

**MINERALOGY OF THE NIEDERSCHLEMA–ALBERODA U – Se – POLYMETALLIC
DEPOSIT, ERZGEBIRGE, GERMANY. V. WATKINSONITE,
NEVSKITE, BOHDANOWICZITE AND OTHER BISMUTH MINERALS**

HANS-JÜRGEN FÖRSTER[§]

Institute of Earth Sciences, University of Potsdam, D-14415 Potsdam, Germany

GERHARD TISCHENDORF

Bautzner Strasse 16, D-02763 Zittau, Germany

DIETER RHEDE

GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany

ABSTRACT

The uranium deposit at Niederschlema–Alberoda, Germany, contains a rich variety of Bi minerals deposited between the Permian and the Cretaceous; these have been studied for paragenetic relations, composition, and conditions of formation. Particular attention is given to the rare Bi selenides watkinsonite, nevskite, and cuproan bohdanowiczite. Whereas watkinsonite and nevskite only occur intergrown with clausthalite, bohdanowiczite is more widespread and also is associated with Cu selenides. Watkinsonite from this second confirmed locality worldwide has an average composition $(\text{Cu}_{1.47}\text{Ag}_{0.49})_{\Sigma 1.96}(\text{Pb}_{1.01}\text{Hg}_{0.01}\text{Fe}_{0.01})_{\Sigma 1.03}\text{Bi}_{3.98}(\text{Se}_{7.98}\text{S}_{0.05})_{\Sigma 8.03}$, ideally $(\text{Cu,Ag})_2\text{PbBi}_4\text{Se}_8$. These findings suggest that the empirical formula of watkinsonite originally proposed for the type specimen from the Otish Mountains uranium deposit in Quebec $[\text{Cu}_{2+x}\text{Pb}_{1+x}\text{Bi}_{4-x}(\text{Se,S,Te})_8, x \approx 0.3]$ requires revision. The composition of nevskite is $(\text{Pb}_{0.06}\text{Bi}_{0.95})_{\Sigma 1.01}\text{Se}_{0.99}$, on average. Bohdanowiczite from the Cu-selenide assemblage shows extensive substitution of Cu^+ for Ag^+ , expressed by the crystallochemical formula $(\text{Ag}_{1.80-0.94}\text{Cu}_{0.16-1.05}\text{Pb}_{0.00-0.05})_{\Sigma 1.98-2.07}\text{Bi}_{\Sigma 1.97-2.03}\text{Se}_{\Sigma 3.96-4.04}$. This observation seems to argue for the natural existence of $\text{Cu}_2\text{Bi}_2\text{Se}_4$, the Se-dominant analogue of emplectite. The Bi selenides were deposited at temperatures of about 100°C, in the Jurassic. The lack of thermodynamic data for all the Bi selenides limits reliable inferences on the fugacities of selenium and sulfur that prevailed during their formation. Other Bi minerals from this locality comprise members of the bismuthinite–aikinite solid-solution series of Permian age and, more importantly, native Bi and Bi sulfides (matildite, bismuthinite, wittichinite), deposited in the Cretaceous.

Keywords: selenium minerals, watkinsonite, nevskite, bohdanowiczite, matildite, wittichenite, bismuthinite, aikinite, solid solution, uranium deposit, Niederschlema–Alberoda, Erzgebirge, Germany.

SOMMAIRE

Le gisement uranifère de Niederschlema–Alberoda, en Allemagne, contient une riche variété de minéraux de bismuth, déposés en épisodes dans un intervalle entre le Permien et le Crétacé. Nous les avons étudiés afin d'en établir les relations paragenétiques, la composition, et les conditions de formation. Nous avons porté une attention particulière aux séléniures de bismuth watkinsonite, nevskite, et bohdanowiczite cuprifère, minéraux rares. Tandis que la watkinsonite et la nevskite ne se présentent qu'en intercroissances avec la clausthalite, la bohdanowiczite est plus répandue et aussi associée aux séléniures de cuivre. La watkinsonite de cette deuxième localité à l'échelle mondiale possède une composition moyenne $(\text{Cu}_{1.47}\text{Ag}_{0.49})_{\Sigma 1.96}(\text{Pb}_{1.01}\text{Hg}_{0.01}\text{Fe}_{0.01})_{\Sigma 1.03}\text{Bi}_{3.98}(\text{Se}_{7.98}\text{S}_{0.05})_{\Sigma 8.03}$, ou idéalement $(\text{Cu,Ag})_2\text{PbBi}_4\text{Se}_8$. Ces données font penser que la formule empirique de la watkinsonite proposée pour l'échantillon-type, provenant d'un gisement d'uranium des monts Otish, au Québec $[\text{Cu}_{2+x}\text{Pb}_{1+x}\text{Bi}_{4-x}(\text{Se,S,Te})_8, x \approx 0.3]$ requiert une révision. La composition de la nevskite est $(\text{Pb}_{0.06}\text{Bi}_{0.95})_{\Sigma 1.01}\text{Se}_{0.99}$, en moyenne. La bohdanowiczite associée à l'assemblage de séléniures de cuivre fait preuve d'une substitution importante de Cu^+ pour Ag^+ , telle qu'exprimée par la formule cristallographique $(\text{Ag}_{1.80-0.94}\text{Cu}_{0.16-1.05}\text{Pb}_{0.00-0.05})_{\Sigma 1.98-2.07}\text{Bi}_{\Sigma 1.97-2.03}\text{Se}_{\Sigma 3.96-4.04}$. Cette observation semble indiquer l'existence dans la nature de $\text{Cu}_2\text{Bi}_2\text{Se}_4$, l'analogue à dominance de Se de l'emplectite. Les séléniures de Bi ont été déposés à une température d'environ 100°C, au Jurassique. Le manque de données thermodynamiques

[§] E-mail address: forhj@gfz-potsdam.de

pour tous ces sélénures de Bi limite la reconstitution des fugacités de sélénium et du soufre lors de leur formation. Parmi les autres minéraux de Bi à cette localité sont les membres de la solution solide entre bismuthinite et aikinite, d'âge permien, et, plus importants encore, le Bi natif et les sulfures de Bi (matildite, bismuthinite, wittichinite), déposés au Crétacé.

