SCHENDLECK-TYPE FAHLORE: AN UNUSUAL VARYING TETRAHEDRITE-TENNANTITE SOLID SOLUTION

by

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Abstract

A rarely occurring complete tetrahedrite-tennantite solid solution has been reported from the Schendleck area (Lower Austria). The fahlores from this region ("Schendleck-type" fahlore) represents an unique type, exhibiting a strong inhomogeneity and a wide range of the Sb/(Sb+As) ratio (from 5 to 95% tetrahedrite-content). The presence of the Schendleck-type fahlore indicates that the complete fahlore solid solution between the nearly pure Sb-endmember and the nearly pure As-endmember exists in nature.

Zusammenfassung

Das seltene Vorkommen einer kompletten Fahlerz-Mischkristallreihe (Tetraedrit-Tennantit) wird aus dem Bereich Schendleck (Niederösterreich) dokumentiert. Die einzigartigen Fahlerze dieses Gebietes ("Schendleck-Typ" Fahlerze) zeigen starke Inhomogenitäten und einen weiten Bereich des Sb/(Sb+As) Verhältnisses (von 5 bis 95% Tetraedrit-Gehalt). Das Auftreten dieses Schendleck-Typ Fahlerzes weist darauf hin, dass die komplette Fahlerz-Mischkristallreihe zwischen dem nahezu reinen Sb-Endglied und dem nahezu reinen As-Endglied in der Natur vorhanden ist.

Introduction

Schendleck (Schendlegg) (15°46′E - 47°42′N) is a small historical mining area between the villages Großau and Kleinau (Semmering area, Lower Austria). The area has been originally mined for iron and copper. Geologically, the area consists mainly of low-grade metamorphic quartz porphyry "Blasseneck Porphyroid" of "Caradocian" age (Upper Ordovicium). The quartz porphyry, which is a part of the Noric Nappe (the upper tectonic unit of the Greywacke Zone) represents in situ the lowest stratigraphic unit in the Schendleck area. Beside the quartz porphyry, the Schendleck area contains siderite veins cutting the quartz porphyry (POHL & BELOCKY, 1994) and also eight to ten meters thick siderite layers with disseminated and fissure-filling chalcopyrite and 15 cm thick fahlore layers (HACKENBERG, 2003).

The chemical formula of the fahlores from Schendleck has been given so far as $(Cu_{10.16}Fe_{1.06}Zn_{1.20}Hg_{0.02}Ag_{0.01})_{12.45}(Sb_{2.26}As_{1.70}Bi_{0.03})_{3.99}S_{13.45}$ (SCHROLL & AZER, 1958; GÖTZINGER et al., 1997).

The fahlore group (tetrahedrite-tennantite solid solution) is one of the most common sulfosalt minerals group, where tetrahedrite $(Cu_{12}Sb_4S_{13})$ and tennantite $(Cu_{12}As_4S_{13})$ are the most common mineral phases. CHARLAT & LÈVY (1974) proposed a general formula for the tennantite-tetrahedrite series as (Cu,Ag)₁₀(Fe,Zn,Cu,Hg,Cd)₂(As,Sb)₄S₁₃. The authors also concluded that within the fahlore group minerals the Sb-rich endmember is most frequently occurring. JOHNSON et al. (1986) gave a generalized formula of naturally occurring fahlore as (Cu,Ag)₆Cu₄(Fe,Zn,Cu,Hg,Cd)₂(Sb,As,Bi,Te)₄(S,Se)₁₃. In general, the classical formulae of the pure tetrahedrite or tennantite endmembers, i.e. Cu₁₂Sb₄S₁₃ or Cu₁₂As₄S₁₃, respectively, have never been reported from natural occurrences (KLÜNDER et al., 2003). In addition, review of published data show that fahlores representing a complete solid solution series from pure Asendmember tennantite to Sb-endmember tetrahedrite are missing in the literature (e.g. NASH, 1975; RAABE & SACK, 1984; LYNCH, 1989; ARLT & DIAMOND, 1998; FOIT & ULBRICH, 2001; DI BENEDETTO et al., 2002; SACK et al., 2002, 2003; GRAMMATIKOPOULOS et al., 2005). The present work aims to investigate the chemically extremely inhomogeneous composition of the fahlore group minerals in the Schendleck area, representing an unique type of fahlores.

