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MINERALOGY OF THE NIEDERSCHLEMA – ALBERODA U–Se–POLYMETALLIC DEPOSIT, ERZGEBIRGE, GERMANY. I. JOLLIFFEITE, NiAsSe, THE RARE Se-DOMINANT ANALOGUE OF GERSDORFFITE

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Abstract

The Niederschlema–Alberoda uranium deposit, in the Erzgebirge region of Germany, contains an uncommon assemblage of metallic minerals, in particular selenides, sulfides, arsenides, tellurides, and native elements, in addition to uraninite and coffinite. The complex mineralogy resulted from the superposition of several mineralizing events over the time interval from the Permian to the Cretaceous; these events introduced and redeposited a great variety of metallic elements within the hydrothermal uranium deposit (Pb, Ag, Cu, Hg, Tl, Bi, Co, Ni, As, Sb, Se, S, Te). One of the exotic minerals is jolliffeite, an arsenoselenide with end-member composition NiAsSe, so far only known from Lake Athabasca, Saskatchewan, Canada. A single, small, anhedral grain of jolliffeite from Niederschlema–Alberoda is included and partly replaced by sulfurian eskebornite. Associated minerals comprise hematite, Ni–Co–Se-bearing löllingite, clausthalite, tiemannite, mercurian hakite–giraudite solid solutions, sulfurian berzelianite, sulfurian umangite, hessite, Ni–Co–As-bearing pyrite, and Se-rich chalcopyrite. The sulfurian jolliffeite has the empirical formula $(Ni_{0.85}Cu_{0.09}Co_{0.05}Fe_{0.02}Ag_{0.01})_{\Sigma 1.02}As_{0.98}(Se_{0.77}S_{0.23})_{\Sigma 1.00}$ and differs from type jolliffeite mainly by substantial substitution of Cu (2.6–3.3 wt.%) for Ni and S (3.2–4.1 wt.%) for Se. Substantial S-for-Se substitution in jolliffeite implies extensive and probably complete miscibility between NiAsSe and its S-dominant analogue, gersdorffite-*Pa*3 (NiAsS). We suggest that a localized accumulation of Ni and As in the Se–(S)-bearing hydrothermal fluid gave rise to the crystallization of jolliffeite at some rare locations at a late stage of formation of the Jurassic selenide assemblage.

Keywords: jolliffeite, eskebornite, gersdorffite, selenium minerals, arsenic, solid solution, uranium deposit, Niederschlema–Alberoda, Erzgebirge, Germany.

Sommaire

Le gisement uranifère de Niederschlema–Alberoda, dans l'Erzgebirge, en Allemagne, contient un assemblage inhabituel de minéraux métalliques, en particulier des séléniures, sulfures, arséniures, tellurures, et éléments natifs, en plus de l'uraninite et la coffinite. Les complexités minéralogiques résultent de la superposition de plusieurs événements minéralisateurs au cours de l'intervalle de temps allant du Permien au Crétacé; ces événements ont introduit et redéposé une grande variété d'éléments métalliques (Pb, Ag, Cu, Hg, Tl, Bi, Co, Ni, As, Sb, Se, S, Te) dans ce système hydrothermal minéralisé en uranium. Un des minéraux exotiques est la jolliffeïte, an arsenoséléniure ayant la formule idéale NiAsSe, connu jusqu'à ce point seulement à sa localité-type, au lac Athabasca, Saskatchewan, au Canada. Un seul grain xénomorphe de jolliffeïte a été trouvé à Niederschlema–Alberoda, inclus et en partie remplacé par l'eskebornite sulfurée. Leurs sont associés hématite, löllingite contenant Ni, Co et Se, clausthalite, tiémannite, la solution solide hakite–giraudite mercurienne, berzélianite sulfurée, umangite sulfurée, hessite, pyrite contenant Ni, Co et As, et chalcopyrite sélénifère. La jolliffeïte sulfurée répond à la formule empirique $(Ni_{0.85}Cu_{0.09}Co_{0.05}Fe_{0.02}Ag_{0.01})_{\Sigma 1.02}As_{0.98}(Se_{0.77}S_{0.23})_{\Sigma 1.00}$; elle diffère de la jolliffeïte holotype par une substitution substantielle de Cu (2.6–3.3%, poids) pour le Ni, et du soufre (3.2–4.1%) pour le sélénium. Une substitution importante de S pour Se dans la jolliffeïte impliquerait une

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miscibilité étendue et probablement complète entre NiAsSe et son analogue à dominance de soufre, la gersdorffite-*Pa*3 (NiAsS). Nous croyons qu'une accumulation locale de nickel et d'arsenic dans la phase fluide hydrothermale porteuse de Se (et de S) a mené à la cristallisation de la jolliffeïte à quelques endroits épars à un stade tardif de formation de l'assemblage de séléniures au Jurassique.

