0.29</sub> interval and these cover the entire range of fahlore composition (from As=4 to As=0). Equidistant spacing of the isopleths is, again, an admittedly oversimplified approximation necessitated by the absence of suitable analytical data of synthesized compounds.

The following salient features of the sulphidation curves (Figs. 1 and 2) are worth mentioning:

1. A large number of sulphosalts are stable in the pyrrhotite field at all temperatures.
2. Some sulphosalts like proustite, seligmannite, tetrahedrite are stable in the pyrite field only at lower temperature and become stable in the pyrrhotite field at high T and high a<sub>S<sub>2</sub></sub>.

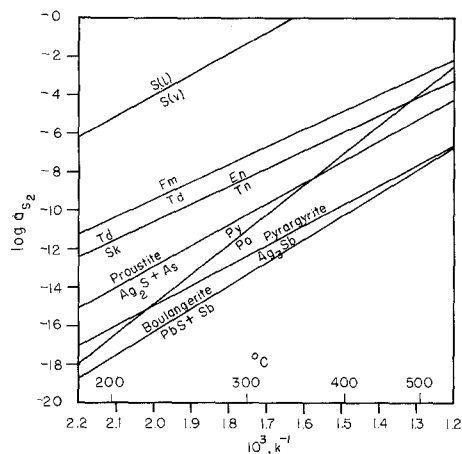


Fig. 1. log a<sub>S<sub>2</sub></sub>-Temperature projection for selected sulphosalts sulphidation curves. Data used from Table 1. Symbols: Fm – Famatinitite, Td – Tetrahedrite, Sk – Skinnerite, En – Enargite, Py – Pyrite, Po – Pyrrhotite, Tn – Tennantite

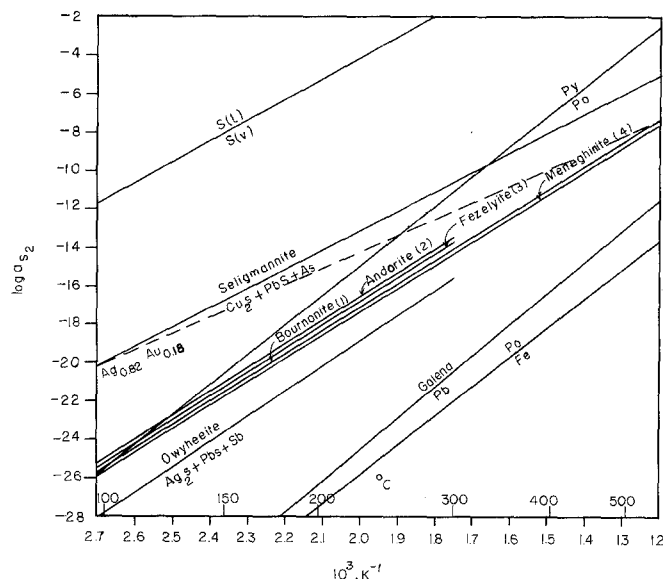


Fig. 2. log a<sub>S<sub>2</sub></sub>-Temperature projection for selected sulphosalts sulphidation curves. Data used from Table 1. Symbols: Py – Pyrite, Po – Pyrrhotite. Sulphidation reactions for lines labelled (1), (2), (3) and (4) are given in Table 1 and are not reproduced for lack of space

Table 2. Calculation of activity of sulphur from univariant assemblages of fahlore (td – tn. ss.) and the 'fcc' phase at 500 °C and 425 °C. (Data from Luce et al., 1977; Barton, 1973)

Sl. No.	Temp. (°C)	td. – tn. ss.	Co-existing 'fcc phase'			S <sub>2</sub> /Cu <sub>2</sub> S	log a <sub>S<sub>2</sub></sub>
			Comp.	S <sub>2</sub>	Cu <sub>2</sub> S		
(1)	(2)	(3)	(4)	(5)	(6)		
			(a)	(b)	(c)		
1	500	Cu <sub>12.50</sub> (Sb <sub>1.45</sub> As <sub>2.60</sub> ) <sub>4.05</sub> S <sub>13</sub>	Cu <sub>1.84</sub> S	4.17	95.83	0.04	-4.5
2	425	Cu <sub>12.64</sub> (Sb <sub>1.42</sub> As <sub>2.60</sub> ) <sub>4.02</sub> S <sub>13</sub>	Cu <sub>1.808</sub> S	5.04	94.96	0.05	-4.8
3	500	Cu <sub>13.46</sub> (Sb <sub>1.41</sub> As <sub>2.89</sub> ) <sub>4.30</sub> S <sub>13</sub>	Cu <sub>1.906</sub> S	3.09	96.91	0.03	-5.0

td. – tn. ss. – Tetrahedrite-tennantite solid solution

3. At any temperature, the As-analogues of most sulphosalts (except fahlore) require higher  $a_{S_2}$  for their formation than their antimonian counterparts (e.g., proustite-pyrargyrite, bournonite-seligmannite, etc.).