(Traduit par la Rédaction)

Mots-clés: minéraux de sélénium, watkinsonite, nevskite, bohdanowiczite, matildite, wittichenite, bismuthinite, aikinite, solution solide, gisement d'uranium, Niederschlema–Alberoda, Erzgebirge, Allemagne.

INTRODUCTION

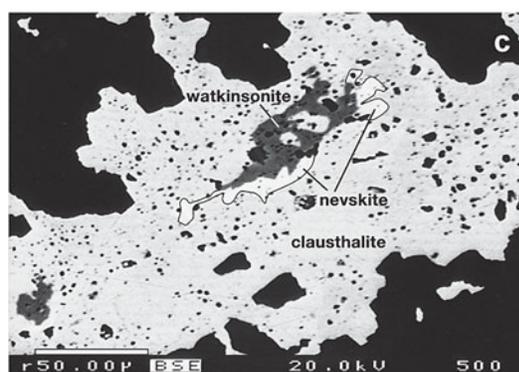
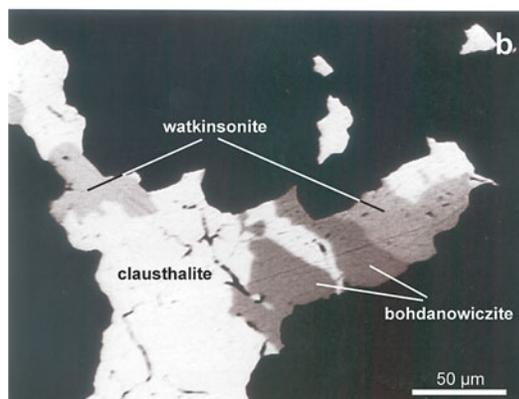
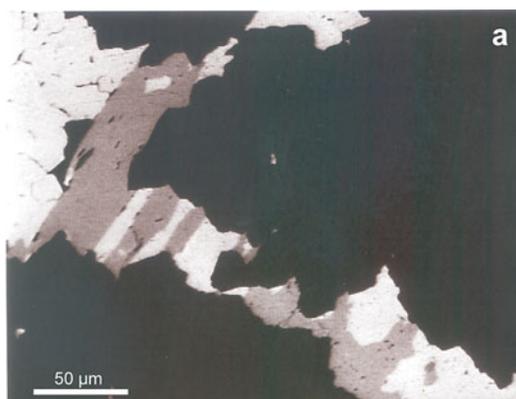
Niederschlema–Alberoda, in the western Erzgebirge of Germany, is an unconformity-related vein-type uranium deposit that hosts important selenide and polymetallic mineralization. The complex assemblage of uranium minerals, selenides, sulfides (Förster 2004b), arsenides (Förster *et al.* 2004), tellurides (Förster 2004a), and native metals was deposited during three major mineralizing events, between the Permian and Cretaceous periods (Förster & Haak 1995).

A recent detailed survey of the mineral parageneses by electron microprobe revealed the occurrence of several rare selenium-bearing species (*i.e.*, Förster *et al.* 2002, 2004) and the new mineral schlemaite, a Cu–Pb–Bi selenide of composition $(\text{Cu}, \square)_6(\text{Pb}, \text{Bi})\text{Se}_4$ (Förster *et al.* 2003). The Bi-selenides watkinsonite, nevskite, and bohdanowiczite are the focus of this fifth part of a series of papers on the mineralogy of this polymetallic deposit. Also described here are the Bi sulfides (wittichenite, matildite, bismuthinite, aikinite–bismuthinite solid solutions) and native bismuth, which complete the assemblage of Bi-bearing minerals at Niederschlema–Alberoda. The geology and formation of the deposit have been described in detail by Förster & Tischendorf (2001), Förster *et al.* (2002, 2003, 2004) and Lipp (2003).

ANALYTICAL PROCEDURE

The Bi minerals were analyzed routinely for Ag, Hg, Cu, Fe, Co, Ni, Zn, Cd, Pb, Pd, Pt, Sb, As, Bi, Te, S, and Se at the GeoForschungsZentrum Potsdam, using an automated Cameca CAMEBAX SX-50 electron microprobe operated in wavelength-dispersion mode. The operating conditions were as follows: accelerating voltage 20 kV, beam current 40 nA, and beam diameter 1–2 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).

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



As, Bi_2Se_3 for Bi and Se, InSb for Sb, and CdS for Cd. Detection limits for the individual elements range between 0.03 and 0.06 wt%.

RESULTS

In Figure 1, we present a selection of back-scattered electron (BSE) and secondary electron (SE) images showing the textures and parageneses of the Bi minerals. The intimate intergrowth of nevkite, bohdanowiczite, and watkinsonite enclosed within clausthalite is reflected in the element-distribution X-ray maps for Bi, Pb, Ag, and Se (Fig. 2).

Petrographic description of the Bi selenides

Watkinsonite and nevkite were observed in only one sample (Sh9) of more than 40 selenide-bearing polished

sections from Niederschlema–Alberoda studied to date. Watkinsonite occurs as anhedral grains (maximum size $120 \times 30 \mu\text{m}$) intergrown with clausthalite (Fig. 1a). In clausthalite, watkinsonite may be associated with bohdanowiczite (Fig. 1b), nevkite (Fig. 1c), or both (Fig. 2). Nevkite either occurs as a small rim between watkinsonite and clausthalite (Fig. 1c) or as small grains ($<20 \mu\text{m}$) associated with watkinsonite and bohdanowiczite in the body of clausthalite (Fig. 2). Schlemaiter is the only other selenide present in section Sh9 (*e.g.*, Förster *et al.* 2003, their Table 7). Bohdanowiczite, the most widespread Bi selenide at Niederschlema–Alberoda, is associated with clausthalite and other selenides and sulfides. In addition to being associated with watkinsonite and nevkite in clausthalite (Figs. 1b, 2), it forms large, anhedral grains up to several hundred μm across in clausthalite (sample R3, Fig. 1d), overgrowing and replacing spherical grains of uraninite.

