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Compositional variations of fahlore group minerals from Austria

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Abstract

Fahlores from seven Austrian localities and from two additional localities in England and Slovakia have been investigated by reflected-light and scanning electron microscopy with energy dispersive analysis (SEM-EDA). The studied fahlores can be divided on the basis of their tetrahedrite (td)-content (td = Sb/(Sb+As) x 100) into chemically homogeneous tetrahedrite (td > 95%), tennantite (td < 5%) and intermediate fahlores with variable compositions. An additional, unique, fahlore type, represented by the "Schendleck-type" fahlore, is extremely inhomogeneous and varies in its td-content from nearly pure endmember tetrahedrite to nearly pure endmember tennantite. The studied samples exhibit a relatively wide range in the Me-element contents (Me = Fe + Zn + Hg + Cd) and show an Me excess (up to 2.5 *apfu*) in practically all fahlore types except tennantite. The measured Vickers microhardness number (VHN) in the studied samples correlates inversely with the Cu-content, which argues for the increase of the VHN with increasing Cu/Me substitution.

Fahlerze von sieben österreichischen Vorkommen und zweier weiterer aus England und der Slowakei wurden mittels Auflicht- und Rasterelektronen-Mikroskopie mit Energie-Dispersiver Analytik (REM-EDX) untersucht. Die untersuchten Fahlerze können auf der Grundlage ihres Tetraedrit (Td)-Gehaltes (Td = Sb (Sb+As) x 100) in chemisch homogene Tetraedrit (Td > 95%) und Tennantit (Td < 5%) sowie in intermediäre Fahlerze mit variabler Zusammensetzung unterteilt werden. Ein zusätzlicher, einzig-artiger Fahlerztyp, repräsentiert durch das „Schendleck-Typ" Fahlerz, ist extrem inhomogen und variiert in seinem Td-Gehalt vom praktisch reinen Tetraedrit- zum reinen Tennantit-Endglied. Die untersuchten Proben weisen einen relativ weiten Bereich in den Me-Elementgehalten (Me = Fe + Zn + Hg + Cd) auf sowie einen Me-Überschuss (bis 2.5 *apfu*) in praktisch allen Fahlerze-typen, ausgenommen Tennantit. Die gemessene Vickers-Mikrohärte (VHN) korreliert gegenläufig mit dem Cu-Gehalt, was auf einen Anstieg der VHN mit steigendem Cu/Me-Ersatz hinweist.

1. Introduction

Fahlores with the generalized formula $(Cu,Ag)_6Cu_4(Fe,Zn,Cu,Hg,Cd)_2(Sb,As,Bi,Te)_4(S,Se)_{13}$ (Johnson et al., 1986) are considered as the most important sulfosalt minerals of epi- to mesothermal ore deposits, polymetallic sulfide veins and sedimentary exhalative and volcanogenic massive sulfides deposits, occurring in a wide range of geological settings and varying in its association (Sack et al., 2003).

Most investigations on fahlores have dealt with synthetic tetrahedrite and tennantite as pure Sb and As endmember
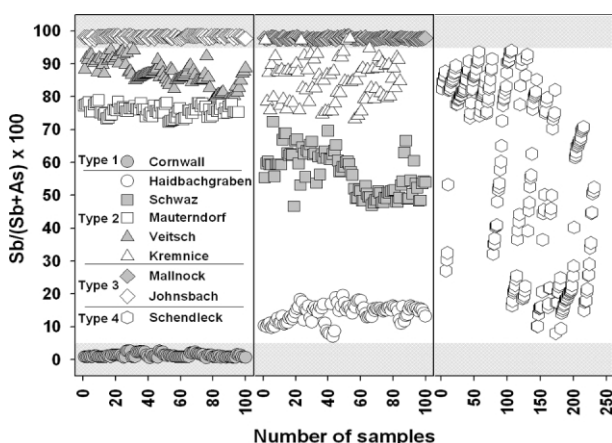

Figure 1: Frequency distribution of the studied fahlores relative to their td-content (Sb/(Sb+As) x 100).
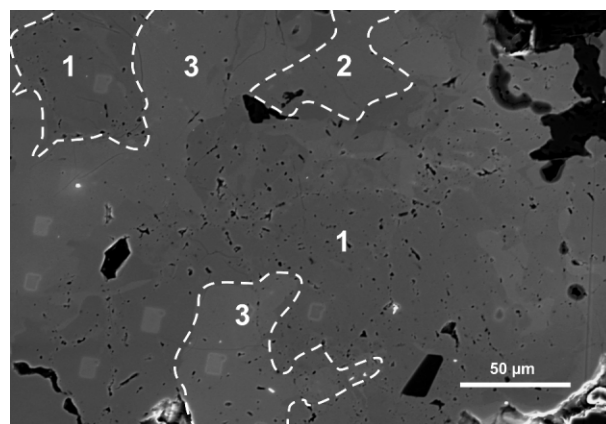

Figure 2: Backscattered SEM micrograph showing fahlores from Schendleck. The dark grey hue (1) is close to tennantite, the medium grey (2) represents intermediate fahlores and the light grey (3) corresponds to tetrahedrite.

phases, respectively, and with Ag-rich natural tetrahedrite as important silver ores (Charlat and Lèvy, 1974; Johnson et al., 1986; Sack and Ebel, 1993). Investigations on naturally occurring Ag-poor, Sb-rich fahlores and on As-rich fahlores are rare. The ideal formulae for the pure Cu-tetrahedrite or Cu-tennantite endmembers (i.e. $Cu_{12}Sb_4S_{13}$ or $Cu_{12}As_4S_{13}$, respectively) have never been reported from natural occurrences (Klünder et al., 2003). Johnson and Jeanloz (1983) mentioned that the classic formula $Cu_{12}Sb_4S_{13}$ is not expected to occur and that fahlores with an approximate composition of $Cu_{10}(Fe,Zn)_2(Sb,As)_4S_{13}$ have a higher stability. Furthermore, the presence of Cu^{2+} in natural tetrahedrite has been reported in only few cases (Pattrick et al., 1993; Di Benedetto et al., 2002). Investigations on synthetic tetrahedrite using L-edge X-ray Absorption Spectroscopy (L-edge XAS) (Pattrick et al., 1993) and Electron Paramagnetic Resonance spectroscopy (EPR) (Di Benedetto et al., 2005) proved the presence of the Cu^{2+}.