### Checking the Validity of Calculation

Dependability of such calculations involving multiple approximations has to be cross-checked by matching the 'derived' phase relations against naturally occurring assemblages and/or experimental observations. The polymetallic sulphide-sulphosalt deposit of Rajpura-Dariba, India, is chosen for this purpose since it contains a host of sulphide-sulphosalt minerals and since the geology (Chauhan, 1977; Deb and Bhattacharya, 1980; Basu, 1981) and mineral chemistry (Basu et al., 1980; 1981a, b, c; 1982) of the deposit have been investigated in detail.

The Rajpura-Dariba deposit, located in Udaipur district, Rajasthan, India, provides an example of biphase metallization (Basu, 1981). The main ore body is composed of sulphide layers interbanded with lithic units (calc-silicates and graphite-schist) and had shared the same post-depositional history as the host rocks which underwent amphibolite facies of metamorphism. Geothermometric/geobarometric data, provided by silicate mineral assemblages as well as by sphalerite geobarometric study, consistently indicate the same metamorphic PT conditions for the banded ore and the host rocks (5.5 Kb, 550 °C, Deb and Bhattacharya, 1980).

A second phase of metallization with totally different paragenesis, chemistry and texture, is superposed in the form of discordant bodies/veins of ultra-coarse grained ore facies within the primary banded ores. The difference between the two 'ore facies' is summarized in Table 3. Basu (1981) has demonstrated that the coarse-grained ore facies is younger in age, was formed at lower temperature and originated from a solution of altogether different chemistry (Basu et al., 1981c). Further, widely varying compositional range of sulphosalt minerals from the same locale is taken to indicate a very rapidly changing physico-chemical condition during the second phase of mineralization.

Three significant features of the 'banded' and the 'ultracoarse discordant' ore facies merit special mention.

1. While the banded ore facies contains predominantly pyrite and subsidiary pyrrhotite, the discordant facies contains only pyrrhotite and completely precludes pyrite.

2. The only sulphosalt mineral present in the banded ore facies is fahlore, while the discordant ore facies contains a host of sulphosalt mineral including fahlore.

3. Intermetallic compounds and native metals occur exclusively in the discordant ore facies.

A survey of log  $a_{S_2}$ -T diagrams (Figs. 1 and 2) reveals a gratifying correspondence between 'derived' and observed phase relations among mineral assemblages in the two ore-facies. This is emphasized below.

1. The 'discordant' facies, which lies completely in the pyrrhotite field, contains all the sulphosalt minerals like

**Table 3.** Mineralogical, textural and chemical differences between 'banded' and 'coarsegrained, discordant' ore facies (Summarized and modified from Basu, 1981)

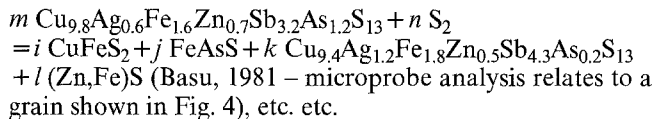
Concordant, banded ore facies	Discordant, coarsegrained ore facies
I. <i>Relation with host rock</i> Occurs as congruent bands interlayered with graphite schist and calc-silicates. Cu-, Pb-Zn and Zn-Fe rich zones within the ore body are roughly concordant with lithic units.	Occurs as discordant patches, lenses, pods and segregation veins exclusively in calc-silicates. Also, transverse to metal zoning in the banded ores.
II. <i>Ore minerals</i> Mainly pyrite, sphalerite, galena and chalcopyrite; subordinate amounts of arsenopyrite, fahlore, pyrrhotite.	Mainly galena with geocronite, fahlore, native As; Subordinate amounts of chalcopyrite and pyrrhotite and exclusive occurrences of owyheeite, bournonite-seligmannite, boulangerite, pyrargyrite-proustite, ramdohrite, meneghinite, rayite <sup>a</sup> $Pb_8(Tl,Ag)_2Sb_8S_{21}$ , Mn-bearing fahlore, an intermetallic compound $(Ag_{74.2}Au_{16.4}Hg_{9.4})$ and gudmundite.
III. <i>Gangue minerals</i> Quartz, mica, graphite, staurolite, kyanite, chert, carbonate, tremolite, fluorite, baryte etc.	Mainly coarse grained diopside, with tremolite, quartz, carbonate, baryte, fluorite ( $\pm$ quartz-carbonate-sulfide veins).
IV. <i>Textural features</i> Perfect textural equilibrium among sulphides and non-sulphides, no replacement relations, poikiloblastic inclusions of fine grained sulphides within staurolite porphyroblast; evidence of recrystallization and partial annealing. Extensive evidence of deformation of all sulphides.	Ore minerals mainly in interstices of coarse diopside grains, as irregular pockets, nebulitic nests; comb structure suggestive of open space filling, no evidence of recrystallization; all minerals except the rarest ones are coarse grained; cross-cutting relations in macroscopic and microscopic scale within banded ore imply a late stage formation. No evidence of deformation of sulphides.
V. <i>Trace metals</i> A. No enrichment in Tl, Ag, Au and Hg known.	A. Distinct enrichment in Tl, Ag, Au and Hg registered by mineral compositions; Tl-bearing geocronite, meneghinite and boulangerite. B. A late stage Mn enrichment is indicated by Mn-bearing fahlore.

