

Schneebergite and nickelschneebergite from Schneeberg, Saxony, Germany: the first Bi-bearing members of the tsumcorite group

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Abstract: Schneebergite and nickelschneebergite are new members of the tsumcorite group; they represent the bismuth analogues of cobaltlotharmeyerite and nickellotharmeyerite. The two minerals were discovered on samples from the former mining area "Am Roten Berg", Schneeberg, Saxony, Germany; associated minerals are scorodite, barium-pharmacosiderite, ferrillotharmeyerite (cobaltoan, bismuthian), preisingerite, and waylandite. Schneebergite and nickelschneebergite are very similar in appearance; they form crystal aggregates up to 1 mm and small tabular crystals (≤ 0.5 mm), elongated parallel to [010]. The colour is brown to beige (depending on the iron content), the streak is pale brown; Vickers hardness is $VHN_{15} = 250$ kg/mm² corresponding to a Mohs' hardness of 4 to 4^{1/2}. Crystallographic forms are $\{\bar{2}01\}$ (dominant), $\{001\}$, $\{101\}$, $\{\bar{1}01\}$, $\{\bar{1}02\}$, $\{\bar{1}11\}$. The optical orientation is Y parallel to [010], $X \approx [001]$, pleochroism is weak to distinct (depending on the iron content) with $X = Z =$ pale yellow and $Y =$ brown (for both minerals). Schneebergite is biaxial positive, $2V = 85(5)^\circ$, $n_x = 1.93(\text{calc.})$, $n_y = 1.95(1)$, and $n_z = 1.98(2)$; nickelschneebergite is biaxial negative, $2V = 77(5)^\circ$, $n_x = 1.92(\text{calc.})$, $n_y = 1.95(1)$, and $n_z = 1.97(2)$. Empirical formulas calculated from electron microprobe analyses and based on 10 oxygen atoms are $(\text{Bi}_{0.74}\text{Ca}_{0.29})_{\Sigma 1.03}(\text{Co}_{1.06}\text{Ni}_{0.75}\text{Fe}_{0.22})_{\Sigma 2.03}[(\text{AsO}_4)_{1.99}(\text{SO}_4)_{0.01}]_{\Sigma 2.00}[(\text{OH})_{1.09}(\text{H}_2\text{O})_{0.91}]_{\Sigma 2.00}$ for schneebergite, and $(\text{Bi}_{0.73}\text{Ca}_{0.28}\text{Pb}_{0.01})_{\Sigma 1.02}(\text{Ni}_{1.18}\text{Co}_{0.64}\text{Fe}_{0.16})_{\Sigma 1.98}(\text{AsO}_4)_{1.99}[(\text{H}_2\text{O})_{1.10}(\text{OH})_{0.93}]_{\Sigma 2.03}$ for nickelschneebergite; the ideal formulas are $\text{BiCo}_2(\text{AsO}_4)_2[(\text{H}_2\text{O})(\text{OH})]$ and $\text{BiNi}_2(\text{AsO}_4)_2[(\text{H}_2\text{O})(\text{OH})]$, respectively. There is a probably complete solid solution involving schneebergite, nickelschneebergite, cobaltlotharmeyerite, and nickellotharmeyerite. Schneebergite/nickelschneebergite are monoclinic, space group $C2/m$, with $a = 9.005(1)/8.995(1)$, $b = 6.211(1)/6.207(1)$, $c = 7.440(1)/7.462(1)$ Å, $\beta = 115.19(1)/115.00(1)^\circ$, $V = 376.5(1)/377.6(1)$ Å³, $Z = 2$, $D_{\text{calc}} = 5.28/5.23$ g/cm³. Structure investigations for schneebergite ($R1 = 0.038$) and nickelschneebergite ($R1 = 0.044$) based on single-crystal X-ray data confirmed isotopy with the tsumcorite-type structure.