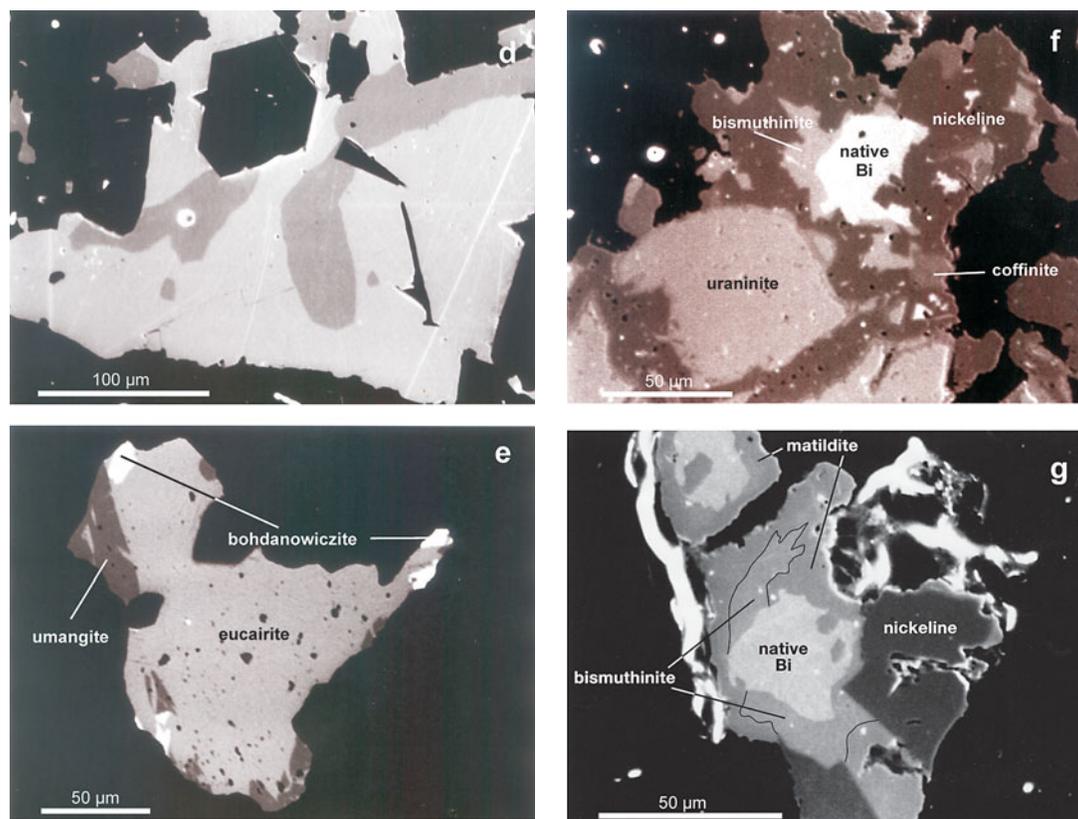


FIG. 1. Back-scattered electron (BSE) and secondary electron (SE) images showing the texture and assemblage of Bi minerals from Niederschlema–Alberoda. a. BSE image of watkinsonite (dark) intergrown with clausthalite (bright) in sample Sh9. b. BSE image of watkinsonite associated with bohdanowiczite and clausthalite (Sh9). c. BSE image of nevkite rimming watkinsonite in clausthalite (Sh9). d. SE image of anhedral bohdanowiczite (dark) associated with clausthalite (bright) in sample R3. e. BSE image of bohdanowiczite and umangite replacing (?) eucairite in sample F2. f. SE image showing the assemblage native Bi + bismuthinite + nickeline + uraninite + coffinite in sample Sh76. g. SE image of native Bi replaced by bismuthinite and matildite (Sh76). Black areas represent gangue minerals.

As part of the Cu-selenide assemblage, bohdanowiczite forms euhedral to subhedral grains up to 50 μm in size enclosed in berzelianite and, together with umangite, subhedral to anhedral grains at the periphery of eucairite (sample F2; Fig. 1e).

Petrographic description of other Bi minerals

Wittichenite invariably is intimately intergrown with Bi-bearing tennantite or Bi-bearing zincian tennantite (sample Sh3). Textural relations indicate that wittichenite is replaced progressively by tennantite. Associated minerals include gersdorffite, löllingite-safflorite solid solutions, chalcopyrite, bornite, and chalcocite. Native Bi, bismuthinite, and matildite occur in the same sample (Sh76) and are associated with chalcopyrite, pyrite, nickeline, löllingite, rammelsbergite, acanthite, native silver, uraninite, and coffinite. Bismuthinite either forms individual grains in the carbonate gangue or is intergrown with nickeline, where it usually overgrows and replaces native Bi (Fig. 1f). Native bismuth forms individual grains in the carbonate matrix and, more generally, occurs enclosed within nickeline, where it typically is overgrown by bismuthinite. Matildite overgrows and replaces native Bi and bismuthinite included in nickeline (Fig. 1g).

In addition to Bi-bearing minerals associated with the Co-Ni-Fe arsenides, another assemblage of Bi sulfides at Niederschlema-Alberoda (sample F16) consists of needles of bismuthinite-aikinite solid solutions, up to several mm long, associated with Bi-bearing galena and Pb-bearing chalcopyrite (*e.g.*, Förster 2004b). At least three Bi-bearing minerals can be distinguished on the basis of brightness contrasts in the BSE image. For the most part, the needles are made up of subhedral to euhedral aikinite, which locally is replaced or overgrown by domains of anhedral bismuthinite less than 100 μm in size. Bismuthinite locally is intergrown with an unidentified Cu-Pb-Bi sulfosalt that forms small, anhedral grains usually less than 30–50 μm in size.

Chemical composition of the Bi selenides

Representative results of analyses and the average composition of watkinsonite in sample Sh9 from Niederschlema-Alberoda are reported in Table 1. An essential feature of this watkinsonite is the invariable presence of significant Ag (2.4–4.1 wt%) substituting for Cu. Silver occupies about a quarter of the Cu site. The extent of substitution of Hg for Pb, and S for Se, is minor. The concentrations of other elements are at or below their detection limits. Watkinsonite has an average composition of $(\text{Cu}_{1.47}\text{Ag}_{0.49})_{\Sigma 1.96}(\text{Pb}_{1.01}\text{Hg}_{0.01}\text{Fe}_{0.01})_{\Sigma 1.03}\text{Bi}_{3.98}(\text{Se}_{7.98}\text{S}_{0.05})_{\Sigma 8.03}$ ($n = 27$).