Based on studies on tetrahedrite, Johnson et al. (1988) proposed the following structural formula: $M(1)_6^{[4]}M(2)_6^{[3]}[X^{[3]}Y_3^{[4]}]_4Z^{[6]}$, where M (1) = Cu^{1+}, Cu^{2+}, Fe, Zn, Mn, Hg, Cd and M (2) = Cu^{1+}, Ag; X = Sb, As, Bi, Te and Y and Z = S, Se with two formula units per unit cell. According to Wuensch (1964), Cu atoms occupy two different sites; Cu(1) is tetrahedrally coordinated by four S(1) atoms whilst Cu(2) is trigonal planar coordinated by one S(2) and two S(1) atoms. Sb and/or As (on a 3-fold axis) are coordinated to three S(1) atoms, thus forming a flat trigonal pyramid.

A summary review of Austrian fahlore compositions was given by Götzinger et al. (1997). Mineralogical studies on fahlores from Klamm Alm (Tyrol) and Schwaz (Tyrol) have been published by Gregurek and Raith (1997) and by Arlt and Diamond (1998), respectively. Gold inclusions in fahlores from Mitterberg and from Hachau (near Filzmoos), Schwemmberg (north of Radstadt) and Ochsen-alm (north of Mandling) have been recorded previously by Bernhard (1965) and Dachs and Paar (1984). More recently, gold inclusions and unusual gold oxysulfides associated with Austrian fahlores have been noted in Veitsch, Erzberg, Mitterberg, Serfaus, St. Martin and

Rottenmann (Kucha et al. 1995, 1997a, b, 2003).

The present work focuses on the chemical composition of naturally occurring Ag-poor fahlores, especially from Austrian localities and aims to deduce some general compositional relationships, thus contributing to the crystal chemistry of this widely occurring mineral group. Detailed reflected light microscopy combined with comprehensive scanning electron microscopy (SEM) studies is the basis of the work.

2. Samples and experimental methods

The studied samples were collected from seven localities in Austria, comprising Haidbachgaben, Schendleck, Veitsch, Johnsbach and Schwaz within the Greywacke zone, Mallnock in the Gurktal Alps and Mauterndorf in the middle part of the Tauern Window. In the Greywacke zone, fahlores are hosted in early Palaeozoic rocks and are of epigenetic origin (Frimmel, 1991; Ofner, 2002). The fahlores from Mallnock and Mauterndorf occur as small encrustations and minor veinlets
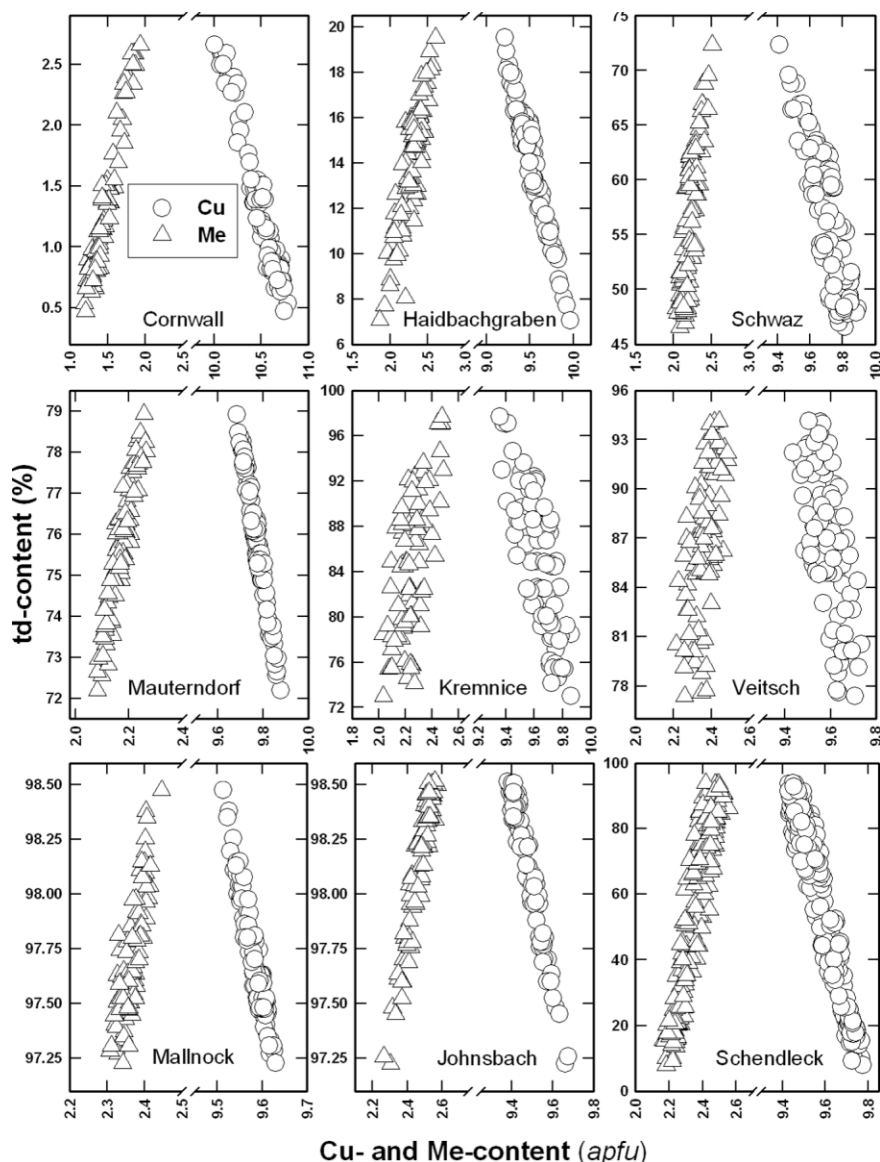