Key-words: schneebergite, nickelschneebergite, new mineral, tsumcorite group, crystal chemistry, crystal structure.

Introduction

The species of the tsumcorite group show a considerable variation regarding chemistry and crystallography; more than 20 species are known up to now (Table 1). The general formula of the tsumcorite-group minerals is $Me(1)Me(2)_2(\text{XO}_4)_2(\text{H}_2\text{O},\text{OH})_2$; $Me(1) = \text{Pb}, \text{Ca}, \text{Na}, \text{Bi}$; $Me(2) = \text{Fe}, \text{Mn}, \text{Cu}, \text{Zn}, \text{Co}, \text{Ni}, \text{Al}, \text{Mg}$; $X = \text{P}, \text{As}, \text{V}, \text{S}$ (Krause *et al.*, 1998a). In the course of the investigation of cobalt- and nickellotharmeyerite, *i.e.*, $\text{Ca}(\text{Co},\text{Fe})_2(\text{AsO}_4)_2(\text{H}_2\text{O},\text{OH})_2$ and $\text{Ca}(\text{Ni},\text{Fe})_2(\text{AsO}_4)_2(\text{H}_2\text{O},\text{OH})_2$ (Krause *et al.*, 1999, 2001b), many samples were found to contain substantial amounts of bismuth substituting for calcium. Subsequent analyses finally revealed Bi-dominant samples, which represent the basis for the present study.

Schneebergite and nickelschneebergite are the first members of the tsumcorite group with a Bi-dominant occupation on the $Me(1)$ site.

The new Bi-Co-Ni-arsenates have been named schneebergite (Co-dominant on the $Me(2)$ position) and nickelschneebergite (Ni-dominant on the $Me(2)$ position), although the name 'schneebergite' had already been in use in former times. According to the IMA guidelines re-use of a discredited name is permitted, if the name has not appeared in the active literature for fifty years (Nickel & Grice, 1998). The name 'schneebergite' had been used for a Ca-Sb-oxide which has later been shown to be identical with roméite. Roméite was described by Damour (1841) from St. Marcel, Piemont, Italy, as a probably tetragonal Ca-Sb-oxide. Later 'schneebergite' was described by

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Table 1. Tsumcorite group minerals.