Electron-microprobe analyses indicate a minor substitution of Pb for Bi in nevskite (Table 2). The small size and intimate intergrowth with other minerals

permitted only a limited number of analyses, which gave, on average, $(\text{Pb}_{0.06}\text{Bi}_{0.95})_{\Sigma 1.01}\text{Se}_{0.99}$ ($n = 2$).

The composition of bohdanowiczite is variable, depending on mineral assemblage (Table 3). Bohdanowiczite associated with clausenthalite in sample R3 (average formula: $\text{Ag}_{1.98}(\text{Bi}_{1.98}\text{As}_{0.01})_{\Sigma 1.99}(\text{Se}_{3.84}\text{S}_{0.18})_{\Sigma 4.02}$, $n = 20$, calculated on the basis of 8 atoms per formula unit, *apfu*) is compositionally similar to bohdanowiczite associated with clausenthalite + watkinsonite + nevskite in sample Sh9 (average formula: $(\text{Ag}_{1.98}\text{Pb}_{0.02})_{\Sigma 2.00}\text{Bi}_{1.99}(\text{Se}_{3.99}\text{S}_{0.01})_{\Sigma 4.00}$, $n = 15$). Only minor substitutions of As (up to 0.5 wt%) for Bi, Pb (up to 1.1 wt%) for Ag, and S (up to 1 wt%) for Se are recorded. Bohdanowiczite associated with Cu selenides in sample F2 is devoid of S and As, but contains between 1.1 and 7.4 wt% Cu substituting for Ag. Its compositional variability is expressed by the crystallochemical formula $(\text{Cu}_{0.16-1.05}\text{Ag}_{1.80-0.94}\text{Pb}_{0.00-0.05})_{\Sigma 1.98-2.07}\text{Bi}_{\Sigma 1.97-2.03}\text{Se}_{\Sigma 3.96-4.04}$ ($n = 16$).

Clausenthalite associated with bohdanowiczite in sample R3 contains about 0.4 wt% Ag, 1 wt% Bi, and 0.4–0.8 wt% S. The Cu content is at the limit of detection. Clausenthalite from sample Sh9 contains similar amounts of Ag and Bi, but no detectable Cu and S.

Chemical composition of other Bi minerals

Wittichenite has a composition close to the ideal end-member, Cu_3BiS_3 (Table 4). The average formula is $(\text{Cu}_{3.00}\text{Ag}_{0.01}\text{Zn}_{0.01}\text{Fe}_{0.01}\text{Ni}_{0.01}\text{Co}_{0.01})_{\Sigma 3.04}(\text{Bi}_{0.96}$

TABLE 1. CHEMICAL COMPOSITION OF WATKINSONITE

	Niederschlema – Alberoda						Olsh Mtns ¹	
	1	2	3	4	ave. <i>n</i> = 27	STDW	ave.	STDW <i>n</i> = 11
Cu wt%	5.63	4.46	4.76	5.47	5.13	0.26	8.62	0.50
Ag	2.41	4.10	3.74	2.46	2.92	0.43		
Hg	0.14	0.06	0.17	0.26	0.11	0.08		
Pb	11.37	11.41	11.48	11.28	11.46	0.11	15.08	0.70
Zn	d.l.	0.03	d.l.	d.l.	0.00	0.01		
Cd	d.l.	d.l.	0.04	0.05	0.01	0.02		
Fe	d.l.	0.04	0.03	d.l.	0.02	0.02		
Co	d.l.	d.l.	d.l.	d.l.	0.00	0.01		
Sb	d.l.	d.l.	d.l.	0.03	0.00	0.01		
Bi	45.52	45.70	45.77	45.60	45.59	0.19	44.52	1.15
S	0.09	0.09	0.08	d.l.	0.08	0.05	3.21	0.11
Se	34.54	34.39	34.70	34.76	34.53	0.26	28.14	0.35
Te							0.34	0.12
Total	100.23	100.30	100.77	99.89	99.86	0.46	99.91	0.41
Cu <i>apfu</i>	1.61	1.28	1.36	1.57	1.47		2.31	
Ag	0.41	0.69	0.63	0.41	0.49			
Hg	0.01	0.01	0.01	0.02	0.01			
Pb	1.00	1.01	1.00	0.99	1.01		1.24	
Cd			0.01	0.01				
Fe		0.01	0.01		0.01			
Bi	3.96	3.99	3.97	3.97	3.98		3.63	
S	0.05	0.05	0.04		0.05		1.71	
Se	7.96	7.95	7.96	8.02	7.98		6.07	
Te							0.05	

d.l.: below detection limit. Blank: not analyzed. STDW: standard deviation. ¹: from Johan *et al.* (1987). Cation proportions are calculated on the basis of 15 *apfu*.

As_{0.01})_{Σ0.97} (S_{2.94}Se_{0.03})_{Σ2.97} ($n = 10$). Silver, Zn, and Fe invariably are present, but at low concentrations, between 0.1 and 0.4 wt%. Nickel and Co sporadically occur in detectable amounts. Between 0.3 and 0.7 wt% Se substitutes for S. Bismuthinite has the average formula (Bi_{1.93}As_{0.04}Ag_{0.01}Fe_{0.01}Ni_{0.01})_{Σ2.00}S_{3.00} ($n = 8$). The grains from the matrix differ from those associated with Ni arsenides and native Bi by having measurable

concentrations of As (2.2 wt%), Ag (0.8 wt%), and Ni (0.3 wt%). The extent of substitution of Se for S is insignificant. In native Bi, no elements other than Bi occur at a level of concentration sufficient to be accounted

TABLE 2. CHEMICAL COMPOSITION OF NEVSKITE

	SLM-ALB		Nevskoe ¹		unnamed ²
Cu wt%	0.03	0.03			
Ag	d.l.	0.20	0.6	0.5	d.l.
Pb	3.47	4.44	3.6	1.9	2.13
Sb	d.l.	d.l.			0.05
Bi	69.71	67.85	69.1	71.2	69.11
S	0.04	0.03	1.8	1.4	0.10
Se	27.05	26.99	24.7	24.8	28.37
Total	100.30	99.53	99.8	99.8	99.76
Ag <i>apfu</i>		0.01	0.02	0.01	
Pb	0.05	0.06	0.05	0.03	0.03
Bi	0.96	0.94	0.92	0.96	0.94
S			0.16	0.12	0.01
Se	0.99	0.99	0.87	0.88	1.02

d.l.: below detection limit. Blank: not analyzed. SLM-ALB: Niederschlema – Alberoda. ¹: Data of Nechelyustov *et al.* (1984). ²: Data of Zhukova & Ordynets (1988). Cation proportions are calculated on the basis of 2 *apfu*.