<sup>a</sup>The mineral is approved by Int. Comm. on New Minerals and Mineral Names (IMA)

boulangerite, bournonite, owyheeite, meneghinite, pyrrhotite, andorite-fezelyite (Ramdohrite), all these minerals are stable well below pyrite-pyrrhotite line at all temperatures.

2. Pure tetrahedrite provides an exception in that it is stable in the pyrite field up to  $T \approx 480^\circ\text{C}$  and  $\log a_{\text{S}_2} \approx -4.5$  beyond which it becomes stable also in the pyrrhotite field. The upper stability limit of pure tennantite (lower limit unknown) virtually coincides with the lower limit of tetrahedrite stability. Equally common occurrence of fahlore (although of different compositions) in pyritic, banded ore facies as well as in the pyrrhotite-bearing, coarse-grained, discordant ore-facies at Rajpura-Dariba can therefore be easily reconciled in terms of  $\log a_{\text{S}_2}$ - $T$  diagrams.

There is however, further textural evidence that fahlore in the banded ore facies often tends to decompose into component sulphides plus a compositionally different fahlore (Fig. 4), implying instability during subsequent episode/s. The type of decomposition exhibited in Fig. 4, has been ascribed to various causes – rearrangement of components due to pressure effect (Gavelin, 1939; Sampson, 1941; Ramdohr, 1969 p. 559), change of redox potential (Bortnikov et al. 1978), reduction of Ag, Sb and increase of S, Fe, As activities (Bespayev et al., 1971), rearrangements of components during cooling (Tarantov and Garvilina, 1969), change of sulphur activity according to a schematic reaction



However, the phase diagram suggests that the most likely effect of sulphidation of tetrahedrite is formation of famatinite and not a decomposition into component phases. Hence it is unlikely that increase of  $a_{\text{S}_2}$  alone could produce such texture. Disproportionately large amount of arsenopyrite in the decomposition product (vis-a-vis the original composition of the parent fahlore – Fig. 4) corroborates such reasoning.

3. Pyrrargyrite and proustite in Rajpura-Dariba always show a consistent textural relation, with a pyrrargyrite core surrounded by a proustite rim. The calculated stability relation (Fig. 1) shows that proustite at all temperatures requires higher sulphur activity for its stabilization and of course high arsenic activity.

The two evidences from decomposition of fahlore and rimming of pyrrargyrite by proustite, taken together, clearly imply increased sulphur and arsenic activities.

4. Close spacing of many of the sulphosalt sulphidation curves in the  $\log a_{\text{S}_2}$ - $T$  space implies that small changes/fluctuations in  $a_{\text{S}_2}$  – even in the scale of microenvironment – would affect the stabilities of a large number of sulphosalt species, giving rise to a varied, complex mineral paragenesis. The unusually large number of sulphosalts reported from Rajpura-Dariba confirms this deduction.

5. It has been stated earlier (Table 3) that the coarse grained ore facies is clearly post-tectonic and formed at a lower PT condition than the metamorphic PT condition (5.5 Kb,  $550^\circ\text{C}$ ) of the primary banded ore facies. The texturally equilibrated assemblage of an intermetallic compound (=  $\text{Ag}_{0.82}\text{Au}_{0.18}$ , neglecting Hg) and owyheeite (Basu et al., 1981a) within the 'exclusively pyrrhotite field'