(Traduit par la Rédaction)

Mots-clés: jolliffeïte, eskebornite, gersdorffite, minéraux de sélénium, arsenic, solution solide, gisement d'uranium, Niederschlema–Alberoda, Erzgebirge, Allemagne.

INTRODUCTION

Selenium minerals in the western Erzgebirge metallogenic province of Germany are associated with unconformity-related vein-type uranium deposits. This setting constitutes one of the four major environments in which hydrothermal Se-bearing polymetallic deposits are found (*e.g.,* Simon *et al.* 1997). The Niederschlema – Alberoda uranium ore deposit (lat. 50°37'N, long. 12°40'E), in the Schneeberg – Schlema – Alberoda ore district, is the major selenide occurrence in the Erzgebirge (Fig. 1).

This is the first part of a series of papers describing rare mineral species from the Niederschlema – Alberoda U–Se–polymetallic deposit. Here, we report the second occurrence of jolliffeite, and discuss its origin and alteration. Jolliffeite is a very rare arsenoselenide with end-member composition NiAsSe, first described from Lake Athabasca, Saskatchewan, by Cabri *et al.* (1991).

BACKGROUND INFORMATION

The first detailed mineralogical and paragenetic studies of the selenide assemblages in the Niederschlema – Alberoda deposit, undertaken in the 1960s and 1970s (Harlass & Schützel 1965, Ryschow 1972), were supplemented in the 1980s by electron-microprobe studies (Dymkov *et al.* 1982, 1989, 1991). As a result of these investigations, the following Se-bearing minerals were identified: clausthalite (PbSe), tiemannite (HgSe), naumannite (Ag_2Se), klockmannite (CuSe), umangite (Cu_3Se_2), berzelianite ($Cu_{2-x}Se$), bukovite ($Cu_3FeTl_2Se_4$), permingeatite (Cu_3SbSe_4), crookesite (Cu_7TlSe_4), eucairite (AgCuSe), and migriite [$(Cu,Fe)_3AsSe_3$].

In the late 1990s and early 2000s, access to previously uninvestigated samples from both institutional and private collections, as well as from the mineralogical archives of the WISMUT GmbH, encouraged the authors to undertake a further, more thorough study of the selenides and associated minerals from this location (*e.g.*, Förster & Tischendorf 2001, Förster *et al.* 2002, Förster 2004). Recent results of this study, which is still under way, have revealed the presence of selenium-, tellurium- and sulfur-bearing minerals previously unknown from Niederschlema – Alberoda, among them also new species. One of these new species is schlemaite, a Cu–Pb–Bi selenide of composition $(Cu,\square)_6(Pb,Bi)Se_4$ (Förster *et al.* 2003).

In addition to new minerals, many rare selenides, sulfides, arsenides, tellurides and native metals are part of the exotic assemblages of minerals from this location. The assemblages resulted from the overlapping effects of three major mineralizing events, which lasted from the Permian to the Cretaceous. These events introduced and redeposited a great variety of ore elements (*e.g.*, Pb, Ag, Cu, Hg, Tl, Bi, Co, Ni, As, Sb, Se, S, Te) within the hydrothermal vein-type uranium deposit.

JOLLIFFEITE AND OTHER SELENIDES OF NI AND CO

The type jolliffeite was discovered on the Shirley Peninsula, Lake Athabasca, Saskatchewan (Cabri *et al.* 1991). It occurs as small, discrete anhedral grains (maximum diameter 145 × 240 μm) in a uraninite-rich fracture zone. Closely associated minerals comprise clausthalite, an unnamed arsenoselenide with formula (Co,Ni)AsSe, and unidentified Bi and Pb–Bi–Ag selenides. Jolliffeite is chemically and crystallographically the Se-dominant analogue of gersdorffite-*Pa*3 (NiAsS).