Samples and experimental

In the studied samples from Schendleck, the fahlores occur as very small encrustations with minor chalcopyrite. The fahlores are hosted in quartz porphyry. For determining the chemical compositions of the studied fahlore samples from the Schendleck locality, a total of 231 spots (every spot represents one mineral grain) in eight carbon-coated polished sections were prepared for quantitative energy dispersive X-ray (EDX) microanalysis investigations. In addition, profiles of 20 point analyses were carried out in eight selected larger mineral grains. The analyses were performed on a Jeol JSM-6400 scanning electron microscope (SEM) equipped with a Link quantitative energy dispersive X-ray (EDX) microanalysis unit. Cobalt was used for internal gain calibration. An acceleration voltage of 20 keV was applied, the channel width was set to 20 eV, matrix absorption and fluorescence effects were corrected by the ZAF-4 algorithm (Link analytical). The standards used were arsenopyrite (As), galena (Pb), pyrite (S) and native Ag, Au, Bi, Cd, Cu, Fe, Hg, Mn, Sb and Zn. The measurements were accurate to ± 2 rel %.

Results

Ore microscopy and SEM

Under the ore microscope, the studied fahlores occur in close association with chalcopyrite. Chalcopyrite (CuFeS₂) occurs as sub- to euhedral interstitial grains and as fracture fillings within the fahlores (Fig. 1). The analyses of the chalcopyrite grains show that the Cu-content ranges from 34.51 to 35.14 wt %. Only with SEM, Ag-rich gold ("electrum") inclusions in chalcopyrite were determined (Fig. 1). The analyses of the gold grains show Au-content ranging between 64 and 69 wt %, Ag-content from 28 to 33 wt % and minor amounts of Hg ranging up to about 4.5 wt % (Tab. 1).

Gold inclusions associated with Austrian fahlores have been noticed before in Veitsch, Mitterberg, Serfaus, St. Martin and Rottenmann by KUCHA et al. (1995; 1997a, b).

Figure 1

Back scattered electrons (BSE) micrograph showing sub- to euhedral grains of chalcopyrite in fahlore masses and Ag-rich gold inclusions in chalcopyrite.

Total



-		-	-	-					
Sample No.	SE11	SE12	SE13	SE21	SE22	SE23	SE36	SE37	SE39
					wt %				
Ag	30.45	30.77	29.27	28.84	28.91	29.69	32.15	30.71	29.42
Hg	3.56	3.88	2.84	2.25	3.64	3.58	3.74	4.21	4.51
Au	65.66	64.95	67.12	68.88	67.06	66.24	64.05	64.89	65.48

99.97

99.61

99.51

99.94

99.81

99.41

Table 1

Representative analyses of Ag-rich gold in Schendleck area.

99.60

99.23

99.67

Fahlore occurs as an- to subhedral grains and masses. Some grains show faint brownish red

internal reflections, which may have higher amounts of As than the other grains. Inclusions of euhedral grains and subhedral masses of chalcopyrite and euhedral quartz occur within the fahlore (Fig. 2).

Figure 2

Back scattered electrons (BSE) micrograph showing chalcopyrite masses and euhedral quartz in fahlores of varying composition (different shades).



Under the SEM fahlores vary in their hue from light to dark grey, apparently due to the different amounts of Sb and As in fahlores (Fig. 2). It is important to note that the different shades under SEM do not represent different mineral phases, but only different ratios between As and Sb.

Chemistry and substitutions

The formulae of all analyzed fahlores of the Schendleck locality are calculated on the basis of 13 S atoms per formula unit (apfu). The studied fahlores show approximately the ideal stoichiometric formula $(Cu,Ag)_{10}(Fe,Zn,Hg,Cd)_2(Sb,As,Bi)_4S_{13}$, but exhibit sums of (Cu + Ag) lower than 10 apfu and sums of Me (Me = Fe + Zn + Hg + Cd) higher than 2 apfu reaching values of about 2.5 apfu, which are far beyond the analytical error. Despite the relatively constant values of the (Cu+Ag) and Me, the formulae of the studied samples vary significantly in their tetrahedrite (td) content [td-content = Sb/(Sb+As) x 100]. As shown in Figure 3, the studied fahlore



samples from Schendleck area reveal a complete solid solution with all possible Sb/(Sb+As) ratios from near-endmember tennantite to near-endmember tetrahedrite (i.e. from 5 to 95 td). Representative analyses are summarized in Table 2.

Figure 3

Frequency distribution of the studied Schendleck-type fahlores relative to their Sb/(Sb+As) ratio (n = 231).