mineral name	ideal chemical formula	S.G. [†]	Z	references*
tsumcorite	Pb(Zn,Fe ³⁺) ₂ (AsO ₄) ₂ (H ₂ O,OH) ₂	C2/m	2	1
mawbyite	Pb(Fe ³⁺ ,Zn) ₂ (AsO ₄) ₂ (OH,H ₂ O) ₂	C2/m	2	2
cobalttsumcorite	Pb(Co,Fe ³⁺) ₂ (AsO ₄) ₂ (H ₂ O,OH) ₂	C2/m	2	3
thometzekite (sulfatian)	PbCu ₂ (AsO ₄ ,SO ₄) ₂ (H ₂ O,OH) ₂	C2/m	2	4
mounanaite	PbFe ³⁺ ₂ (VO ₄) ₂ (OH) ₂	C2/m	2	4
krettnichite	PbMn ³⁺ ₂ (VO ₄) ₂ (OH) ₂	C2/m	2	5
lotharmeyerite	Ca(Mn ³⁺ ,Zn) ₂ (AsO ₄) ₂ (OH,H ₂ O) ₂	C2/m	2	4, 6
cobaltlotharmeyerite	Ca(Co,Fe ³⁺) ₂ (AsO ₄) ₂ (H ₂ O,OH) ₂	C2/m	2	7
ferrilotharmeyerite	Ca(Fe ³⁺ ,Zn) ₂ (AsO ₄) ₂ (OH,H ₂ O) ₂	C2/m	2	4
nickellotharmeyerite	Ca(Ni,Fe ³⁺) ₂ (AsO ₄) ₂ (H ₂ O,OH) ₂	C2/m	2	3
cabalzarite	Ca(Mg,Al) ₂ (AsO ₄) ₂ (H ₂ O,OH) ₂	C2/m	2	8
schneebergite	BiCo ₂ (AsO ₄) ₂ [(H ₂ O)(OH)]	C2/m	2	this work
nickelschneebergite	BiNi ₂ (AsO ₄) ₂ [(H ₂ O)(OH)]	C2/m	2	this work
natrochalcite	NaCu ₂ (SO ₄) ₂ [(H ₂ O)(OH)]	C2/m	2	9
gartrellite	PbCuFe ³⁺ (AsO ₄) ₂ [(H ₂ O)(OH)]	P1	1	4
zinggartrellite	Pb(Zn,Cu)(Zn,Fe ³⁺)(AsO ₄) ₂ (H ₂ O,OH) ₂	P1	1	10
phosphogartrellite	PbCuFe ³⁺ (PO ₄) ₂ [(H ₂ O)(OH)]	P1	1	11
lukrahnite	CaCuFe ³⁺ (AsO ₄) ₂ [(H ₂ O)(OH)]	P1	1	12
helmutwinklerite	PbZn ₂ (AsO ₄) ₂ ·2H ₂ O	P1	4	4, 10, 13
rappoldite	PbCo ₂ (AsO ₄) ₂ ·2H ₂ O	P1	4	10
thometzekite	PbCu ₂ (AsO ₄) ₂ ·2H ₂ O	P1?	4?	4, 10, 13
† space group				
* references (with emphasis on structural studies, if available); 1: Tillmanns & Gebert (1973); 2: Kharisun <i>et al.</i> (1997); 3: Krause <i>et al.</i> (2001b); 4: Krause <i>et al.</i> (1998a); 5: Brugger <i>et al.</i> (2001); 6: Kampf <i>et al.</i> (1984); 7: Krause <i>et al.</i> (1999); 8: Brugger <i>et al.</i> (2000); 9: Giester & Zemmann (1987); 10: Effenberger <i>et al.</i> (2000); 11: Krause <i>et al.</i> (1998b); 12: Krause <i>et al.</i> (2001a); 13: Schmetzer <i>et al.</i> (1985).				

Table 2. Physical data of schneebergite and nickelschneebergite.

	schneebergite (sample #358)	nickelschneebergite (sample #374)
morphology	{201}, {001}, {102}, {111}	{201}, {001}, {101}, {101}, {111}
habit	tabular on {201}, elongated // [010]	tabular on {201}, elongated // [010]
lustre	adamantine	adamantine
diaphaneity	transparent	transparent
colour*	brown to beige	brown to beige
streak*	light brown to nearly white	light brown to nearly white
fluorescence	none	none
hardness	Mohs 4 - 4½, VHN ₁₅ 250 kg/mm ²	Mohs 4 - 4½, VHN ₁₅ 250 kg/mm ²
tenacity	brittle	brittle
cleavage	none observed	none observed
fracture	conchoidal	conchoidal
density (calc.)	5.28 g/cm ³	5.23 g/cm ³
optical character	positive	negative
n _x (calc.)	1.93	1.92
n _y	1.95(1)	1.95(1)
n _z	1.98(2)	1.97(2)
2V	85°(5)	77°(5)
dispersion	not determined	not determined
pleochroism**	distinct Y brown, X = Z pale yellow	weak Y light brown, X = Z pale yellow
orientation	Y = b, X ≈ c	Y = b, X ≈ c
* depending on the iron content		
** depending on the iron content; samples with little iron exhibit only weak pleochroism		

Brezina (1880) from Schneeberg, Tyrol, Austria, as a cubic Ca-Sb-oxide. Brezina supposed that 'schneebergite' could be a polymorph of roméite. Finally Zedlitz (1932) and Machatschki (1932) showed by X-ray analyses that roméite and 'schneebergite' are identical. Therefore the name roméite had to be maintained for priority reasons (Hintze, 1938). Roméite, $(\text{Ca}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Na})_2(\text{Sb}, \text{Ti})_2\text{O}_6(\text{O}, \text{OH}, \text{F})$, is now known to be a member of the stibiconite group.