Nickel- and cobalt-dominant species are among the scarcest selenides. Only eight selenium minerals are known in which Ni is the predominant cation. In addition to jolliffeite, these selenides are sederholmite and mäkinenite (the hexagonal and trigonal variants of NiSe), trüstedtite and wilkmannite (the cubic and monoclinic variants of Ni_3Se_4), penroseite [$(Ni,Co,Cu)Se_2$], kullerudite ($NiSe_2$), and kitkaite (NiTeSe). Most of these selenides have only one or two occurrences. Of these eight minerals, six (sederholmite, mäkinenite, wilkmannite, kullerudite, trüstedtite, kitkaite) have the same type locality, the U-mineralized diabase sills from Kuusamo, Finland (Vuorelainen *et al.* 1964, Häkli *et al.* 1965). With seven occurrences, penroseite is the most widespread Ni selenide (*e.g.*, Herzenberg & Ahlfeld 1935, Johan *et al.* 1972, Deliens 1975, Dubakina *et al.* 1985, Grundmann *et al.* 1990, Stanley *et al.* 1990, Wallis 1994, Paar *et al.* 1996).

GEOLOGICAL SETTING

The Niederschlema – Alberoda uranium deposit is located in the vicinity of the town of Hartenstein in the western Erzgebirge of Germany. The sample containing jolliffeite was collected from the dike complex "Ruhmvoll", at the –510-m level, in gallery 414, at cross cut 804. Of the three uranium deposits forming the Schneeberg – Schlema – Alberoda ore district (Schneeberg, Oberschlema, Niederschlema – Alberoda; Fig. 1), Niederschlema – Alberoda was the richest in both uranium and selenium. Mining activities for selenium between 1961 and 1965 resulted in a total production of 1472 tonnes of selenium ore containing on average 0.52 wt.% Se.

In the western Erzgebirge U deposits, three uraniferous vein-mineral associations can be distinguished: comb quartz – calcite – uraninite (*kku*), magnesian carbonate – uraninite – fluorite (*mgu*), and bismuth – cobalt – nickel ± silver ± uranium (*biconi*) (*e.g.*, Schuppan *et al.* 1994, and references therein). The formation of the primary *kku* association took place during the early Permian (~270 Ma; Förster & Haack 1995). Colloform, reniform-botryoidal uraninite was deposited in veins containing quartz, calcite, fluorite, coffinite, hematite, and sulfide minerals such as aikinite, galena, bismuthinite, chalcopyrite, and pyrite. During the Jurassic (~190 Ma), oxidizing hydrothermal solutions overprinted and altered the early-formed veins and introduced new elements (Mg, Se, Ag, Pb), giving rise to the *mgu* mineral association. Most of the new components were probably mobilized from the metamorphic wallrocks (alteration halos developed in felsic pelite, mica schist and gneiss, limestone, skarn, metadiabase, and mafic amphibolite). During this event, Permian uraninite was destabilized, and the mobilized U was redeposited as another generation of spherical aggregates of uraninite accompanied by dolomite, ankerite, fluorite, hematite, and diverse sulfides (chalcopyrite, galena, bornite, tennantite) and selenides. This association is most prominent at Niederschlema – Alberoda. Hydrothermal activity in response to tectonic processes in the early Cretaceous (~120 Ma) again gave rise to alteration of earlier-formed mineral assemblages. Pre-existing uraninite, coffinite, and selenides were partially dissolved by the infiltrating fluids and replaced by the telescopic *biconi* association comprising native minerals (Ag, Bi, As), Co–Ni–Fe arsenides (skutterudite, safflorite, rammelsbergite, löllingite, nickeline), and Bi sulfides. Quartz, fluorite, barite, siderite, and dolomite form the gangue of the *biconi* association and the remobilized U- and Se-bearing minerals.