Sample No.	SE173	SE148	SE217	SE174	SE197	SE79	SE117	SE84	SE133	SE86	SE203	SE201	SE167	SE95	SE5	SE105
	wt %															
Cu	39.55	39.48	39.10	38.90	39.08	38.03	37.45	36.53	36.77	35.92	35.79	35.33	34.90	34.64	34.62	33.00
Ag	0.38	0.34	0.38	0.38	0.38	0.35	0.35	0.35	0.35	0.36	0.41	0.40	0.37	0.37	0.54	0.81
Hg	4.75	3.59	4.30	3.73	3.80	4.56	5.53	5.59	4.56	6.54	6.20	6.22	7.63	8.25	5.87	9.39
Fe	4.34	4.05	3.66	4.60	5.09	4.82	3.87	3.21	3.29	3.60	3.57	4.45	3.59	3.41	4.69	2.74
Zn	2.03	3.22	3.13	2.51	1.63	1.86	2.40	3.06	3.14	2.15	2.38	1.93	1.76	1.90	1.29	1.80
Cd	0.73	0.36	0.41	0.41	0.73	0.38	0.87	0.90	0.97	0.98	0.75	0.44	1.04	1.06	0.83	1.07
As	17.32	16.33	15.31	14.50	13.42	11.61	10.11	9.03	8.44	7.37	6.39	5.56	4.57	3.86	2.30	0.98
Sb	2.43	4.21	5.41	6.69	8.64	10.99	12.98	13.54	15.18	16.37	17.74	18.92	20.19	21.29	23.75	24.75
Bi	0.80	0.71	0.80	0.80	0.80	0.71	0.73	1.74	0.73	0.73	0.83	0.82	0.76	0.75	1.09	0.76
S	26.55	26.59	26.33	26.33	26.43	25.82	25.49	24.95	25.01	24.55	24.51	24.38	24.01	23.93	23.98	22.91
Total	98.88	98.88	98.83	98.85	100.00	99.13	99.78	98.90	98.44	98.57	98.57	98.45	98.82	99.46	98.96	98.21
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Cu	9.77	9.74	9.74	9.69	9.70	9.66	9.64	9.61	9.65	9.60	9.58	9.51	9.53	9.50	9.47	9.45
Ag	0.05	0.05	0.06	0.06	0.06	0.05	0.05	0.05	0.05	0.06	0.06	0.06	0.06	0.06	0.09	0.14
Hg	0.37	0.28	0.34	0.29	0.30	0.37	0.45	0.47	0.38	0.55	0.53	0.53	0.66	0.72	0.51	0.85
Fe	1.22	1.14	1.04	1.30	1.44	1.39	1.13	0.96	0.98	1.09	1.09	1.36	1.12	1.07	1.46	0.89
Zn	0.49	0.77	0.76	0.61	0.39	0.46	0.60	0.78	0.80	0.56	0.62	0.50	0.47	0.51	0.34	0.50
Cd	0.10	0.05	0.06	0.06	0.10	0.05	0.13	0.13	0.14	0.15	0.11	0.07	0.16	0.16	0.13	0.17
Total	12.00	12.03	12.00	12.01	11.99	11.98	12.00	12.00	12.00	12.01	11.99	12.03	12.00	12.02	12.00	12.00
As	3.63	3.42	3.24	3.07	2.83	2.50	2.21	2.01	1.88	1.67	1.45	1.27	1.06	0.90	0.53	0.24
Sb	0.31	0.54	0.70	0.87	1.12	1.46	1.74	1.86	2.08	2.28	2.48	2.66	2.88	3.05	3.39	3.70
Bi	0.06	0.05	0.06	0.06	0.06	0.06	0.06	0.14	0.06	0.06	0.07	0.07	0.06	0.06	0.09	0.07
Total	4.00	4.01	4.00	4.00	4.01	4.02	4.01	4.01	4.02	4.01	4.00	4.00	4.00	4.01	4.01	4.01
S	13.00	13.00	13.00	13.00	13.00	13.00	13.00	13.00	13.00	13.00	13.00	13.00	13.00	13.00	13.00	13.00
Total	29.00	29.04	29.00	29.01	29.00	29.00	29.01	29.01	29.02	29.02	28.99	29.03	29.00	29.03	29.01	29.01
Sb/(Sb+As) x 100	7.87	13.64	17.77	22.08	28.35	36.87	44.05	48.06	52.53	57.72	63.10	67.68	73.10	77.22	86.48	93.91

Table 2

Representative EDX analyses of fahlores in Schendleck area.

The Cu-content of the studied fahlores varies and decreases generally relative to the increase of the td-content, where the highest Cu-content (39.58 wt % - 9.77 apfu) corresponds to lowest td-content and inversely the lowest Cu-content (33.00 wt % - 9.43 apfu) to the highest td-content (Fig. 4). In contrast to the Cu-content, the Me-content increases with increasing td-content (Fig. 4). The studied fahlores contain very low contents of Ag (maximum 0.82 wt % - 0.14 apfu, minimum 0.25 wt % - 0.05 apfu, respectively).



Figure 4

Cu- and Me-contents (Me = Fe + Zn + Hg + Cd) related to the Sb/(Sb+As) ratio (td-content).



