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Tennantite Decomposition: Evidence from the Kedabek Copper Deposit, Azerbaijan

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Summary

A microscopic study of ores of the Kedabek deposit revealed unusual microtextures of intimate intergrowths of fine grains of chalcopyrite, fahlore (tetrahedrite), arsenopyrite and sphalerite. These textures result from fahlore (tennantite) decomposition. A detailed study of the chemical composition of earlier and later generations of ore minerals and the bulk composition of the products of decomposition of tennantite suggest that the decomposition of tennantite is due to an increase in the activity of antimony. The reason for such an increase is the crystallization of earlier generations of arsenopyrite and tennantite which caused a depletion of arsenic and an increase in the antimony/arsenic ratio in residual solutions.

Zusammenfassung

Die Zerfallsbedingungen von Tennantiten aus der Kedabek-Lagerstätte, Aserbaidschan, G.U.S.

Mikroskopische Untersuchungen von Erzen der Lagerstätte Kedabek belegen ungewöhnliche Mikrostrukturen, nämlich feinkörnige Verwachsungen von Zinkblende mit Kupferkies, Fahlerz (Tetraedrit) und Arsenkies, die durch den Zerall von Tennantit entstanden sind. Eine detaillierte chemische Untersuchung der verschiedenen Generationen von Erzmineralien und deren Gesamtchemismus führt zum Schluß, daß diese Umwandlung von Tennantit durch eine Zunahme der Aktivität des Antimons bedingt ist. Diese Zunahme ist durch die Kristallisation einer früheren Generation von Arsenopyrit und Tennantit verursacht, die zu einer Verarmung der Restlösung an Arsen und einer Erhöhung des Antimon/Arsen-Verhältnisses geführt haben.

Introduction

There is much textural evidence to support the reequilibration of ore minerals as a result of postdepositional changes in the physico-chemical environment. Unique mineral intergrowth textures may often be generated by these processes. Among such textures, the fine aggregates of chalcopyrite, fahlore, arsenopyrite and sphalerite in chalcopyrite ores at the Kedabek deposit (Azerbaijan) are of great interest. According to Genkin (1958), these textures first described by Betekhtin (1940), were formed during fahlore decomposition.

As chemical features of tennantite decomposition have not been discussed previously, we have performed studies of the chemical composition of earlier and later generations of ore minerals associated with fahlore, and of the bulk composition of the tennantite decomposition products. The results obtained are the object of this paper.

Geological Setting

The Kedabek deposit was one of the most important copper mines in the Caucaus Mountains. Exploitation ceased in 1920 (Alizade, 1975). The deposit is located within a zone where the Dashkesan synclinorium and the Shamhor anticlinorium join (Kerimov, 1963). This zone consists of volcanogenic and sedimentary rocks of Jurassic age. The lower unit is porphyrite of Middle Jurassic age which has been metamorphosed into garnet and epidote hornfels. These rocks are unconformably overlain by quartz porphyries. The upper unit of the sequence is composed of effusive-pyroclastic rocks including diorite, hornblende and plagioclase porphyries, their tuffs and tuffobreccias. Carbonate beds overlie the volcanogenic rocks. These rocks form an anticlinal fold striking North-West. Major North-West to South-East trending faults transsect the Kedabek ore field. A plagiogranite-porphyry and granitoid intrusives intrude the volcanogenic sequence. The early Cretaceous granitoid intrusive is polyphase; the first phase consists of gabbro, gabbronorite, diorite, while the second phase includes quartz diorite, granodiorite and tonalite.

Ore bodies are located within quartz porphyries which are altered to secondary quartzites in the Misdag Mountains near a large intrusion of quartz diorite. There are two types of ore bodies: veins and zones of a veinlet—disseminated mineralization are recognized (Alizade, 1975). Three stages have been established in the mineral paragenesis. The products of the earliest stage consist of pyrite, pyrrhotite and arsenopyrite. The principal minerals of second stage are pyrite, arsenopyrite, chalcopyrite, sphalerite and fahlore. Gold, molybdenite and pyrite were deposited during the third stage.