TABLE 3. CHEMICAL COMPOSITION OF BOHDANOWICZITE

Sample Anal.	R3 1	R3 2	R3 3	Sh9 4	F2 5	F2 6	F2 7	F2 8
Cu wt%	d.l.	0.04	0.03	d.l.	7.37	6.90	2.42	1.60
Ag	22.91	22.78	22.92	21.89	11.22	11.72	18.29	20.26
Au					0.08	d.l.	d.l.	d.l.
Hg	0.18	0.14	0.16	0.05	d.l.	d.l.	d.l.	0.13
Pb	0.09	0.09	0.10	1.30	d.l.	d.l.	1.16	d.l.
Fe	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	0.05	0.06
As	d.l.	0.26	0.47	d.l.	d.l.	d.l.	d.l.	d.l.
Bi	43.83	43.91	43.46	43.78	46.43	46.41	44.50	44.88
S	0.21	0.54	0.80	0.04	d.l.	d.l.	d.l.	d.l.
Se	32.81	31.91	32.16	33.27	34.60	34.27	33.02	33.77
Total	100.02	99.67	100.10	100.32	99.70	99.31	99.43	100.70
Cu <i>apfu</i>		0.01			1.05	1.00	0.36	0.24
Ag	2.01	1.99	1.97	1.93	0.94	1.00	1.60	1.75
Hg	0.01	0.01	0.01					0.01
Pb				0.06			0.05	
Fe							0.01	0.01
As		0.03	0.06					
Bi	1.98	1.98	1.93	1.99	2.02	2.03	2.02	2.00
S	0.06	0.16	0.23	0.01				
Se	3.93	3.82	3.79	4.00	3.98	3.98	3.96	3.99

d.l.: below detection limit. Blank: not analyzed. Cation proportions were calculated on the basis of 8 atoms per formula unit (*apfu*).

TABLE 4. CHEMICAL COMPOSITION OF BI SULFIDES AND NATIVE BI

	wittichenite				bismuthinite				matildite		native bismuth			
Cu wt%	38.34	38.94	38.34	38.45	d.l.	0.04	0.11	d.l.	d.l.	0.25	d.l.	d.l.	d.l.	
Ag	0.27	0.30	0.33	0.33	0.85	d.l.	0.12	27.95	27.84	d.l.	d.l.	d.l.	d.l.	
Hg	d.l.	0.16	d.l.	d.l.	d.l.	d.l.	0.09	0.16	0.06	d.l.	0.13	0.06	d.l.	
Zn	0.13	0.07	0.09	0.24	0.04	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	
Fe	0.05	0.08	0.05	0.12	0.14	d.l.	d.l.	0.17	0.11	0.10	d.l.	0.05	d.l.	
Co	0.17	0.44	0.19	0.33	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	
Ni	0.12	0.35	0.13	0.26	0.32	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	
As	d.l.	0.89	d.l.	d.l.	2.27	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	
Bi	40.77	40.16	40.67	40.84	76.39	80.73	80.83	80.48	55.20	54.89	99.11	100.01	100.18	
S	18.92	19.22	19.06	19.16	19.25	19.04	18.85	19.08	16.60	16.59	d.l.	d.l.	d.l.	
Se	0.67	0.29	0.42	0.42	d.l.	0.13	d.l.	d.l.	0.20	0.25	0.65	0.14	0.12	
Total	99.44	100.90	99.28	100.16	99.26	99.93	99.81	100.13	100.13	99.67	100.14	100.26	100.30	
Cu <i>apfu</i>	3.00	2.98	3.00	2.98				0.01			0.01			
Ag	0.01	0.01	0.02	0.02	0.04			0.01	1.98	1.98				
Zn	0.01	0.01	0.01	0.02										
Fe		0.01		0.01	0.01			0.02	0.02	0.01				
Co	0.01	0.04	0.02	0.03										
Ni	0.01	0.03	0.01	0.02	0.03									
As		0.06			0.15									
Bi	0.97	0.93	0.97	0.96	1.80	1.97	1.98	1.95	2.02	2.01	0.97	0.99	1.00	
S	2.94	2.92	2.95	2.94	2.97	3.02	3.01	3.01	3.96	3.97				
Se	0.04	0.02	0.03	0.03		0.01			0.02	0.02	0.02			

d.l.: below detection limit. Cation proportions calculated on the basis of 1 *apfu* (native Bi), 5 *apfu* (bismuthinite), 7 *apfu* (wittichenite), and 8 *apfu* (matildite).

for in the formula. One analysis of a grain included in carbonate revealed the presence of 0.25 wt% Cu and 0.65 wt% Se in the structure. The average composition of matildite is $(\text{Ag}_{1.98}\text{Fe}_{0.01})_{\Sigma 1.99}\text{Bi}_{2.02}(\text{S}_{3.96}\text{Se}_{0.02})_{\Sigma 3.98}$ ($n = 2$). Among the minor elements, only Fe and Se were found to be present above the limits of detection.

Bismuthinite from the bismuthinite–aikinite series contains appreciable amounts of Pb (3.1–5.8 wt%) and minor concentrations of Cu (1.1–2.1 wt%) and Se (0.8–1.2 wt%) (Table 5). The average composition of bismuthinite from this assemblage is to $(\text{Cu}_{0.13}\text{Pb}_{0.11}\text{Bi}_{1.76})_{\Sigma 2.00}(\text{S}_{2.94}\text{Se}_{0.06})_{\Sigma 3.00}$ ($n = 4$). In contrast to bismuthinite, aikinite is poor in minor elements. Its average formula is $\text{Cu}_{1.00}(\text{Pb}_{1.00}\text{Fe}_{0.01})_{\Sigma 1.01}\text{Bi}_{0.98}\text{S}_{3.00}$ ($n = 2$). The third Bi-bearing species has the best stoichiometric fit if the formula is calculated on the basis of 14 *apfu*, that is, $\text{Cu}_{1.00}\text{Pb}_{1.03}\text{Bi}_{3.99}(\text{S}_{7.76}\text{Se}_{0.22})_{\Sigma 7.98}$ ($n = 2$), or ideally $\text{CuPbBi}_4\text{S}_8$. A mineral of this composition is not yet known. However, because of the small grain-size and intimate intergrowth with bismuthinite and aikinite, the analytical results may reflect contamination with the neighboring minerals. The unidentified mineral is chemically similar to paarite, $\text{Cu}_{1.7}\text{Pb}_{1.7}\text{Bi}_{6.3}\text{S}_{12}$, and salzburgite, $\text{Cu}_{1.6}\text{Pb}_{1.6}\text{Bi}_{6.4}\text{S}_{12}$, two recently discovered derivatives of the bismuthinite–aikinite series (Topa *et al.* 2000, 2005, Makovicky *et al.* 2001).