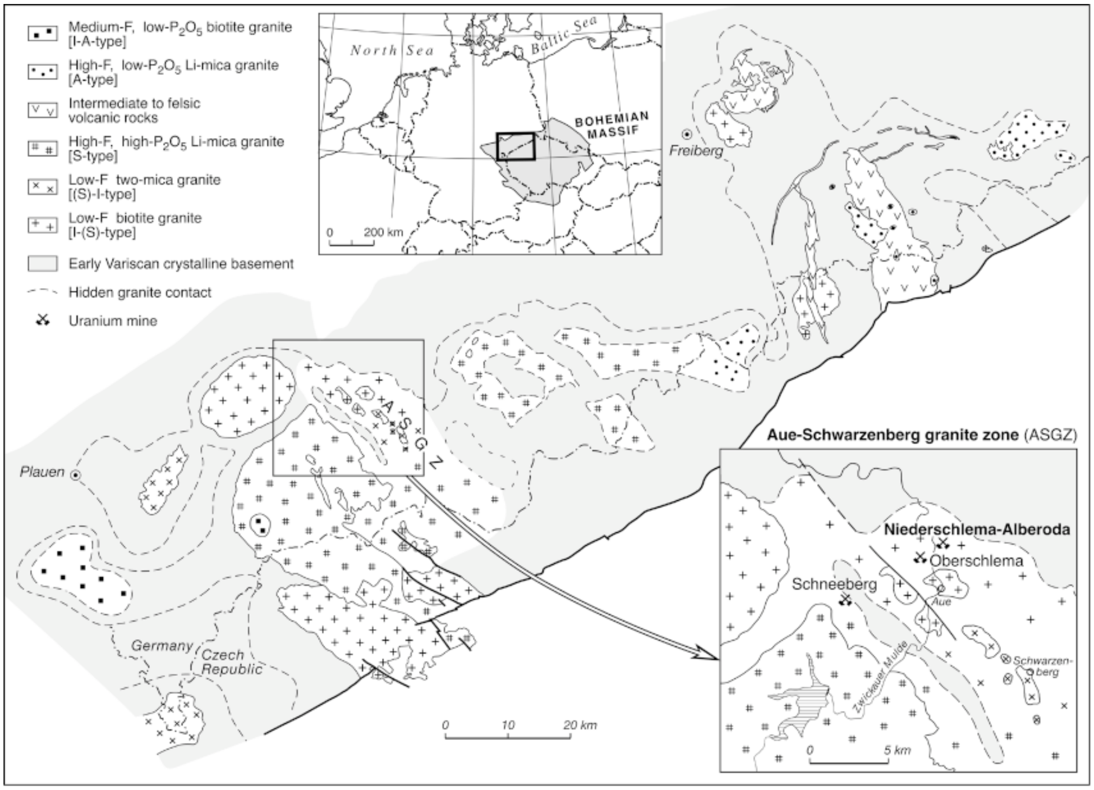

FIG. 1. Geological sketch-map, showing the location of the three uranium deposits forming the Schneeberg – Schlema – Alberoda ore district and the distribution of the various groups of Variscan granites in the Erzgebirge of Germany.

ANALYTICAL CONDITIONS

Jolliffeite and the associated metallic minerals were analyzed for Ag, Hg, Cu, Fe, Co, Ni, Zn, Cd, Pb, Pd, Pt, Sb, As, Bi, Te, S, and Se with an automated CAMEBAX SX–50 electron microprobe at the GeoForschungs-Zentrum Potsdam using wavelength-dispersion techniques. The operating conditions were as follows: accelerating voltage 20 kV, beam current 40 nA, and beam diameter 1 to 2 μm. The counting times on the peak were 50 s, and 25 s for background counts on each side of the peak. Data reduction was done with a PAP correction procedure (Pouchou & Pichoir 1985).

Lines measured were $K\alpha$ for Fe, Co, Ni, Cu, Zn, Se, and S, $K\beta$ for As, $L\alpha$ for Hg, Pd, Pt, Cd, Sb, and Te, $L\beta$ for Ag, $M\alpha$ for Bi, and $M\beta$ for Pb. Primary standards included pure metals for Co, Ag, Pd, and Pt, chalcopyrite for Fe, Cu, and S, pentlandite for Ni, sphalerite for Zn, Ag_2Te for Ag and Te, cinnabar for Hg, galena for Pb, GaAs for As, Bi_2Se_3 for Bi and Se, InSb for Sb, and CdS for Cd.

In all mineral analyses, the concentrations of Au, Pd, and Pt were found to be below the detection limits of the electron microprobe used.

RESULTS

Petrographic descriptions

Jolliffeite is among the scarcest selenides at Niederschlema – Alberoda. In the 40 polished sections examined so far, it was observed in only one sample; in all, only one grain was found (Fig. 2). This anhedral and corroded grain has an approximate size of 30 × 30 μm and is located at the margin of anhedral eskebornite embedded in dolomite. Outside of the area shown in Figure 2, one small grain of clausthalite is also included in the eskebornite, which shows a typical cracked appearance. The textural relations suggest that jolliffeite became replaced by eskebornite, which itself is slightly younger than clausthalite. Other minerals present in the section include hakite–giraudite solid solution, tennantite–giraudite solid solution, tiemannite, berzelianite, umangite, hessite, chalcopyrite, löllingite, and probably native tellurium. Thus, jolliffeite from Niederschlema – Alberoda is paragenetically distinct from the virtually unaltered type-locality jolliffeite described by Cabri *et al.* (1991).