FIGURE 3: Cu- and Me-contents (Me=Fe + Zn + Hg + Cd) related to the td-content.

hosted within Early Palaeozoic carbonate rocks and dolomites of Triassic age, respectively. Under the ore microscope, the studied fahlores are associated with pyrite, chalcopyrite, ± sphalerite, ± galena, ± enargite, ± gersdorffite, and ± bournonite. Ag-rich gold "electrum" inclusions in chalcopyrite were determined only under the SEM in the Schendleck samples. Analyses of the electrum grains show that Ag contents range from 28.9 to 32.2 wt %, Au contents range between 64.9 and 68.9 wt % and minor amounts of Hg reach up to 4.5 wt %.

For determining the chemical compositions of the studied fahlores from the seven Austrian localities, a total of 827 point analyses (every point represents one mineral grain) in 32 carbon-coated polished sections were performed. Due to the lack of pure As-fahlore (tennantite) in the Austrian samples, a total of 100 points in 2 carbon-coated polished sections in samples from Cornwall (SW England) were analyzed to obtain data for the tennantite endmember. Additional samples from Kremnice (Slovakia), with a relatively wide range in

the Sb/(Sb+As) ratio, were also analyzed. Both the Cornish and Kremnica samples are from the collection of the Institute of Mineralogy and Crystallography, University of Vienna. The analyses of the Cornish and Kremnica samples were included with the analyses of the Austrian samples, increasing the number of localities to nine and expanding the range of fahlore chemical compositions.

The analyses were performed on a Jeol JSM-6400 SEM equipped with a Link quantitative energy dispersive X-ray microanalysis (EDA) 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). Arsenopyrite (As), galena (Pb), pyrite (S) and native Ag, Au, Bi, Cd, Cu, Fe, Hg, Mn, Sb and Zn standards were used. The measurements are accurate to ± 2 rel. %, with chemical analyses recalculated on the basis of 13 S *apfu* and 29 *apfu*. In both cases, the calculated formulae yielded similar values. However, the formulae obtained by recalculating on the basis of 13 S *apfu* were preferred, since these avoid any loss of cations for sulfur and also reduce the number of correlations between the different positively charged elements and sulfur.

The Vickers microhardness of the studied fahlores was measured using the Paar MHT-4 microhardness tester. The total of 129 measurements were made with a load of 100 g (applied for 15 seconds) prior to the chemical analyses of the samples.

3. Classification of the fahlores

According to the literature, the name "fahlore(s)" is used for naturally occurring mineral phases of the tetrahedrite-tennantite solid-solution series. However, it is difficult to set boundaries among fahlore group minerals because of their complex and variable chemical composition and there is no generally accepted classification for the fahlores based of their Sb/ (Sb+As) ratio. On the basis of the tetrahedrite content (td), defined as [Sb *apfu* / (Sb *apfu* +As *apfu*) x 100], the studied fahlores have been divided into four types (Fig. 1). These types comprise: (1) tennantite Sb/(Sb+As) < 5 td, repre-
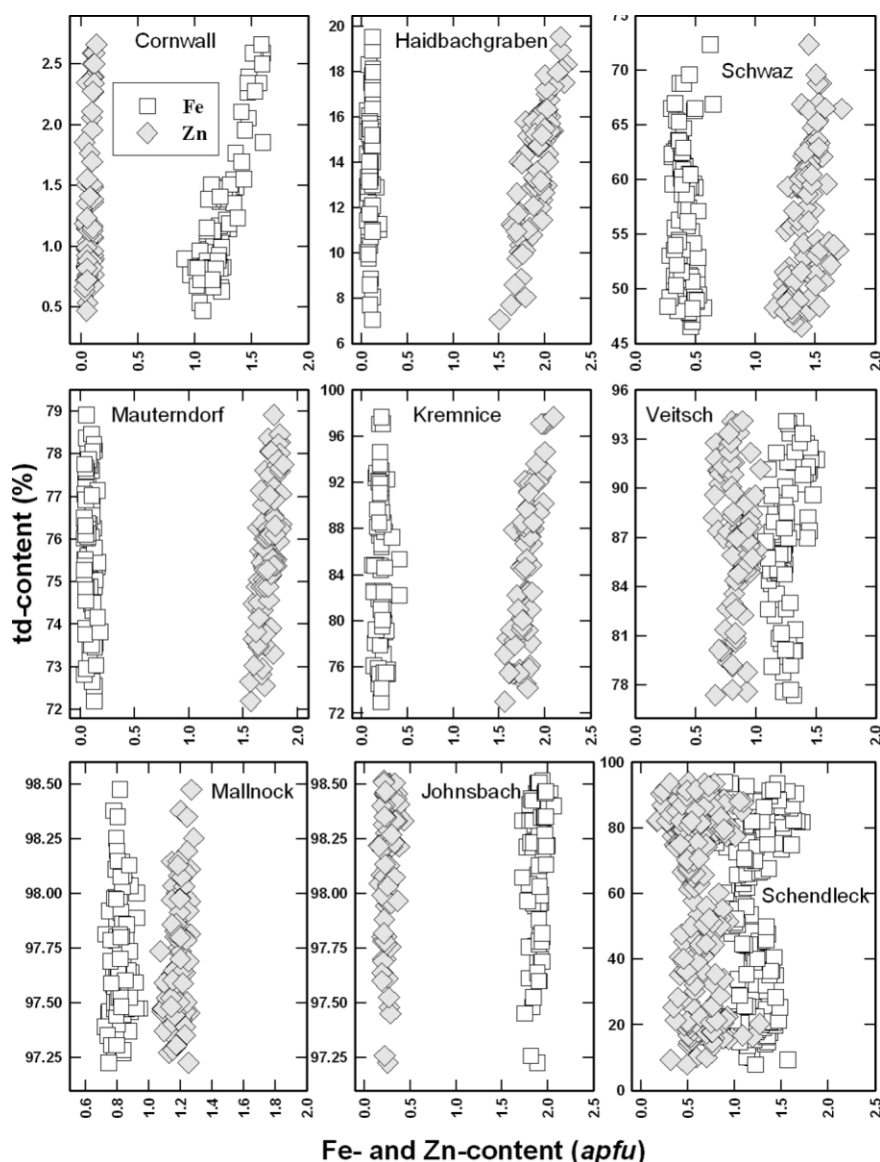