DISCUSSION

Occurrence of the Bi selenides

Niederschlema–Alberoda represents the second reported occurrence of watkinsonite. The type locality is

TABLE 5. CHEMICAL COMPOSITION OF BISMUTHINITE, AIKINITE, AND UNNAMED $\text{CuPbBi}_4\text{S}_8$

	bismuthinite		aikinite		unnamed		salz-	paar-	
							burgite ¹	ite ²	
Cu wt%	2.06	1.81	1.15	11.00	11.02	4.60	4.67	4.65	4.79
Hg	0.07	d.l.	d.l.	0.21	d.l.	d.l.	d.l.		
Pb	5.85	4.75	3.14	35.84	36.10	15.55	15.37	15.97	16.70
Zn	0.05	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.		
Fe	d.l.	d.l.	d.l.	0.12	0.10	d.l.	d.l.	0.05	0.08
Sb	0.06	0.04	0.03	d.l.	d.l.	d.l.	0.05		
Bi	71.80	73.13	75.58	35.52	35.15	60.46	60.69	61.58	60.80
S	18.62	18.74	18.97	16.74	16.65	18.19	18.01	17.79	17.83
Se	1.22	0.94	0.83	0.12	d.l.	1.00	1.53		
Te	0.02	d.l.	d.l.	0.05	d.l.	d.l.	d.l.		
Total	99.74	99.40	99.69	99.55	99.02	99.80	100.31	100.04	100.20
Cu <i>apfu</i>	0.16	0.14	0.09	1.00	1.00	1.00	1.01		
Hg				0.01					
Pb	0.14	0.11	0.08	0.99	1.01	1.03	1.02		
Fe				0.01	0.01				
Sb							0.01		
Bi	1.71	1.75	1.81	0.98	0.97	3.98	3.99		
S	2.90	2.93	2.97	3.00	3.01	7.81	7.71		
Se	0.08	0.06	0.05	0.01		0.17	0.27		

d.l.: below detection limit. Cation proportions were calculated on the basis of 5 *apfu* (bismuthinite), 6 *apfu* (aikinite), and 14 *apfu* (unnamed). ¹: Data from Topa *et al.* (2000). ²: Data from Makovicky *et al.* (2001).

the Otish Mountains uranium deposit, Quebec, Canada (Johan *et al.* 1987), where watkinsonite occurs in a dolomite matrix and is associated with a complex assemblage of selenides, tellurides, and sulfides comprising skippenite, poubaite, součekite, clausenthalite, aikinite, wittichenite, molybdenite, pyrite, chalcocopyrite, galena, digenite, covellite, argentian gold, native bismuth, and several other bismuth selenides.

Nevskite is known from three localities. At its type locality, the Nevskoe tin deposit in northeastern Russia, nevskite occurs in quartz–cassiterite veins (Nechelyustov *et al.* 1984). Associated minerals include ferberite–hübnerite solid-solution, cassiterite, natanite, guanajuatite, and other Bi-bearing species. The second occurrence is the site of an unnamed metasomatic uranium ore (Zhukova & Ordynets 1988), where nevskite is accompanied by uraninite and coffinite and forms intimate intergrowths with clausenthalite. The Otish Mountains uranium deposit may be a third occurrence of nevskite (no compositional data reported), where it occurs as veinlets in aggregates of watkinsonite associated with clausenthalite and chalcocopyrite (Johan *et al.* 1987).

Several occurrences of bohdanowiczite are reported in the literature. Bohdanowiczite was first described from the uranium – polymetallic mineralization near Kletno, Poland, where it is associated with Bi-bearing clausenthalite and wittichenite (Banaś & Ottemann 1967, Banaś *et al.* 1980). The mineral is considered to have formed by exsolution from its Cu–Bi–Ag–S-bearing clausenthalite host. The same mode of origin has been proposed for bohdanowiczite inclusions in clausenthalite from the epithermal vein-type selenide deposit of Tannenglasbach, Thuringia, Germany (Anspach 2001). Bohdanowiczite from the Kidd Creek volcanogenic massive sulfide deposit, Ontario, Canada, typically forms blebs in bornite or an intergrowth with cobaltite and clausenthalite (Pringle & Thorpe 1980). Nesterov *et al.* (1985) described bohdanowiczite intergrowth with clausenthalite, naumannite, chalcocopyrite, and bornite from a sulfide deposit in eastern Transbaikalia, Russia. Wallis (1994) noted the presence of bohdanowiczite in selenide-bearing calcite–quartz veins from the ancient St. Andreasberg silver deposit, Harz Mountains, Germany. Polymetallic grains with bohdanowiczite, clausenthalite, eucairite, and umangite associated with other Bi minerals (wittichenite, bismuthinite) were reported from the Iron Monarch sedimentary iron deposit in South Australia (Pring 1998). Bohdanowiczite–kawazulite intergrowths associated with wittichenite and included in chalcocopyrite occur in the Ocna de Fier – Dognecea Fe–Cu skarn deposit (Cook & Ciobanu 2001).

Composition of the Bi selenides

To confirm that the Cu–Pb–Bi selenide from this study is actually watkinsonite, X-ray analysis of a powder mount was conducted using a Debye–Scherrer

powder camera 57.3 mm in diameter. The dearth of material (contamination with the enclosing clausenthalite) allowed us only to acquire a rather weak, somewhat spotty film. However, the prominent diffraction lines and intensities are consistent with the data published for watkinsonite (Johan *et al.* 1987), taking into account a slight shift due to chemical variations.