The joint occurrence of bismuth, cobalt, nickel, and arsenic is characteristic for the mining material of the Schneeberg area in Saxony, Germany. Considering the presence of these elements in the new minerals we proposed the names schneebergite and nickelschneebergite, respectively. Schneeberg is known for more than 600 years of famous mining history in that area; in addition Schneeberg is the type locality for more than 30 mineral species.

The two new minerals and their names have been approved by the IMA Commission on New Minerals and Mineral Names (schneebergite 99-027; nickelschneebergite 99-028). Type material is preserved in the collection of the "Staatliches Museum für Mineralogie und Geologie", Dresden, Germany, under catalogue numbers 18332Sa(MMG) (schneebergite) and 18333Sa(MMG) (nickelschneebergite).

Occurrence and physical data

The type locality of schneebergite and nickelschneebergite is the mining area "Am Roten Berg", which was reported to be mined for hematite in former times. The dumps are located approximately 4.8 km southwest of the centre of Schneeberg, Saxony, Germany. The two new minerals may be considered as *in situ* formations in the near to the surface oxidation zone; primary minerals were not reported, probably because mining activities at that time were restricted close to the surface. The type specimen of schneebergite (sample #358), approximately 3 cm in diameter, was found in November 1997. Aggregates of elongated crystals are grown in small vugs of coarse quartz; associated minerals are scorodite and barium-pharmacosiderite. The type specimen of the second new mineral (sample #374, approximately 6 cm in diameter, found in May 1997) consists also mainly of coarse quartz with dense aggregates and acicular crystals of nickelschneebergite; no associated minerals could be observed. On other schneebergite/nickelschneebergite samples associated minerals are Co/Ni bearing ferrilotharmeyerite, cobaltlotharmeyerite, nickellotharmeyerite, preisingerite, waylandite, and zeunerite. Preisingerite could also be confirmed by microprobe analyses as minute inclusions in schneebergite / nickelschneebergite aggregates. Due to solid solution the composition normally covers a certain range so that both schneebergite and nickelschneebergite may occur even on the same specimen.

Physical data of schneebergite and nickelschneebergite are compiled in Table 2. Refractive indices were determined by immersion in higher-refractive-index liquids (Cargill oils); both minerals show a slow decomposition in such liquids. SEM micrographs of the two minerals and a crystal drawing including the optical orientation are shown

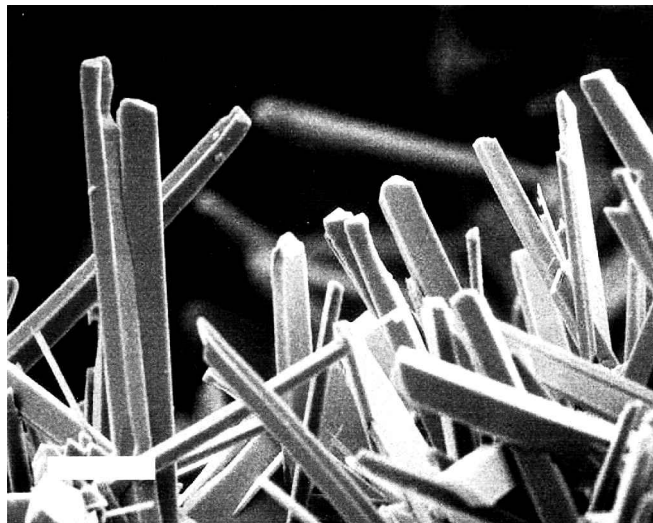


Fig. 1. Schneebergite crystals – SEM micrograph; scale bar is 20 μm .