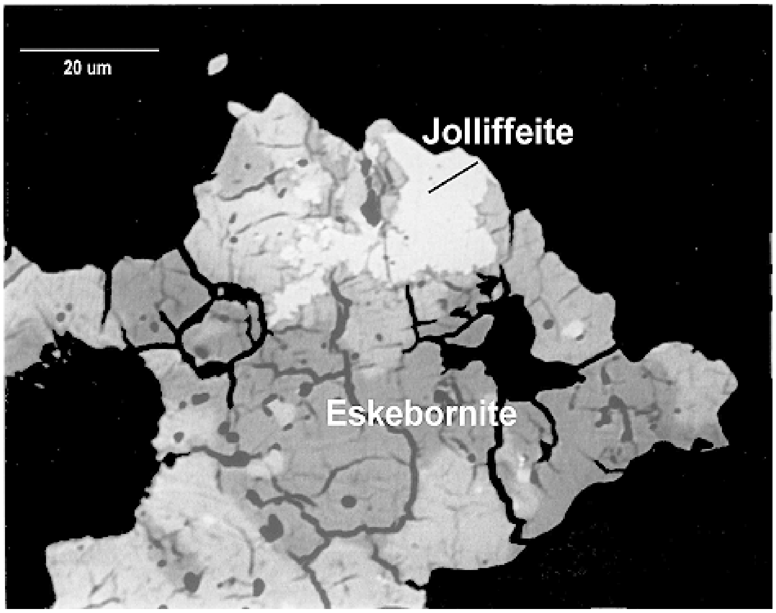

FIG. 2. Back-scattered electron image of jolliffeite in sulfurian eskebornite. Note the cracked appearance and the different brightness of eskebornite, which is a reflection of variable ratio of selenium to sulfur.

Chemical composition

Table 1 lists representative results of electron-microprobe analyses and the average composition of jolliffeite from Niederschlema – Alberoda (sample HS106), together with the compositional average of type jolliffeite from Lake Athabasca (Cabri *et al.* 1991). Atom proportions were calculated on the basis of three atoms per formula unit (*apfu*). Element correlations and compositional zoning of the polymineralic jolliffeite – eskebornite grain are shown as X-ray element-distribution maps for Ni, Cu, Fe, As, Se, and S (Fig. 3). The position of the jolliffeite grain in the eskebornite is displayed best in the Cu, Ni, Se, and As distribution maps. No significant internal zoning is visible in both selenium species.

The average empirical formula (based on 3 *apfu*) for jolliffeite from Niederschlema – Alberoda is $(Ni_{0.85}Cu_{0.09}Co_{0.05}Fe_{0.02}Ag_{0.01})_{\Sigma 1.02}As_{0.98}(Se_{0.77}S_{0.23})_{\Sigma 1.00}$. It has a composition distinct from that of the type material from Lake Athabasca, the average formula of which is $(Ni_{0.81}Cu_{0.01}Co_{0.19})_{\Sigma 1.01}As_{0.98}(Se_{1.00}S_{0.01})_{\Sigma 1.01}$, in its significantly higher contents of Cu (2.6–3.3 wt.% or 8–10 mol.%) and S (3.2–4.1 wt.%; 20–25 mol.%), but lower abundances of Co (1.1–1.5 wt.%; 4–5 mol.%) (Table 1). Iron (0.4–0.8 wt.%; 2–3 mol.%), Ag (0.3–0.4 wt.%; 1 mol.%), and Te (0.05–0.08 wt.%) are consistently present above their detection limits. The contents of Hg, Pb, Zn, and Sb are insignificant and at their detection limits, whereas Bi and Cd were not detected. Because of the extensive substitution of S for Se, jolliffeite from Niederschlema – Alberoda is described as sulfurian.

Representative results of electron-microprobe analyses of ore minerals accompanying jolliffeite in sample HS106 are given in Table 2. Se-poor löllingite and S-poor mercurian giraudite constitute the As-dominant minerals other than jolliffeite. Minor concentrations of As are present in pyrite, chalcopyrite, hessite, and eucairite. Löllingite and pyrite contain minor Ni and Co. The copper selenides umangite and berzelianite are enriched in S, thus being of the sulfurian variety. This also holds for the eskebornite replacing the jolliffeite grain, which, however, contains no measurable contents of Ni and As. The selenides clausthalite and tiemannite are devoid of detectable sulfur.