The analytical data from this study fit perfectly a $(\text{Cu}+\text{Ag}) : \text{Pb} : \text{Bi} : (\text{Se} + \text{S})$ stoichiometry of 2:1:4:8 for watkinsonite from Niederschlema–Alberoda. The empirical formula, $(\text{Cu},\text{Ag})_2\text{PbBi}_4(\text{Se},\text{S})_8$, calculated on the basis of 15 *apfu*, contrasts with that obtained by Johan *et al.* (1987) for the type specimen of watkinsonite. Calculated on the basis of 15 *apfu*, the empirical formula of watkinsonite from the Otish Mountains uranium deposit averages to $\text{Cu}_{2.31}\text{Pb}_{1.24}\text{Bi}_{3.63}(\text{Se}_{6.07}\text{S}_{1.71}\text{Te}_{0.05})_{\Sigma 7.83}$ (Table 1). The relative deficit in Bi atoms and the corresponding excess of Pb and Cu atoms with respect to the simplified formula does not hold for watkinsonite from this study. This discrepancy does not support the ideal formula of watkinsonite proposed

by Johan *et al.* (1987), $\text{Cu}_{2+x}\text{Pb}_{1+x}\text{Bi}_{4-x}(\text{Se},\text{S},\text{Te})_8$, $x \approx 0.3$. The reason for the deviation from ideal stoichiometry is unknown, but may be related to analytical problems during the electron-microprobe work on type watkinsonite.

The element-distribution X-ray maps for Ag (Fig. 2a) and Pb (Fig. 2d) suggest locally minor Ag, but uniform and moderate contents of Pb in nevkite from Niederschlema–Alberoda. However, the small size and intimate association of nevkite with clausenthalite and the other Bi selenides pose analytical difficulties. We have omitted all electron-microprobe data from our set of results in which Pb contents are in excess of 3.5 wt% and Ag contents exceed 0.2 wt%, because they may represent analytical artefacts, *i.e.*, contamination from adjacent grains.

The highest content of Cu in bohdanowiczite measured thus far is 2.15 wt% (Cook & Ciobanu 2001). However, results of recalculation of that particular composition yielded a formula, $(\text{Cu}_{0.32}\text{Ag}_{2.15}\text{Fe}_{0.10})_{\Sigma 2.57}\text{Bi}_{1.87}(\text{Se}_{3.39}\text{Te}_{0.15})_{\Sigma 3.54}$, on the basis of

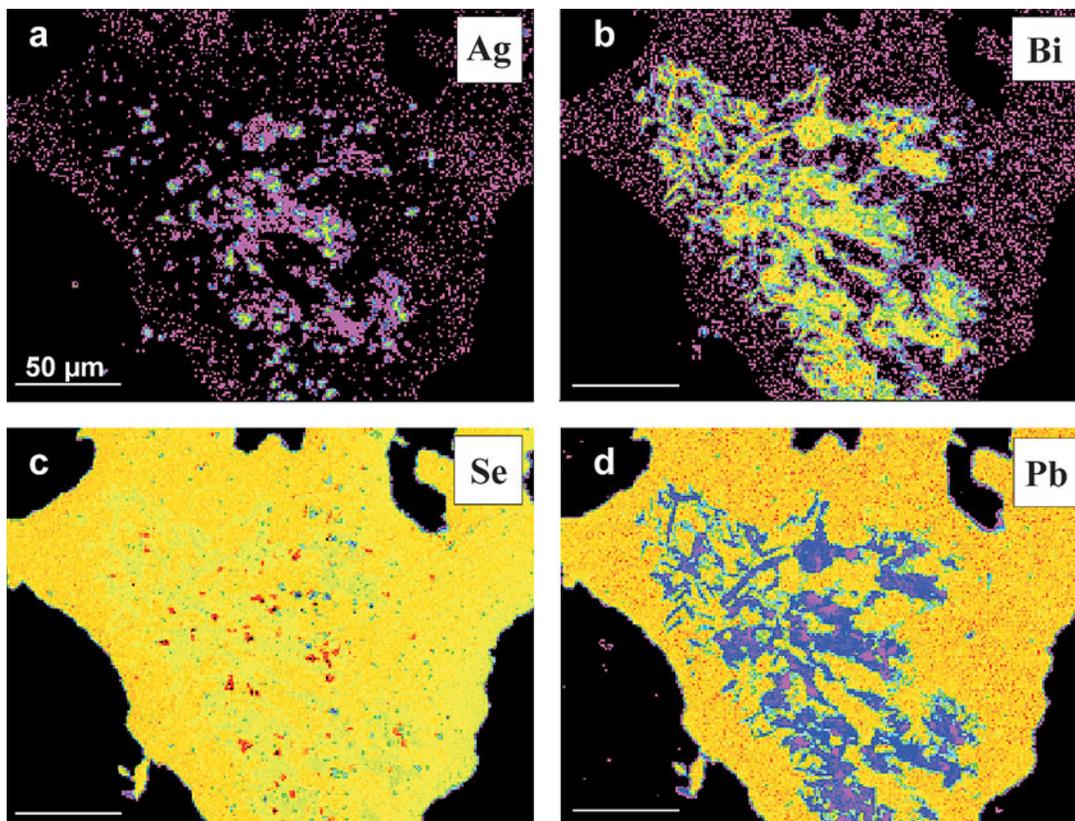


FIG. 2. X-ray element-distribution maps for Ag (a), Bi (b), Se (c), and Pb (d) showing the intimate intergrowth of nevkite (yellow-red in b, green in c, deep purple in d) and bohdanowiczite (yellow-green in a, green in b, red in c) with minor watkinsonite (green in d) in clausenthalite (yellow-red in d).