From Figure 5 it is evident that the Fe- and Zn-contents of the fahlores from Schendleck are strongly varying. The maximum Fe-content amounts to 5.61 wt % (1.72 apfu) and the minimum content to 2.33 wt % (0.73 apfu). The highest Zn-content is 5.27 wt % (1.26 apfu) and the lowest is 0.63 wt % (0.17 apfu). The Hg-contents in Schendleck fahlores are relatively high. Maximum values reach up to 10.30 wt % (0.93 apfu) and the lowest Hg-content amounts to 2.95 wt % (0.23 apfu, Fig. 5). The Cd-content in the studied fahlore ranges between 1.78 wt % (0.45 apfu) and 0.11 wt % (0.02 apfu). The fahlores of the present study have very small contents of Bi. The highest Bi-content amounts to 1.84 wt% (0.16 apfu) and the lowest to 0.13 wt% (0.01 apfu). No significant correlation exists between the Cu-content and the Feand Zn-content (Fig. 5). In fahlores with low td-content, Hg shows a slightly negative correlation with the Cu-content (Fig. 5).

Figure 5 (*a*) *Fe- and Hg-contents and (b) Zn- content related to the Cu-content.*

Figure 6 displays the relationship between the Fe-content, the Zn- and the Hg-content, revealing a clearly negative correlation between Fe and Zn, whereas constant relations occur between Fe and Hg. Two specific types of zoning have been observed in selected grains from the Schendleck fahlore related to the td-content: Decreasing Cu-content at the center and increasing Cu-content at the rims of the grains is represented by fahlores close to tetrahedrite in composition (Fig. 7, grains 1, 2, 3 and 4). The inverse situation occurs in grains that are represented by fahlores close to tennantite in composition (Fig. 7, grains 5, 6, 7, 8). However, the selected zoned grains are rarely occurring and are significantly larger (up to 8.1 mm, Fig. 7) than the usually homogeneous grains.



Figure 6 Zn- and Hg-contents related to the Fecontent.



Figure 7

Profile of point analyses (Cu and Sb/(Sb+As); grains 1-4 close to tetrahedrite composition, grains 5-8 correspond to tennantite composition. Size of the selected mineral grains in parenthese.

Discussion and conclusion

It is evident from Figure 3 that an extremely inhomogeneous fahlore, varying in its Sb/(Sb+As) ratio from nearly pure tetrahedrite to nearly pure tennantite, is represented by the Schendleck samples. Such an extremely inhomogenous fahlore has never been observed before. The "Schendleck-type" fahlores apparently represent an unique fahlore type. A review of published literature data indicates that most of the fahlore samples fall between 0 and 20% td and between 50 and 100% td, respectively (e.g. NASH, 1975; RAABE & SACK, 1984; ARLT & DIAMOND, 1998; FOIT & ULBRICHT, 2001; DI BENEDETTO et al., 2002; LYNCH 1989; SACK et al., 2002; SACK et al., 2003; GRAMMATIKOPOULOS et al., 2005). The lack of fahlores between 20 and 50 td may suggest as a miscibility gap. However, from the Sb/(Sb+As) ratio of the Schendleck fahlores varying from 5 to 95 td, it must be concluded that a complete solid solution series from pure As- to pure Sb-fahlores does exist.

In addition, the Schendleck-type fahlores exhibit a relatively wide range in the Me-element contents. Furthermore, the presence of Me2+ excesses (i.e. larger than 2 apfu) in the Schendlecktype fahlores argues for the absence of Cu²⁺. No evidence exists for a late replacement of Cu²⁺ by Me²⁺. In addition, the increase of the Cu-content toward the As-endmember tennantite indicate the affinity of Cu for As. This observation has been noticed before by CHARLAT & LÈVY (1974). Therefore, one may speculate whether the affinity of Cu for As and that of Me for Sb were responsible for the formation of the Schendleck type fahlore. In a first stage, the crystallization of tennantite $(Cu_{12}As_4S_{13})$ could be expected. However, natural tennantite with 12 Cu apfu is not a stable phase (JOHNSON & JEANLOZ, 1983; JEANLOZ & JOHNSON, 1984; BULLET, 1987). The stability of the mineral will be achieved by replacement of two Cu atoms by two Me elements (KLÜNDER et al. 2003). Since Me elements show great affinity for Sb, the replacement of Cu by Me elements will be facilitated by the substitution of As by Sb. Figure 4 clearly indicates that the Cu-Me substitution increases with increasing td-content. However, inspection of Figure 5 reveals practically no relations between the Cu and the individual Me elements, which confirm the affinity of the Me elements for Sb and explain the inhomogeneity of the studied fahlores.

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