Intergrowth of Ore Minerals at the Kedabek Deposit

The samples examined consist of sulphide aggregates with grains 3–5 mm across. The most widespread mineral among the sulphides is chalcopyrite. Varying proportions of sphalerite, pyrite, fahlore, arsenopyrite and pyrrhotite were observed. Sphalerite occurs as large, sometimes polysynthetically twinned, grains. The pyrite grains are rounded, but rarely idiomorphic. Occasionally they contain inclusions of sphalerite and fahlore. A later generation of pyrite, sometimes intergrown with
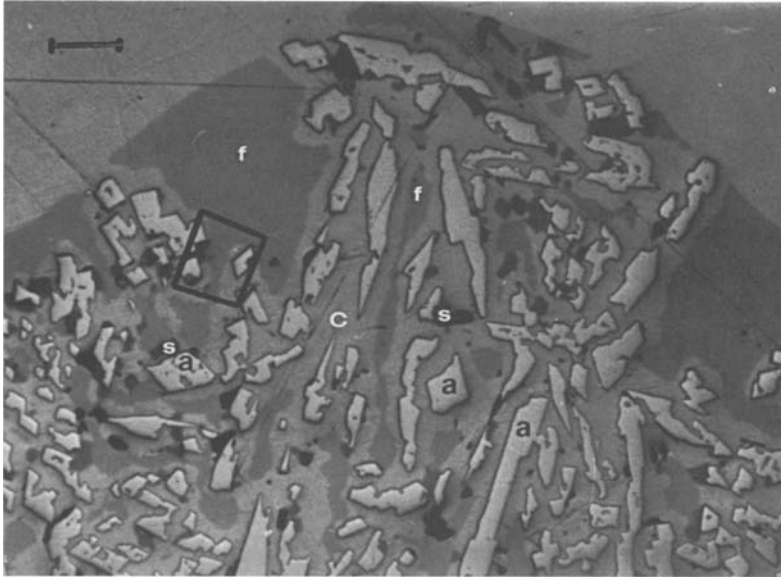
Fig. 1. The final stage of tennantite decomposition: intergrowths of arsenopyrite (a), newly-formed tetrahedrite (f), sphalerite (s), chalcopyrite (c). Area marked □ is the scanning region of Fig. 4. Polished section. Scale bar is 100 micrometers

marcasite, replaces pyrrhotite. The aggregates of fahlore are smaller than those of other sulphides. There is evidence that fahlore was deposited after sphalerite because it overgrows sphalerite grains. However, smooth boundaries between the grains of sphalerite and fahlore were also observed. The lack of observed replacement textures implies contemporaneous deposition of these minerals.

The salient feature of ores at the Kedabek deposit is the sporadic presence of intimate intergrowths of small grains of fahlore, arsenopyrite, chalcopyrite and sphalerite resembling myrmekite and eutectoid textures (Fig. 1). In these intergrowths, fahlore forms 20–30 μm grains while arsenopyrite occurs as oblong 30 × 300 μm and irregular 5 × 500 μm grains. Tiny sphalerite grains up to 10 mm overgrow arsenopyrite and fahlore. The fine-grained aggregates are composed of chalcopyrite. In contrast to the earlier coarse-grained chalcopyrite generation, newly-formed chalcopyrite grains are polysynthetically twinned. Several successive stages of tennantite decomposition have been distinguished.