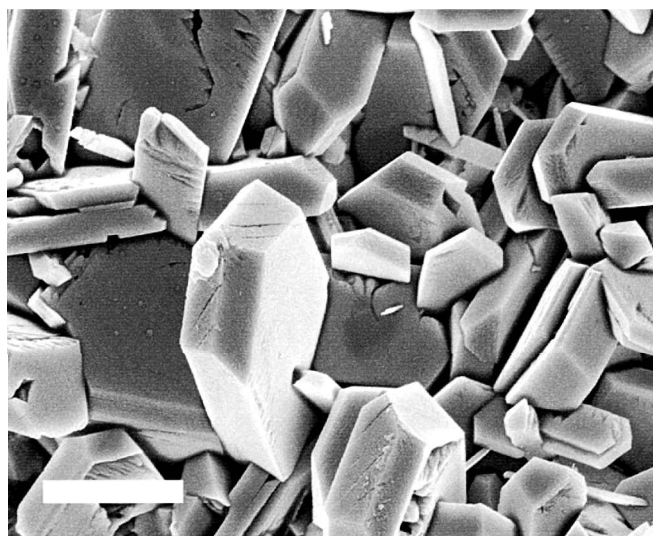


Fig. 2. Nickelschneebergite crystals – SEM micrograph; scale bar is 10 μm .

in Fig. 1, 2 and 3. Crystallographic forms were determined with the optical equipment of the 4-circle X-ray diffractometer and confirmed by optical 2-circle goniometer measurements. Most crystals are tabular on $\{201\}$ and more or less elongated parallel to $[010]$; the length to thickness ratio is normally 3:1 to 10:1. The nickelschneebergite crystal used for the crystal structure determination showed a somewhat different morphology with $\{101\}$ (dominant) and $\{T01\}$; the crystals of Fig. 2 exhibit a combination of $\{201\}$, $\{101\}$, $\{T11\}$ and probably $\{110\}$. Morphology and optical orientation are very similar to those of tsumcorite. The crystals of both schneebergite and nickelschneebergite reach up to 0.5 mm in length. Compatibility indices according to the Gladstone-Dale relationship (Mandarino, 1981) are -0.022 (schneebergite) and -0.030 (nickelschneebergite), which are both rated as excellent. The colour of the nickelschneebergite type material is pale olive-brown