TABLE 1. CHEMICAL COMPOSITION OF JOLLIFFEITE

	Niederschlema–Alberoda							Lake Athabasca	
	1	2	3	4	5	average (n=5)	STDW	average (n=7)	STDW
Cu	2.62	2.63	2.89	3.19	3.26	2.92	0.30	0.18	0.37
Ag	0.30	0.36	0.32	0.32	0.32	0.32	0.02		
Hg	d.l.	d.l.	d.l.	0.07	0.03				
Pb	d.l.	0.05	d.l.	d.l.	d.l.				
Zn	d.l.	d.l.	d.l.	d.l.	0.04				
Fe	0.61	0.82	0.55	0.42	0.54	0.59	0.15	0.07	0.08
Co	1.53	1.32	1.14	1.45	1.26	1.34	0.15	5.31	2.99
Ni	24.94	25.11	24.57	24.03	24.48	24.63	0.42	22.40	3.29
As	35.96	35.87	36.46	35.96	36.19	36.09	0.24	34.49	1.46
Sb	d.l.	0.06	0.03	0.06	0.04	0.04	0.02	0.03	0.06
S	3.84	3.20	4.10	3.59	3.32	3.61	0.37	0.11	0.18
Se	30.10	30.47	29.53	30.25	30.36	30.14	0.37	37.34	1.26
Te	0.05	0.08	0.08	0.08	0.08	0.07	0.01		
Total	99.95	99.97	99.67	99.42	99.92	99.75	0.24	99.93	0.96
Cu	0.08	0.08	0.09	0.10	0.10	0.09		0.01	
Ag	0.01	0.01	0.01	0.01	0.01	0.01			
Fe	0.02	0.03	0.02	0.02	0.02	0.02			
Co	0.05	0.05	0.04	0.05	0.04	0.05		0.19	
Ni	0.86	0.87	0.85	0.83	0.85	0.85		0.81	
As	0.97	0.97	0.98	0.98	0.98	0.98		0.98	
S	0.24	0.20	0.26	0.23	0.21	0.23		0.01	
Se	0.77	0.78	0.76	0.78	0.78	0.77		1.00	

d.l.: below detection limit, blank: not analyzed. Electron-microprobe data, reported in wt.%.

STDW: standard deviation. Cation proportions calculated on the basis of 3 *apfu*.