The initial stages of tennantite decomposition are documented by the development of small elongated patchy areas composed of chalcopyrite and small crystals of arsenopyrite along the cracks (Fig. 2). An intermediate stage of alteration is registered by further coarsening of grains. Finally, interlocking "eutectoid" intergrowths formed, composed of chalcopyrite, arsenopyrite, sphalerite and fahlore with elongated arsenopyrite crystals. They may consist of arsenopyrite, sphalerite and chalcopyrite ± fahlore. While in similar neighbouring aggregates fahlore forms "sheath-like" rims, the central parts of the grains are composed of fine intergrowths of arsenopyrite, sphalerite and chalcopyrite (Fig. 3). It should be noted that both intact fahlore grains and fine grained aggregates of the decomposition products may be observed in the same polished section. The size and shape of fine-grained aggregates correspond to those of the early fahlore generation grains. These inter-
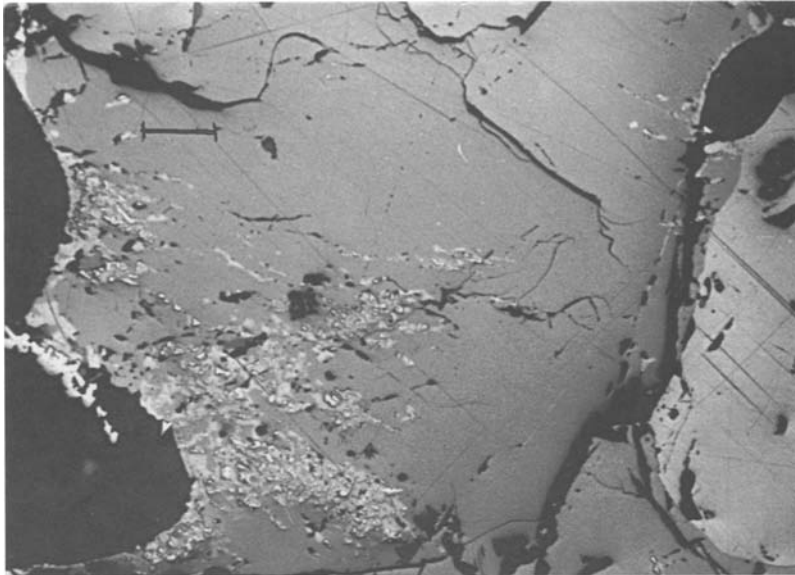
Fig. 2. The initial stage of tennantite decomposition: finegrained aggregates of arsenopyrite (white) and chalcopyrite (light grey) developing along fissures and on the periphery of coarse tennantite grains (grey) of the early generation. On the left—quartz (black), on the right—chalcopyrite of early generation (light grey). Polished section. Scale bar is 100 micrometers
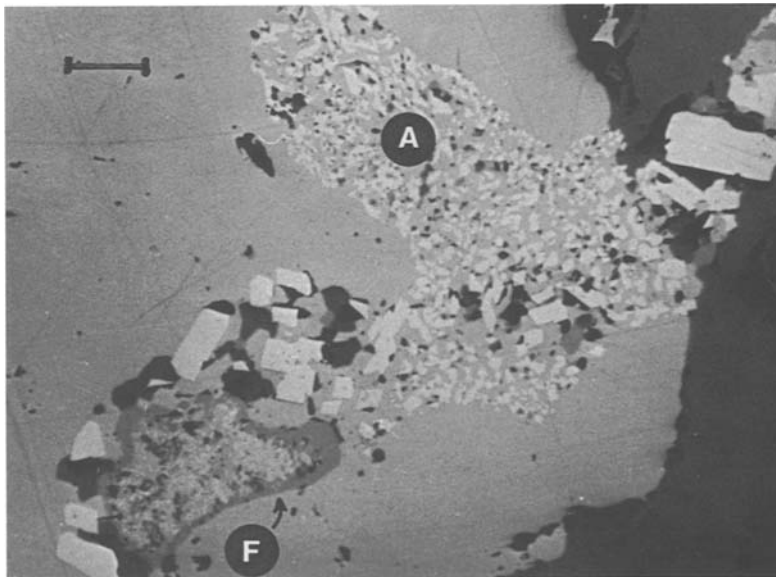
Fig. 3. Fine-grained intergrowths of arsenopyrite, chalcopyrite and sphalerite (A) and intergrowths of similar mineral composition, rimmed by fahlore (dark grey) (F). Both intergrowths are in chalcopyrite of early generation (light grey). Black—quartz. Polished section. Scale bar is 100 micrometers

growth textures permit us to conclude that two paragenetic associations with slightly different compositions formed at different times in the Kedabek deposit ores. The main minerals, both in the earlier and later associations, are arsenopyrite,

chalcopyrite, sphalerite and fahlore. A mineral paragenetic association is here defined as an assemblage of minerals, formed synchronously or successively under similar physical and chemical conditions without clearly displayed disequilibrium relations between these minerals.

Significantly, the later paragenetic association originated during the decomposition of fahlore which belonged to the earlier paragenesis. An understanding of changes in the chemical composition of heterochronous generations of the same mineral and of what chemical alterations occur during fahlore decomposition might shed light on the reasons for this phenomenon.