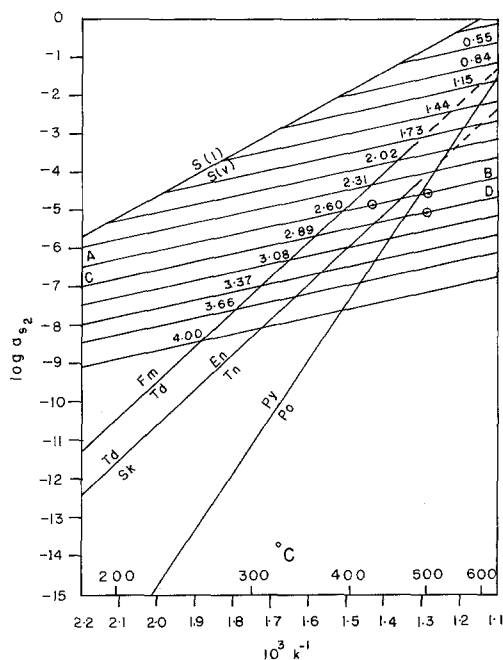


Fig. 3.  $\log a_{\text{S}_2}$ -Temperature projection for sulphidation of various fahlore compositions (atomic fraction of As indicated). The sulphidation curves for tetrahedrite (Td), Famatinite (Fm) (from Craig and Barton, 1973) and Pyrite (Py) (from Barton and Skinner, 1979) are shown as references. Circles denote actual data points

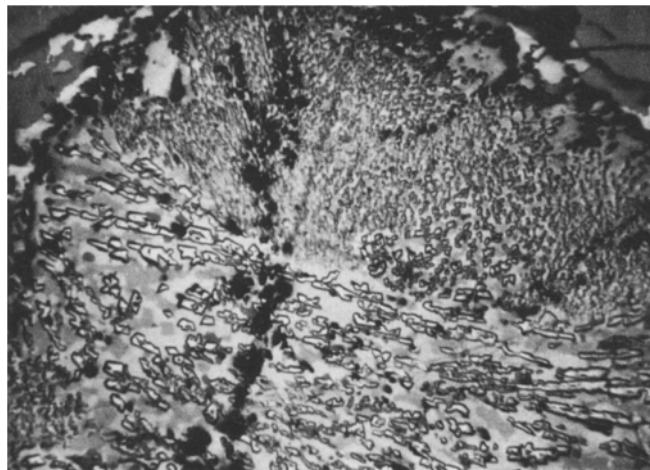


Fig. 4. Photomicrograph showing decomposition of a fahlore grain to arsenopyrite, chalcopyrite (white), sphalerite (dark grey) and a compositionally different fahlore. Border zone of the parent fahlore grain is practically undecomposed. Incident light,  $\times 90$

of this facies, sets a very narrow uppermost limit of the possible ranges of  $a_{\text{S}_2}$  ( $10^{-12}$  to  $10^{-15.8}$ ) at a temperature  $\approx 300^\circ\text{C}$ , the uppermost thermal stability limit of owyheeite (Hoda and Chang, 1975). The uppermost stability limit of Ramdohrite solid solution series is also around  $300^\circ\text{C}$  (Hoda and Chang, 1975).

6. Proustite is stable in the temperature range between  $190$ – $490^\circ\text{C}$  (Roland, 1970). Occurrence of proustite exclusively in the 'pyrrhotite field' indicates a minimum temperature of  $360^\circ\text{C}$  and a minimum  $\log a_{\text{S}_2} = -8.5$  (Fig. 1).

7a. The coarse grained ore facies shows textural equilibrium among arsenopyrite, fahlore and native As. Microprobe analysis of arsenopyrite ( $\text{Fe}_{0.99}\text{As}_{0.96}\text{S}_{1.05}$ ) corresponds to 32 at. percent of As and that of coexisting fahlore shows 3.33 atoms of As per formula unit.

The univariant equilibrium between arsenopyrite-native As ranges between 341–436 °C and a  $\log a_{\text{S}_2}$  corresponding to the upper limit (i.e., 436 °C) is  $-6.2$  (Kretschmar and Scott, 1976; Fig. 7).

The 3.37 As-isopleth (in Fig. 3) of fahlore at 436 °C gives a corresponding value of  $\log a_{\text{S}_2} \approx -6.3$ , thus providing a good match.

Thus evidence cited in (5), (6) and (7a) confirm the geological finding that minerals of the coarse-grained ore facies formed at a temperature lower than that of the peak of regional metamorphism.

7b. In another sample from the banded ore facies showing textural equilibrium between fahlore, pyrite and arsenopyrite (but the fahlore is *internally* decomposed, as in Fig. 4), microprobe analysis of arsenopyrite gives at.% As = 33.30. This composition corresponds to 491 °C, the invariant point (Kretschmar and Scott, 1976; Fig. 7) and represents a  $\log a_{\text{S}_2}$  value =  $-4.5$ . The coexisting fahlore (i.e., undecomposed margin of original grain) shows a formula content of 1.19 As.

However, the 1.20 As-isopleth (Fig. 3) at 491 °C gives a  $\log a_{\text{S}_2}$  value  $\approx -2.0$ . The mismatch here can be logically assigned to a metastable existence of fahlore which clearly shows instability by its tendency to decompose internally.

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