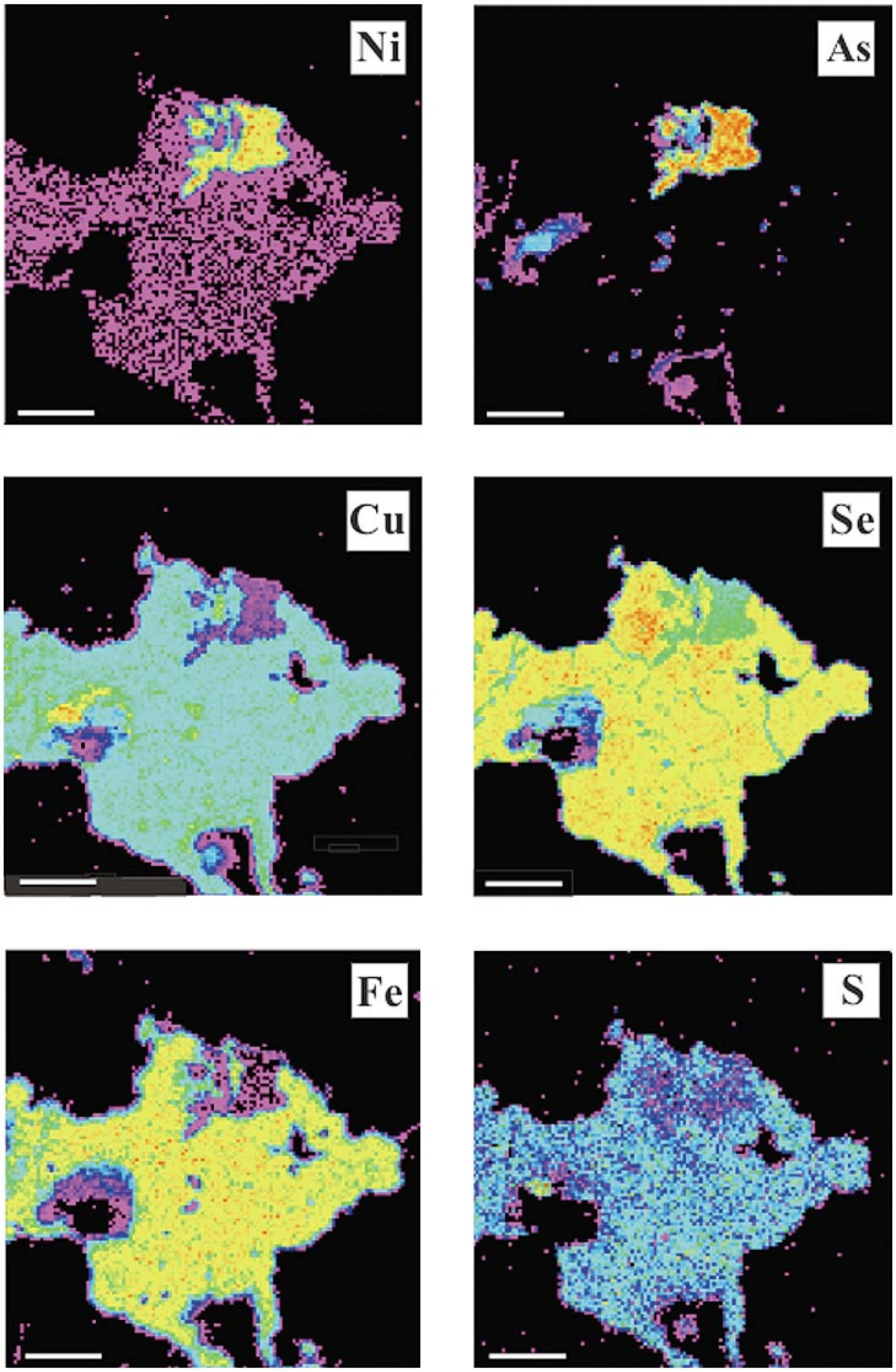

FIG. 3. X-ray element-distribution maps for Ni, As, Cu, Se, Fe, and S in jolliffeite and eskebornite. The scale bar is 20 μm.

DISCUSSION

The formation and replacement of jolliffeite

Both the assemblage and composition of the associated minerals suggest that jolliffeite is part of the *mgu* mineral association. Minerals such as native bismuth, wittichenite, bismuthinite, nickeline, rammelsbergite, safflorite, and gersdorffite, typical of the *biconi* mineral assemblage at Niederschlema – Alberoda, are not associated with jolliffeite. This origin is further supported by the composition of the accompanying löllingite, which contains 1–2 wt.% Cu replacing Fe and about 1 wt.% Se substituting for As. Löllingite of the *biconi* assemblage is virtually free of Cu and Se, but characteristically contains varying contents of S replacing As, and several weight percent Ni and Co replacing Fe.

The thermodynamic properties of jolliffeite and the associated eskebornite remain unknown. Clausthalite, the other intimately associated species, has a wide field of stability in terms of temperature and the fugacities of selenium and sulfur (Simon & Essene 1996). Tiemannite, umangite, berzelianite, giraudite, hessite, and löllingite are not intimately associated with jolliffeite and are not necessarily cogenetic with it. Therefore, any inferences on the T–*X* conditions of formation of jolliffeite from the stability relations of these species would not be quite pertinent.

TABLE 2. CHEMICAL COMPOSITION OF METALLIC MINERALS FROM SAMPLE HS106

Anal. No.	1	2	3	4	5	6	7	8	9	10	11
Cu	2.00	26.36	0.08	33.38	d.l.	25.37	57.48	66.49	25.36	2.07	0.58
Ag	d.l.	1.23	d.l.	d.l.	63.01	42.93	0.04	d.l.	d.l.	d.l.	d.l.
Hg	d.l.	16.85	d.l.	0.13	d.l.	d.l.	d.l.	0.13	0.12	0.25	70.74
Pb	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	69.47	d.l.
Cd	d.l.	0.05	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	0.04	0.41
Fe	25.05	0.12	43.43	28.99	d.l.	d.l.	0.06	0.09	21.58	d.l.	0.15
Co	0.44	d.l.	0.73	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
Ni	0.33	d.l.	1.07	d.l.	d.l.	d.l.	d.l.	0.03	d.l.	d.l.	d.l.
As	71.63	12.61	3.65	2.62	0.40	0.24	d.l.	d.l.	d.l.	d.l.	d.l.
Sb	d.l.	d.l.	0.06	0.12	0.28	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
Bi	d.l.	0.05	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
S	0.22	0.21	49.00	29.97	d.l.	0.02	4.44	6.10	6.76	d.l.	d.l.
Se	1.16	42.56	1.37	4.68	1.52	31.26	37.39	26.95	45.60	28.68	28.29
Te			d.l.	d.l.	35.91	0.03			0.05		
Total	100.87	100.04	99.37	99.89	101.10	99.85	99.41	99.79	99.48	100.50	100.16
Cu	0.06	9.80		1.01		1.00	2.98	1.99	1.01	0.09	0.03
Ag		0.27			1.96	1.00					
Hg		1.99									0.97
Pb										0.92	
Cd		0.01									0.01
Fe	0.91	0.05	0.97	1.00					0.98		0.01
Co	0.02		0.02								
Ni	0.01		0.02								
As	1.95	3.98	0.06	0.07	0.02	0.01					
Sb					0.01						
Bi		0.01									
S	0.01	0.16	1.91	1.80			0.46	0.36	0.54		
Se	0.03	12.74	0.02	0.11	0.06	0.99	1.56	0.65	1.47	0.99	0.99
Te					0.95						