Figure 4: Fe- and Zn-contents related to the td-content.

sented by the homogeneous Cornish sample; (2) intermediate fahlores, 5 ≤ Sb/(Sb+As) ≤ 95 td, including samples from Haidbachgraben, Schwaz, Mauterndorf, Veitsch and Kremnice, varying in their Sb/(Sb+As) ratios within a relatively small range; (3) tetrahedrite Sb/(Sb+As) >95 td, represented by the homogeneous samples from Johnsbach and Mallnock; (4) the Schendleck-type fahlore, represented by the Schendleck sample, which contains unusual fahlores varying over a wide range in their Sb/(Sb+As) ratio (5 ≤ td ≤ 95). Under the SEM, Schendleck-type fahlores vary in their hue from light to dark-grey, apparently due to differing amounts of Sb and As. It is important to note that the different shades under the SEM do not represent different mineral phases, but only different As/Sb ratios. The majority of the Schendleck-type fahlores are close to tetrahedrite. As shown in Figure 2, intermediate fahlores and fahlores close to tennantite composition in the Schendleck type fahlore are also present. Although this fahlore type is very rare, it was noted by Hackbarth and Petersen (1984) in one sample from Casapalca (Peru).

4. Results

4.1 Composition of fahlores

The studied fahlores are close to the ideal stoichiometric formula $(Cu,Ag)_{10}(Fe,Zn,Hg,Cd)_2(Sb,As,Bi)_4S_{13}$ (Tab. 1). However, excepting the Cornish samples (tennantite in composition), sums of (Cu + Ag) are lower than 10 *apfu* and sums of Me (Me = Fe + Zn + Hg + Cd) are larger than 2 *apfu* (Fig. 3). Me excesses of a similar magnitude were observed in natural Sb-rich fahlore endmember tetrahedrite, when the analyses were normalized to 13 S *apfu* by Lynch (1989) or to 29 *apfu* by Sack et al. (2002, 2003). As observed in the Cornish sample, a Cu excess in natural tennantite has also been described previously by Charlat and Lèvy (1974), Cesbron et al. (1985) and Marcoux et al. (1994), when the analyses were normalized to 13 S *apfu* (Table. 1).

The Cu-content of the studied fahlores decreases significantly relative to the increase of td-content, from type 1 (tennantite) to type 3 (tetrahedrite). In addition, the highest and lowest Cu-contents in type 4 fahlores correspond to the lowest and