8 *apfu*), that significantly deviates from stoichiometry, which calls into question the validity of the analytical data. Indeed, further high-resolution scanning-electron microscope studies on this sample of Cu-bearing bohdanowiczite revealed evidence of inhomogeneity and submicroscopic intergrowths on a scale less than 5 μm (N.J. Cook, pers. commun., 2004). The near-stoichiometric composition of Cu-rich bohdanowiczite from Niederschlema–Alberoda and the strong antipathetic relations between Cu and Ag argue for extensive simple isovalent substitution of Cu^+ for Ag^+ . Composition 5 in Table 3 does not represent bohdanowiczite, but its yet unknown Cu-dominant analogue, ideally $\text{Cu}_2\text{Bi}_2\text{Se}_4$. These results seem to suggest complete solid-solution between $\text{Ag}_2\text{Bi}_2\text{Se}_4$ (bohdanowiczite) and unnamed $\text{Cu}_2\text{Bi}_2\text{Se}_4$, the Se-dominant analogue of emplectite ($\text{Cu}_2\text{Bi}_2\text{S}_4$), in nature. However, the small grain-size of the most Cu-rich bohdanowiczite grains from Niederschlema–Alberoda (<25 μm) precluded an X-ray analysis of this material, which would be necessary to support the suggestions of miscibility along the $\text{Ag}_2\text{Bi}_2\text{Se}_4$ – $\text{Cu}_2\text{Bi}_2\text{Se}_4$ join and the possible existence of a Cu-dominant analogue of emplectite made in this paper. Moreover, recent experimental studies of the system Cu–Bi–Se conducted at moderate to high temperatures (300–700°C) led to the successful synthesis of $\text{Cu}_4\text{Bi}_4\text{Se}_9$, but to failure to synthesize the selenide analogue of emplectite (Karup-Møller 2003).

Origin of the Bi minerals

Bismuth minerals were deposited during all three major mineralizing events that the Niederschlema–Alberoda deposit experienced between the Permian and the Cretaceous.

Stage I (Permian): Previous investigators of the ore-mineral assemblages of this deposit suggested formation of the assemblage aikinite + galena contemporaneous with precipitation of primary uraninite in veins in Permian time, at about 275 Ma (*e.g.*, Schuppan *et al.* 1994). The absence of associated Se, Co, Ni, and Ag minerals implies that this early origin also may hold for the aikinite and the associated Bi-bearing minerals (bismuthinite, unnamed $\text{CuPbBi}_4\text{S}_8$) in sample F16. Fluid-inclusion data are not available for this particular assemblage, but they are for the associated uraninite mineralization (90–230°C, Krylova *et al.* 2000). At a temperature of 100°C, galena + bismuthinite + chalcopyrite form an equilibrium assemblage at $\log f(\text{S}_2)$ between –17 and –22.5, which is consistent with $\log f(\text{Se}_2)$ between –19.5 and –25 (Simon & Essene 1996, their Figs. 12 and 13). Higher temperatures would shift the fugacities of sulfur and selenium toward higher values, that is, by about 10 orders of magnitude at $T = 300^\circ\text{C}$.

Stage II (Jurassic): The Bi selenides seem to have been deposited in the Jurassic (~190 Ma), when oxidizing hydrothermal solutions overprinted and

altered the early-formed uraninite veins and introduced new elements (Mg, Se, Pb, Ag, Cu) from the metamorphic wallrocks of the veins. During this event, the 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 sulfide and selenide minerals. This association is the most prominent at Niederschlema–Alberoda. The lack of thermodynamic data for all Bi selenides limits reliable inferences on the T–X conditions that prevailed during their formation. Nevskite and watkinsonite only are associated with clausenthalite, which has the widest field of stability of all Se minerals yet studied in terms of selenium and sulfur fugacities (*e.g.*, Simon & Essene 1996). The association of bohdanowiczite with Cu selenides (umangite, berzelianite, eucairite), and the intergrowth of umangite and tiemannite, provide more rigorous constraints on the condition of formation of this particular paragenesis (sample F2). Umangite decomposes into berzelianite and klockmannite at $T \approx 110^\circ\text{C}$ (Chakrabarti & Laughlin 1981). Thermometric measurements on fluid inclusions in quartz and calcite from the Jurassic mineralization at Niederschlema–Alberoda and elsewhere in the Erzgebirge imply temperatures between 90 and 140°C (Thomas & Tischendorf 1987, Krylova *et al.* 2000). Both sets of observations suggest the formation of the bohdanowiczite – Cu-selenide assemblage at around 100°C. At this temperature, the presence of umangite, and the absence of klockmannite and krutaite, set upper limits for $\log f(\text{Se}_2)$ (~–14.5) and $\log f(\text{S}_2)$ (~–22.5) (see Simon & Essene 1996, their Fig. 13). At these low fugacities of sulfur, tiemannite is only stable at $\log f(\text{Se}_2) > -21.2$, which may be considered as a lower limit of $f(\text{Se}_2)$.

Previous investigators have attributed the formation of bohdanowiczite to exsolution from its Cu–Bi–Ag-bearing clausenthalite host (*e.g.*, Banaš *et al.* 1980, Anspach 2001). Textural relations and mass-balance calculations do not lend support to this mode of origin for the Bi selenides from Niederschlema–Alberoda, not even for the complex, but small-size domains of the Bi-selenide association in the Bi–Ag-bearing, Cu-free clausenthalite from sample Sh9 shown in Figure 2. Similarities in the trace-element pattern between clausenthalite and the associated Bi minerals are rather a reflection of their common deposition from complex, Pb–Bi–Cu–Ag–Se–(S)-bearing hydrothermal solutions.

Stage III (Cretaceous): Wittichenite, matildite, and bismuthinite + native Bi are considered to have formed in response to hydrothermal activity associated with tectonic processes in the early Cretaceous (~120 Ma). In addition to these Bi minerals, the telescopic Bi–Co–Ni–Ag–U association comprises native metals (Ag, As), acanthite, Co–Ni–Fe arsenides (skutterudite, safflorite, rammelsbergite, löllingite, nickeline), tennantite–tetrahedrite solid solutions, and remobilized U minerals (uraninite, coffinite). Fluid-inclusion ther-

mometry indicates low temperatures for this third major mineralizing event, between 90 and 110°C (Thomas & Tischendorf 1987). The replacements of native Bi by bismuthinite and native Ag by acanthite observed in our samples place constraints on the evolution of sulfur fugacities in the mineralizing fluids. At 100°C, the fluids became increasingly more S-rich and passed the Ag–Ag₂S univariant reaction at $\log f(S_2) \sim -21.4$ and the Bi–Bi₂S₃ univariant reaction at $\log f(S_2) \sim -22.5$ (see Simon & Essene 1996, their Figs. 12 and 13). The absence of naumannite (AgSe) and guanajuatite (Bi₂Se₃) defines a value of $\log f(Se_2) \sim -24$ as an upper limit of selenium fugacity during the deposition of native Ag and Bi, which likely holds also for the deposition of their sulfides.

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