Materials and Methods of Investigation

Chemical composition was investigated with a Cameca MS-46 electron probe microanalyser at 20 kV and a beam current of 0.02 mA. The beam diameter was

Table 1. *Microprobe analyses of fahlores from the Kedabek deposit*

Analysis number	As	Sb	Fe	Zn	Cu	Ag	S	Total	As / Sb+As	Fe / Zn+Fe	Ag / Cu+Ag
1	18,79	2,44	5,92	2,10	42,87	0,55	28,82	101,49	0,93	0,77	0,007
	3,66	0,29	1,55	0,47	9,85	0,07	13,12				
2	18,91	2,51	5,72	2,03	42,72	0,54	28,63	101,06	0,93	0,77	0,007
	3,70	0,30	1,50	0,46	9,86	0,07	13,09				
3	18,52	2,57	5,72	1,98	42,44	0,52	28,53	100,28	0,92	0,77	0,007
	3,65	0,31	1,51	0,45	9,87	0,07	13,15				
4	18,85	2,49	5,89	2,09	42,66	0,50	28,21	100,69	0,93	0,77	0,007
	3,71	0,30	1,56	0,47	9,90	0,07	12,98				
5	18,77	2,68	5,95	1,85	24,19	0,59	27,82	99,87	0,92	0,79	0,008
	3,72	0,33	1,59	0,42	9,89	0,08	12,93				
6	10,96	15,09	5,98	2,35	39,81	1,23	27,95	103,37	0,54	0,75	0,018
	2,21	1,87	1,62	0,54	9,45	0,17	13,16				
7	10,65	17,43	5,96	2,40	37,91	1,43	27,08	102,77	0,50	0,74	0,020
	2,19	2,21	1,64	0,57	9,13	0,13	13,02				
8	9,61	16,81	6,00	2,25	38,49	1,51	27,06	101,73	0,48	0,76	0,023
	1,99	2,14	1,67	0,53	9,39	0,22	13,09				
9	9,27	19,02	5,82	2,60	37,58	1,53	26,90	102,72	0,44	0,72	0,023
	1,92	2,43	1,62	0,62	9,18	0,22	13,03				
10	8,37	18,46	5,63	2,69	38,81	1,47	27,35	102,78	0,42	0,74	0,022
	1,72	2,34	1,55	0,63	9,41	0,21	13,14				
11	6,95	22,00	5,02	2,64	38,62	2,03	25,03	102,29	0,34	0,69	0,03
	1,49	2,89	1,43	0,65	9,72	0,30	12,49				
12	4,68	25,00	4,97	2,93	36,84	2,50	25,51	102,54	0,23	0,66	0,04
	1,01	3,31	1,43	0,72	9,34	0,37	12,81				
13	3,43	26,73	4,87	3,13	36,36	3,07	24,81	102,48	0,17	0,65	0,05
	0,75	3,59	1,43	0,78	9,35	0,47	12,65				
14	3,03	27,02	5,36	3,43	35,92	3,03	24,47	102,16	0,15	0,65	0,05
	0,66	3,64	1,57	0,86	9,27	0,46	12,51				

2–3 μm. The following standards and wavelengths were used: synthetic $CuFeS_2$ (for CuKα and FeKα, synthetic NiAs (As Lα), natural stoichiometric FeAsS (for FeKα), CdS (for CdKα and SKα), pure metals Ag (for AgLα), Zn (for ZnKα) and Sb (for SbLα). The measured X-ray intensities were processed by the "PUMA" correction program. To determine the bulk chemical composition of the fahlore decomposition products, ten areas of the fine-grained chalcopyrite-arsenopyrite-sphalerite-fahlore intergrowths were analysed by scanning with a broadened electron beam. The squares examined were 300 × 150 μm in size. Modal analysis of five areas composed of these intergrowths of 100 × 100 μm were also performed using "Magiscan-2". The quantitative proportions of the minerals obtained were used to calculate the bulk composition of the examined aggregates. The results are listened in Tables 1–3.

Table 2. *Comparison of the chemical composition of unaltered tennantite and the bulk chemical composition of the products originated at the early tennantite decomposition*

Components	Unaltered tennantite		Products of the tennantite decomposition		
	1		2	3	
	wt%	atom%	wt%	wt%	atom%
Cu	42,30	34,1	18,3–27,9	20,81	16,2
Ag	0,54	0,2		0,07	
Fe	5,80	5,3	21,9–30,5	26,12	23,1
Zn	1,99	1,6	2,86–7,05	5,09	3,8
As	18,65	12,7	10,65–19,11	15,20	10,0
Sb	2,53	1,1	1,92–6,26	3,13	1,3
S	28,20	45,0	28,3–32,3	29,66	45,0