highest td-contents (Fig. 3). The Fe-content in all types shows a slight positive to constant relationship with respect to the td-content (Fig. 4); constant to slightly positive correlations between Zn- and td-contents were also noticed in the fahlores (Fig. 4). Although the Hg-contents in the studied fahlores are generally low, the Hg-content in type 4 reaches up to 10.30 wt % (0.93 *apfu*) (Fig. 5). The Cd-content in the studied fahlores ranges between 1.78 wt % (0.45 *apfu*) in type 4 and 0.10 wt % (0.01 *apfu*) in type 1. The very small Cd-content in the fahlores can be attributed to the preferential substitution of Cd into sphalerite, which is usually associated with fahlores (Pattrick, 1984). Correlations between the Cu-content and the Fe-, Zn- and Hg-contents show nearly constant to slightly negative relationships (Fig. 5). It is evident from Fig. 3 that the increase of the Me-contents (Me = Fe + Zn + Hg + Cd) in all fahlore types of the present study generally corresponds to an increase of the td-content (Sb/(Sb+As) ratio). This observation also holds for only narrow ranges in the Sb/(Sb+As)
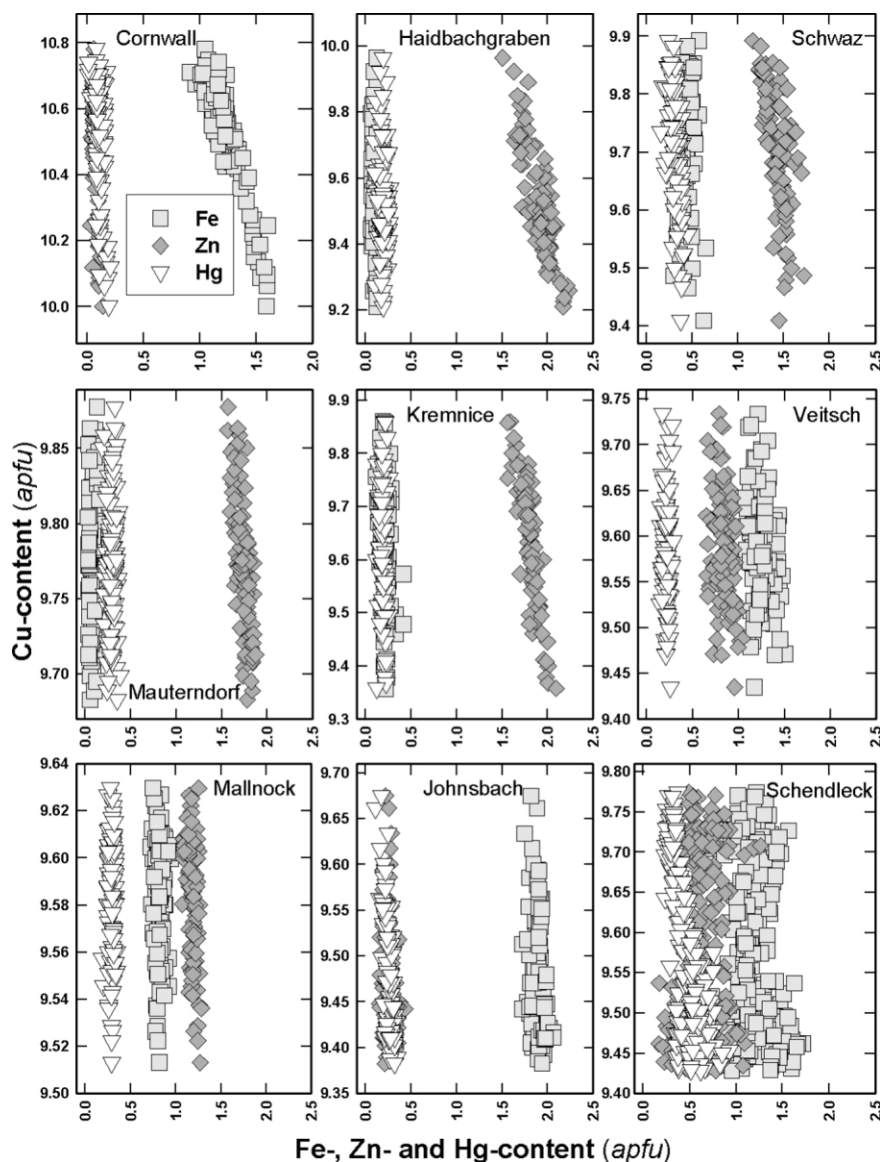
Figure 5: Fe-, Zn- and Hg-contents related to the Cu-content.

Locality	Cu	Ag	Hg	Fe	Zn	Cd	Σ Me	As	Sb	Bi	Total	S	Total
	wt%	wt%	wt%	wt%	wt%	wt%		wt%	wt%	wt%		Wt%	wt%
	apfu	apfu	apfu	apfu	apfu	apfu	apfu	apfu	apfu	apfu	apfu	apfu	apfu
Cornwall	44,42	0,33	1,04	4,55	0,24	0,17		19,38	0,33	0,71		27,58	98,75
	10,57	0,05	0,08	1,23	0,06	0,02	12,01	3,91	0,04	0,05	4	13	29,01
Haidbachgraben	38,74	0,61	3,24	0,31	8,54	0,35		16,33	4,34	0,55		26,77	99,78
	9,5	0,09	0,25	0,09	2,03	0,05	12,01	3,4	0,55	0,04	3,99	13	29
Schwaz	38,11	0,44	3,11	1,74	4,96	0,49		8,65	14,99	0,9		25,37	98,76
	9,85	0,07	0,25	0,51	1,25	0,07	12	1,9	2,02	0,07	3,99	13	28,99
Mauterndorf	36,08	0,4	3,95	0,32	6,49	0,44		3,85	21,71	0,78		24,32	98,34
	9,73	0,06	0,34	0,1	1,7	0,07	12	0,88	3,06	0,06	4	13	29
Kremnice	35,32	0,77	2,54	0,69	6,93	0,29		1,51	25,67	0,5		24,22	98,44
	9,57	0,12	0,22	0,21	1,82	0,04	11,98	0,35	3,63	0,04	4,02	13	29
Veitsch	35,8	0,4	2,57	4,54	2,66	0,29		1,68	25,44	0,51		24,42	98,31
	9,62	0,06	0,22	1,39	0,69	0,04	12,02	0,38	3,57	0,04	3,99	13	29,01
Mallnock	34,91	0,4	2,96	2,65	4,67	0,54		0,33	27,39	0,25		24	98,1
	9,54	0,06	0,26	0,82	1,24	0,08	12	0,08	3,91	0,02	4,01	13	29,01
Johnsbach	34,9	0,35	3,08	6,31	0,88	0,39		0,3	27,82	0,23		24,21	98,47
	9,46	0,06	0,26	1,95	0,23	0,06	12,02	0,07	3,93	0,02	4,02	13	29,04
Schendleck	34,53	0,6	6,27	4,48	1,33	1,09		2,6	23,21	1,03		23,99	99,13
	9,44	0,1	0,54	1,39	0,35	0,17	11,99	0,6	3,31	0,09	4	13	28,99
	37	0,36	4,83	3,02	3,68	0,39		8,51	14,72	1,38		25,15	99,04
	9,65	0,05	0,4	0,9	0,93	0,06	11,99	1,88	2	0,11	3,99	13	28,98
	39,18	0,33	3,28	4,06	3,22	0,36		15,28	5,63	0,71		26,42	98,47
	9,73	0,05	0,26	1,15	0,78	0,05	12,02	3,22	0,73	0,05	4	13	29,02