d.l.: detection limit, blank: not analyzed. Electron-microprobe data, reported in wt.%.
1: löllingite, 2: mercurian giraudite, 3: pyrite, 4: chalcopyrite, 5: hessite, 6: eucairite,
7: sulfurian umangite, 8: sulfurian berzelianite, 9: sulfurian eskebornite, 10: clausthalite,
11: tiemannite. Cation proportions calculated on the basis of 2 *apfu* (anal. 10+11),
3 *apfu* (anal. 1, 3, 5, 6, 8), 4 *apfu* (anal. 4, 9), *5 apfu* (anal. 7), and *29 apfu* (anal. 2).

However, we know from the stability relations of umangite (Förster & Tischendorf 2001) and fluid-inclusion data (Thomas & Tischendorf 1987) that the selenide mineralization formed at temperatures between about 150 and 90°C. Therefore, jolliffeite must be a stable phase at these low temperatures. The alteration of jolliffeite probably is not caused by a decrease in temperature, but may be related to a decrease of the $f(Se_2)$ / $f(S_2)$ ratio in the mineralizing fluid.

Largely on the basis of compositional features of the associated minerals, the following scenario may be invoked for the origin and replacement of jolliffeite. At some rare locations, a localized accumulation of Ni and As in the Se-rich hydrothermal fluid gave rise to the formation of jolliffeite during crystallization of the *mgu* mineral assemblage in the Jurassic. Cogenetic minerals may include Ni–Co–Se-bearing löllingite, mercurian giraudite, and S-poor tiemannite and clausthalite. This assemblage was deposited from As-bearing fluids at conditions of a high Se_2 / S_2 fugacity ratio. The crystallization of the As- and Se-dominant minerals caused a decrease in arsenic and selenium, and an increase of the sulfur fugacity of the fluid, from which subsequently were deposited the sulfurian selenides umangite, berzelianite, and eskebornite. Jolliffeite became unstable at these conditions and was partially replaced by eskebornite. The released elements Ni and As were transported away or became fixed preferentially in pyrite and chalcopyrite.

At Niederschlema – Alberoda, the crystallization of clausthalite and tiemannite commonly postdate the formation of S-poor Cu selenides. The reverse sequence of crystallization and the S-rich nature of the Cu selenides in the jolliffeite-bearing sample imply that formation and replacement of the jolliffeite took place on the retrograde path of the hydrothermal fluids, after the peak in selenium fugacity indicated by the formation of umangite and klockmannite.

Phase relations in the system Ni–Co–Cu–Fe–As–Se–S

As already emphasized by Cabri *et al.* (1991), little is known about phase relations in the system Ni–Co–Cu–Fe–As–Se–S. Electron-microprobe data on type jolliffeite indicated to them significant solid-solutions involving Co-for-Ni substitution, which point to the existence of cubic pyrite-type (*Pa*3) CoAsSe in nature (Cabri *et al.* 1991). Likewise, considerable Cu-for-Ni substitution observed in jolliffeite from Niederschlema–Alberoda indicates that a mineral species represented by the end-member formula CuAsSe-*Pa*3 may form in nature. Experimental investigations on synthetic materials are needed to resolve the many unanswered questions on mineral stabilities in the system Ni–Co–Cu–Fe–As–Se–S. On the other hand, extensive S-for-Se substitution in the jolliffeite studied here is in accordance with extensive and probably complete miscibility between NiAsSe and its chemical S-dominant analogue, gersdorffite-*Pa*3 (NiAsS).

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