1—average from 5 analysis; 2—the compositional range; 3—average from 10 analysis

Table 3. *Modal analysis of constituents within the decomposition area*

Mineral	Density	Molecular weight	Volume of minerals in μm^3					Average from 5 analys.	Contents in moles
			1	2	3	4	5		
Sphalerite	4,088	96,46	590	591	637	652	587	612	25,93
Tetrahedrite	4,936	1659,97	2083	2041	2260	2000	2073	2091	6,22
Chalcopyrite	4,2	183,52	4518	4591	4200	4463	4518	4518	102,02
Arsenopyrite	6,163	162,83	2809	2772	2903	2885	2882	2839	107,45
Tennantite	4,581	1482,75	10000	10000	10000	10000	10000	10000	30,90

Note: Density and molecular weight of tennantite and tetrahedrite are calculated on the basis of the microprobe analysis from Table 1 and their cell dimensions obtained from the equation (*Mozgova, Tsepin,* 1983). Density and molecular weight of other minerals from *Naumov* et al. (1971)

Chemical Features of Tennantite Decomposition

The chemical compositions of different fahlore generations varied greatly. Undecomposed fahlore is virtually the arsenic end member of the tennantite-tetrahedrite series with a minor antimony concentration (Table 1, analysis 1–5). It contains small amounts of silver. Iron predominates over zinc in this generation. The chemical composition of the later fahlore generation is radically different. Firstly, it is richer in the tetrahedrite component (Table 1, analysis 6–14). In some cases newly-formed fahlore is actually the antimony end member of the tennantite-tetrahedrite series (Table 1, analysis 12–14). Secondly, a wide variation in composition was found within the minerals of the later generation. The $As/(Sb + As)$ ratio ranges from 0.15 to 0.54. The $Ag/(Ag + Cu)$ ratio has a narrower range of variation from 0.018 to 0.05. There is a correlation between the antimony and silver contents in fahlore. Within small areas consisting of the decomposition products, the fahlore composition varies insignificantly (Table 1, analyses 6, 7, 11–14). Scanning electron microscopy has shown that the relict grains of earlier fahlore are surrounded by thin rims of later fahlore enriched in silver and antimony (Fig. 4).

In contrast to the composition of fahlore, both earlier and later generations of sphalerite and arsenopyrite are practically indistinguishable. Both sphalerite generations are iron-poor varieties (2.04–3.60 wt.% Fe or 6–7 mole % FeS) and contain 0.4–1.0 wt.% Cu and 0.4–0.5 wt.% Cd.
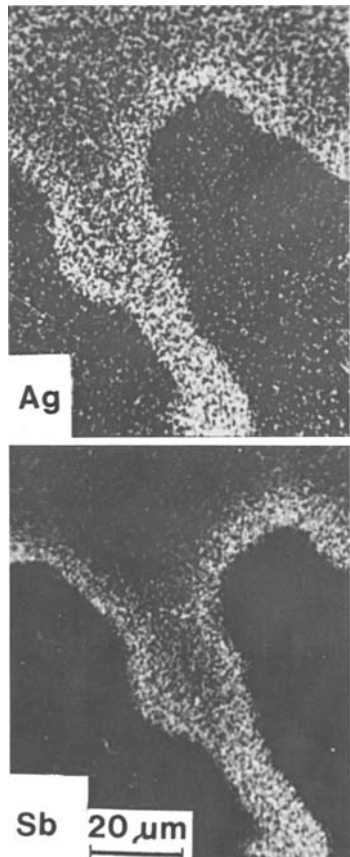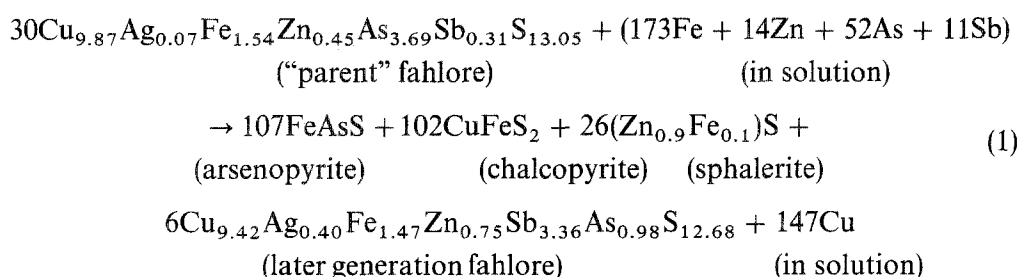

Fig. 4. Element distribution a) $AgK\alpha1$ b) $SbK\alpha1$ scanning pictures of a relic grain of fahlore from the intergrowth marked (A) on Fig. 1

The above data suggest that if the tennantite is replaced by an aggregate of newly-formed minerals, the compositions of sphalerite and arsenopyrite remain virtually costant while the later fahlore generation is enriched in antimony and silver relative to the early generation of this mineral.