TABLE 1: Representative chemical analyses of the studied fahlores.

ratio. The Fe-content usually shows slightly negative correlations with Zn and Hg.

The fahlores of the present study contain very small amounts of Ag and Bi. However, the highest and lowest Ag-contents (2.08 wt % - 0.30 apfu, 0.24 wt % - 0.04 apfu, respectively) were obtained in intermediate fahlores (type 2). The highest Bi-content (1.91 wt% - 0.15 apfu) corresponds to type 2 and the lowest (0.13 wt% - 0.01 apfu) to type 4 fahlores. It was also noticed that relatively high Bi-contents are usually associated with samples that have high Zn-contents. This observation agrees well with Förster et al. (1987), who noted that a high Bi content in natural fahlore is most likely to occur in the material with a high Zn content.

The distribution of Cu, Fe and Zn within individual fahlore grains with respect to element zoning was determined by plotting a profile of point analyses. No specific behavior of Cu, Fe and Zn occurs in the types 1, 2 and 3 fahlore grains. In contrast, two specific relations have been observed in type 4 fahlore corresponding to the td-content. Grains in which the Cu-content decreases in the core and increases towards the rims, are represented by fahlores close to tetrahedrite in composition (Fig. 6, grains 1, 2, 3 and 4) and inversely in grains that are represented by fahlores close to tennantite in composition (Fig. 6, grains 5, 6, 7, 8). No specific zoning behavior of Fe and Zn has been observed in Schendleck-type fahlore.

4.2 Fahlore hardness microindentations

The impression shape of the indentation in the studied fahlores is a strong "straight edge". The shape of the fracturing associated with the impression is either a star radial or a combination of star radial and concentric shell. This agrees well with observations by Craig and Vaughan (1994), who mentioned that straight edge indentation type and radial and shells fractures are common in sulfosalts.

The standard Vickers microhardness number (VHN) values of some fahlore types, published by the Commission of Ore Mineralogy (COM) in the IMA/Com Data File (Criddle and Stanley, 1993), are summarized in Table 2, together with the minimum and maximum VHN values obtained for the studied samples; these simply show that the measured samples lie within the standard VHN ranges. A plot of Cu-content versus VHN shows that the Cu-content of all the studied fahlore types correlates negatively with the VHN (Fig. 7). In contrast, only a very slight positive correlation has been observed between the td-content and the VHN (Fig. 8), except in the Schendleck sample, for which a strong positive correlation is evident.

5. Discussion and conclusion

Although the ranges specified for the fahlore end-members is very small (from 0-5 td % for tennantite and from 95 to 100 td % for tetrahedrite), both end-members (type 1 and type 3, respectively) are considered to be very homogeneous in their td-content. The difference between the lowest and highest td-content in samples of tetrahedrite and tennantite composition does not exceed two td %. Fig. 1 also indicates that intermediate fahlores (type 2) have slightly varying Sb/(Sb+As) ratios from grain to grain. The most inhomogeneous fahlores within this type are represented by the samples from Schwaz and Kremince. The Kremince sample also contains grains of pure tetrahedrite endmember composition. The most homogenous intermediate fahlore is represented by the sample from Mau-

terndorf. An extremely inhomogeneous fahlore, varying in its Sb/(Sb+As) ratio from nearly pure endmember tetrahedrite to endmember tennantite, is represented by the Schendleck sample (type 4). This sample apparently represents a unique fahlore type.

Fig. 1 also shows that most of the fahlore samples fall between 0 and 20 % td and between 50 and 100 % td, respectively. This may lead to the suggestion of a miscibility gap between 20 and 50 % td as a review of published literature data also indicates that As-rich intermediate fahlores are extremely rare (e.g. Nash, 1975; Burkart-Baumann, 1984; Raabe and Sack, 1984; Arlt and Diamond, 1998; Foit and Ulbricht, 2001; Di Benedetto et al., 2002; Lynch, 1989; Sack et al., 2002; Sack et al., 2003; Grammatikopoulos et al., 2005). However, from the varying Sb/(Sb+As) ratio of the Schendleck-type fahlores, it must be concluded that a complete solid solution series from pure As- to pure Sb-fahlores does exist.

The fahlores of the present study exhibit a relatively wide range in the Me-element contents (Fig. 3). Data from other studies of Greywacke zone fahlores indicate that they formed under similar geological conditions, represented by temperatures of about 300 °C and pressures of 2.5 kbar (Arlt and Diamond, 1996; Frimmel, 1991; Pohl and Belocky, 1994; Kucha et al., 1995; Ofner, 2002). Apparently, the distribution of the Me-elements in fahlores depends mainly on the availability of the elements at the time of their formation.