A comparison between earlier fahlore compositions and the bulk composition of its decomposition products (Table 2) shows that the decomposition process resulted in depletion of copper and enrichment in iron. A more accurate estimate of the component mass ratio can be gained by calculating molecular amounts of the fahlore-substituting minerals, assuming constant volume under metasomatic processes. The quantitative data on volume proportions of newly-formed minerals measured with "Magiscan-2" in 100 μm^2 was converted to molecular ratios using data on the chemical composition of minerals, determined by microprobe analyses, as well as their density and molecular weight (Table 3). These calculations suggest that the fahlore decomposition can be expressed by the reaction of:

$$30Cu_{9.87}Ag_{0.07}Fe_{1.54}Zn_{0.45}As_{3.69}Sb_{0.31}S_{13.05} + (173Fe + 14Zn + 52As + 11Sb)$$

("parent" fahlore)   (in solution)

$$\rightarrow 107FeAsS + 102CuFeS_2 + 26(Zn_{0.9}Fe_{0.1})S +$$

(arsenopyrite)   (chalcopyrite)   (sphalerite)   (1)

$$6Cu_{9.42}Ag_{0.40}Fe_{1.47}Zn_{0.75}Sb_{3.36}As_{0.98}S_{12.68} + 147Cu$$

(later generation fahlore)   (in solution)

The technique we have employed can not accurately estimate the balance of components. Therefore, approximate coefficients are given for reaction (1). To balance this reaction some quantities of Ag and S should be added to the reactant side. Since amounts of these elements are minor in comparison with the mass of these elements participating in the reaction, it is possible that these differences are a consequence of the ambiguous analysis of minerals and their ratio calculations. We shall therefore ignore them. Thus, semiquantitative data we have obtained from these calculations indicate that fahlore decomposition is accompanied by a removal of copper and an increase in iron, zinc, arsenic and antimony.

Discussion

The mechanisms and conditions of fahlore decomposition have been previously discussed in the literature. *Genkin* (1958) suggested that intergrowths of chalcopyrite, fahlore, arsenopyrite and sphalerite resulting from tennantite decomposition were generated under the action of reducing solutions, which led to the reduction of As^{+3} (or Sb^{+3}) in fahlore to As^{-1} in arsenopyrite (or Sb^{-1} in gudmundite). He assumed that introduction of Fe and liberation of Cu occurred during this process as well. A different conclusion was reached by *Ramdohr* (1980) who believed that fahlore decomposition was isochemical and due to a rearrangement of components between minerals in response to pressure. Instability of fahlore was also attributed to a change in the redox conditions with an associated loss of copper and arsenic and a gain of antimony and silver (*Bespayev* et al., 1971). *Basu* et al. (1984), who were the first to study the mass balance during tetrahedrite replacement, showed that this

phenomen was due to an increase in activity of As, Fe, S and loss of Cu, Zn, Ag and Sb.

We would like to stress that the previous work paid attention only to changes that had occurred during fahlore substitution and ignored the mineral compositions in the earlier and later paragenetic associations and the chemical compositions of ore minerals (arsenopyrite and sphalerite) other than fahlore. However, we believe that knowing the compositions of minerals composing the early and later paragenetic associations may contribute to our understanding of the reasons which lead to fahlore decomposition.

There is little information on the factors that affect the distribution of arsenic and antimony between the minerals of the tennantite-tetrahedrite series and hydrothermal solutions (*Mishra* and *Mookherjee*, 1986; *Sack* and *Loucks*, 1985; *Sack* et al., 1987). The analytical formulation of *Mishra* and *Mookherjee* (1986) indicates that the exchange reactions Fe–Zn and As–Sb between coexisting sphalerite and fahlore and seligmanite series depend on temperature and sulfur fugacity. A similar conclusion was arrived at by *Prokof'ev* et al. (1988) on the basis of studies of fluid inclusions in sphalerite and chemical composition of coexisting sphalerite and tennantite-tetrahedrite minerals. *Hackbarth* and *Petersen* (1984) found a progressive increase in Ag/(Cu + Ag) and Sb/(As + Sb) ratios in the tennantite-tetrahedrite minerals from earlier generations to the latest ones in zoned crystals. Samples from the central or deeper parts of a deposit contained less Ag and Sb. A fractional crystallization model was proposed by *Hackbarth* and *Petersen* (1984) to explain the compositional variability of fahlore in time and space. The main conclusion was that crystal energies and As–Sb fractionation between fahlore and hydrothermal solutions determine the composition of minerals and are responsible for zonality in crystals and deposits.

Sack et al. (1987) suggested that there is a strong dependence of the distribution coefficients of the As-Sb exchange reactions between fahlores and hydrothermal solutions. However this consideration does not give an answer to the question of what processes may be responsible for the fahlore decomposition phenomenon. *Sack* and *Loucks* (1985) pointed out that the model proposed was correct when tennantite-tetrahedrite dominating minerals crystallized from hydrothermal solutions. If other sulfides such as pyrite, arsenopyrite, sphalerite and chalcopyrite are coprecipitated with fahlore, there are other factors which affect the composition of tennantite-tetrahedrite minerals.

It is evident, that, where spalerite and iron sulfides are codeposited with fahlore, sulfur fugacity should be considered. The principal difference between the two nonsynchronous mineral associations in the ores lies in the fahlore chemical composition (i.e. the early association contain tennantite, the late one involves tetrahedrite), whereas those of early and late generations of sphalerite and arsenopyrite are practically identical. Clearly, fahlore of a specific composition was unstable during the ore transformation, i.e. tennantite was in disequilibrium under conditions different from those present at the time of ore deposition and was replaced by tetrahedrite, while the iron content in sphalerite and the As/S ratio in arsenopyrite were not re-equilibrated. This observation led us to the assumption that physico-chemical parameters such as temperature and sulfur activity, should remain constant, based on studies of the systems Fe–Zn–S and Fe–As–S, which show these parameters control the iron content in sphalerite and the As/S ratio in arsenopyrite equilibrated

with the iron sulfides (*Barton* and *Skinner*, 1979). The presence of newly-formed fahlore with Sb^{+3} and As^{+3} in the late paragenetic association implies that the variations in the valency of these elements did not occur during fahlore decomposition. Consequently, tennantite instability can not be considered as a result of the differences in redox conditions during the postdepositional episodes. The changes in the contents of copper and iron which occurred during the process did not affect the replacement of other minerals or cause an alteration of their chemical compositions, but rather produced a change in the quantitative ratios of minerals only. Consequently, an increase in antimony activity or a change in the antimony/arsenic activity ratio caused the tennantite instability. The latter might be due to differing stabilities of the complexes of these elements in the mineral-forming solutions.

In order to understand the cause of the fahlore decomposition, data are needed on the dominant aqueous species of arsenic and antimony. The exchange reaction, written in terms of dominant arsenic and antimony complexes (e.g. *Spycher* and *Reed*, 1989) may be as follow:

$$Cu_{10}Fe_2Sb_4S_{13} + 2HAS_3S_6^{-2} + H^+ = Cu_{10}Fe_2As_4S_{13} + 3HSb_2S_4^{-1} \quad (2)$$
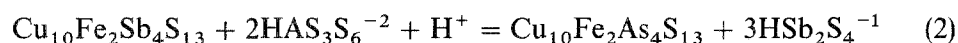
Reaction (2) demonstrates clearly that the distribution of these elements between minerals and fluid depends on pH. Acidification stabilizes tetrahedrite relative to tennantite. The processes causing the increase of pH require clarification. Mixing with acid sulfate water might play an important role in driving acidification (*Spycher* and *Reed*, 1989). The reasonable assumption can be made that crystallization of arsenopyrite and tennantite decreased the arsenic concentration in the residual solution and this caused the increase in the Sb/As ratio.

Conclusions

Evidently, changes in the contents some elements (copper, iron and zinc) cause a variation in the proportions of minerals rather than an alteration in the mineral composition of ores or in the chemical composition of minerals; i.e., the stability of minerals does not depend on activities of these components (such components were called the inert components by *Korzhinsky* (1955)). Rather, the activities of other components such as arsenic and antimony control the chemical composition of fahlore (i.e. these metals are the perfectly mobile components, according to *Korzhinsky*, 1955).

However, it is possible that similar textures produced during fahlore decomposition may have resulted from different processes. Ramdohr's words should be remembered: "It is most emphatically pointed out that many textures can form in a variety of ways and that even where at present only one mode of formation is known, the possibility of several modes of formation exists" (*Ramdohr*, 1980, p. 195).

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