The presence of excess Me^{2+} cations (i.e. up to 2.5 *apfu*) in practically all fahlore types (except the type 1, tennantite samples from Cornwall) argues for the absence of Cu^{2+}. The appearance of the Me^{2+} excess in the studied samples indicates that only monovalent Cu^+ occurs in the tetrahedrally and

Type	Mineral name	COM	Studied samples	
		VHN (kg/mm²)	Locality	VHN (kg/mm²)
1	(Fe)tennantite	294-380	Cornwall	295-388
2	(Zn) As-rich fahlore	312-390	Haidbachgraben	317-344
	(Zn-Fe) intermediate fahlores		Schwaz	310-341
	(Zn) Sb-rich fahlore	239-376	Mauterndorf	305-337
			Kremnice	315-337
	(Fe-Zn) Sb-rich fahlore		Veitsch	318-344
3	(Zn-Fe) tetrahedrite		Mallnock	323-340
	(Fe) tetrahedrite	312-351	Johnsbach	330-362
4	Schendleck-type fahlore		Schendleck	325-365

TABLE 2: VHN values of the studied fahlores compared with standard VHN values [after Commission of Ore Mineralogy (COM), Criddle and Stanley, 1993].
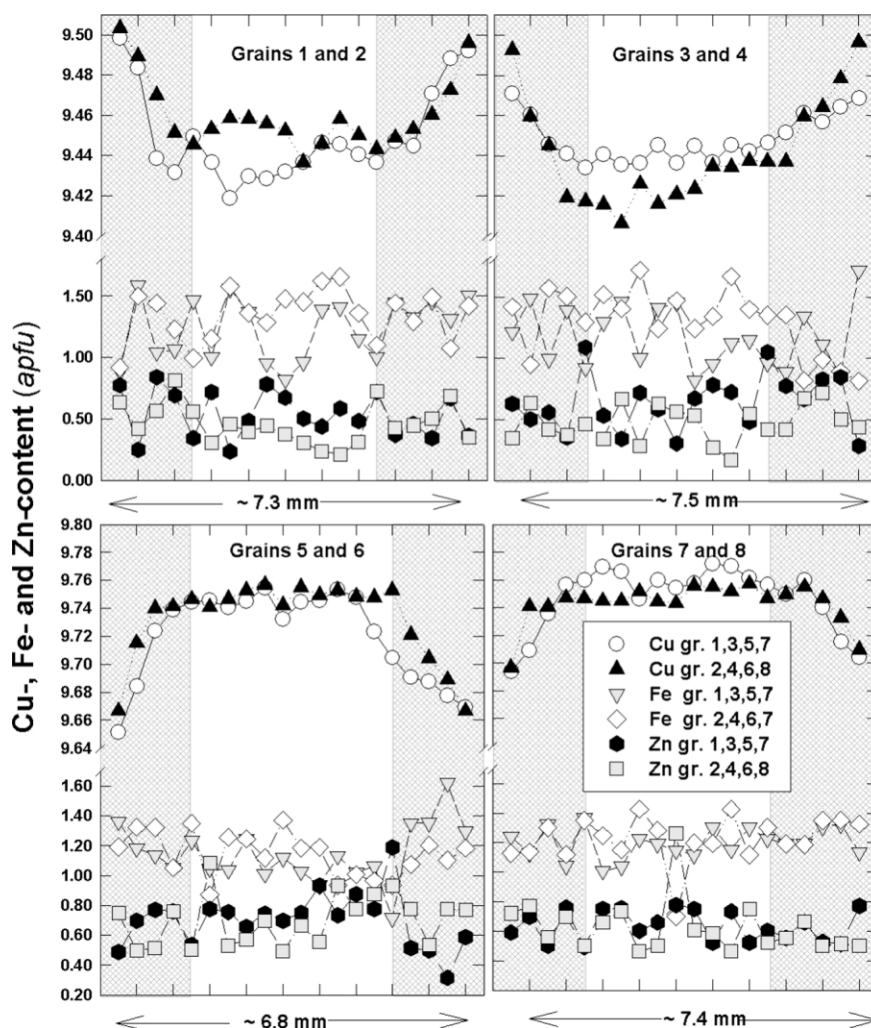

FIGURE 6: Schendleck-type fahlore, profile of point analyses of Cu, Fe and Zn, grains 1-4 close to tetrahedrite composition, grains 5-8 correspond to tennantite composition. Dashed areas represent the rims of the grains.
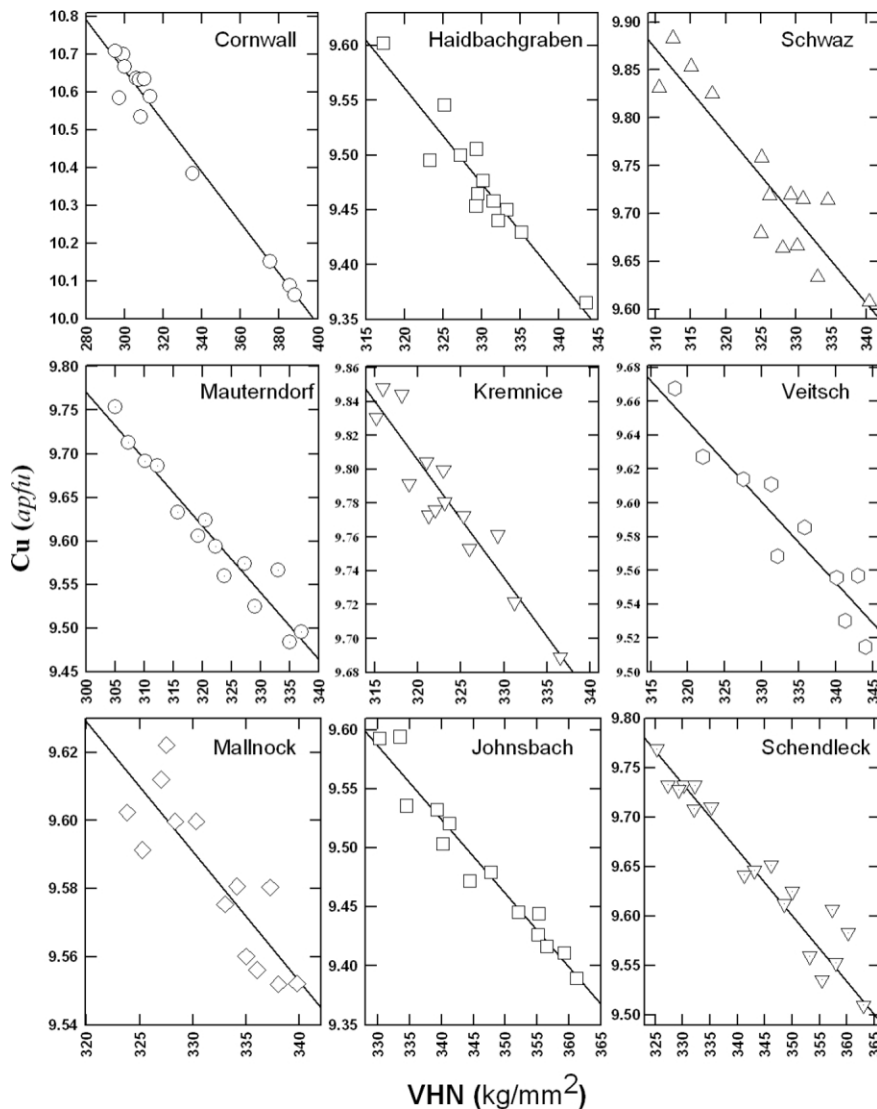
FIGURE 7: Relation between Cu-content and VHN.
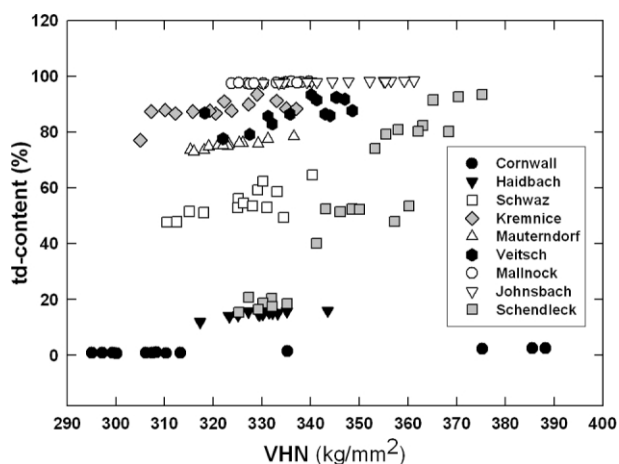
FIGURE 8: Relation between td-content and VHN.

observations agree with Pattrick and Hall (1983), who noted that, in most natural fahlores, the two Cu^{2+} atoms are replaced by divalent elements. Makovicky and Karup-Møller (1994) stated that the most accepted formula of natural tetrahedrite, $(Cu,Ag)_{10}(Fe,Zn,Hg,Cd,…)_2(Sb,As)_4S_{13}$, requires definite stoichiometric ratios between the formally mono- and divalent elements, trivalent metalloids and sulfur. Klünder et al. (2003) stated that pure Cu-fahlore is very rare in nature, as the stability of the mineral is vastly improved by the addition of two apfu of typically divalent metals. Makovicky et al. (2005) also mentioned that the majority of natural samples of fahlore are fully substituted by divalent elements, leaving only 10 (Cu,Ag) apfu. Therefore, it can be tentatively concluded that the absence of Cu^{2+} and the cation excess of Me-elements in tetrahedrite, intermediate fahlore and Schendleck-type fahlore can be attributed to the affinity of Me-elements for Sb.

The studied tennantite from Cornwall (type 1) as well as tennantite (< 5 % td) reported in the literature (e.g. Charlat and Lèvy, 1974; Cesbron et al., 1985; Marcoux et al., 1994) all show a Cu excess (i.e. larger than 10 *apfu*). The Cu excess is explained by the affinity of Cu to As. The charge balance could be provided by the presence of Cu^{2+} (Pattrick et al., 1993; Di Benedetto et al., 2005). The studied tennantite (type 1) and nearly all tennantite samples reported in literature (< 5 % td) are relatively rich in Fe. This observation may lead to the conclusion that Cu^{2+} may also be absent in tennantite, where the charge balance is related to the presence of Fe^{3+} (Charnock et al., 1989; Marcoux et al., 1994).

The inverse correlation between the Cu-content in the studied fahlores and the VHN (Fig. 7) reflects that VHN increases with increasing substitution of Cu by Me. This result confirms the observations of Hall (1972), who noticed that VHN of substituted tetrahedrite increases with substitutions of Cu by Zn and Fe (+ 20 VHN/1.0 at % Cu substituted) and decreases with the substitution of Cu by Ag. In contrast, it does not seem to be possible to set limits or to derive a relationship between the td-content and VHN (Fig. 8). However, a slightly positive correlation is evident and exceptionally well shown by the Schendleck type.

trigonal planar coordinated positions. Fig. 5 clearly demonstrates that at each locality only one of the Me-elements (Fe, Zn, Hg) correlates negatively with the Cu-content. There is no evidence for a late replacement of Cu^{2+} by Me^{2+}. The above

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