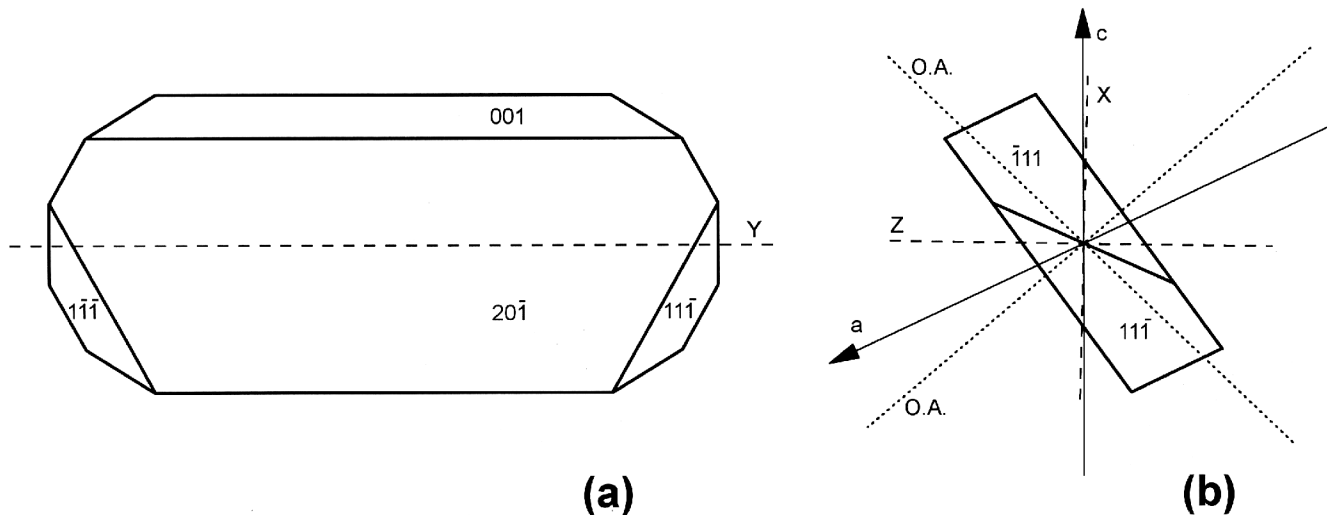


Fig. 3. Crystal drawing of schneebergite including part of the optical data: (a) view perpendicular on $(20\bar{1})$; (b) view parallel to $[010]$.

and differs from the usual brown to beige of other samples; however, the pale brown streak is very similar for all samples of the schneebergite and nickelschneebergite series. In general the colour depends on the iron content, turning from brown to beige to nearly colourless with decreasing iron content. Due to the negative correlation of bismuth and iron (see chemical data), samples with low iron contents represent approximate end-member compositions regarding the occupation of the *Me*(1) site with Bi atoms. Since physical and X-ray data are very similar, a reliable distinction between schneebergite, nickelschneebergite, cobaltlotharmeyerite and nickellotharmeyerite should be based on careful microprobe analyses. EDX

analyses, however, provide merely semiquantitative information and a clear assignment is only possible if the composition is markedly shifted to that of the end members. The distinctly higher refractive indices can serve as a rough indication for samples rich in bismuth.

Chemical data

An electron microprobe (Cameca CAMEBAX, 10 nA, 20 kV, beam diameter 5 μm) was used for chemical analyses (Table 3). Standards used were mimetite (Pb, As), Co metal (Co), NiO (Ni), andradite (Fe, Ca), CaSO_4 (S),

Table 3. Microprobe analyses of schneebergite and nickelschneebergite (in wt.-%).

	schneebergite (#358) [†]			nickelschneebergite (#374) [§]			nickelschneebergite (#357) [‡]		
	mean	range	calculated	mean	range	calculated	mean	range	calculated
CaO	2.72	1.68 - 3.58	2.65	2.68	1.99 - 4.17	2.55	3.91	2.93 - 5.58	3.82
NiO	9.35	8.55 - 10.75	9.34	14.75	13.70 - 15.66	15.10	14.36	13.54 - 14.92	14.08
CoO	13.31	11.49 - 14.89	13.17	7.98	7.21 - 9.34	8.08	8.37	7.60 - 9.51	8.11
ZnO	<0.05	-	0.00	0.09	0.03 - 0.16	0.00	<0.05	-	0.00
PbO	0.11	0.00 - 0.21	0.00	0.35	0.16 - 0.74	0.00	0.32	0.00 - 0.86	0.00
Fe ₂ O ₃	2.95	1.61 - 4.42	2.97	2.19	1.39 - 2.93	2.15	4.18	3.28 - 5.47	4.18
Bi ₂ O ₃	29.01	26.73 - 30.92	28.35	28.54	25.90 - 31.27	28.66	25.35	20.62 - 29.20	24.81
P ₂ O ₅	<0.05	-	0.00	0.08	0.02 - 0.12	0.00	<0.05	-	0.00
As ₂ O ₅	38.42	37.58 - 39.35	38.85	38.26	37.29 - 40.39	38.73	39.34	38.36 - 41.11	40.13
SO ₃	0.11	0.05 - 0.22	0.00	<0.05	-	0.00	0.10	0.05 - 0.16	0.00
H ₂ O *	4.40		4.66	4.72		4.72	4.86		4.86
total	100.38		100.00	99.64		100.00	100.81		100.00

[†] type material; mean of 12 analyses; calculated for $\text{Bi}_{0.72}\text{Ca}_{0.28}\text{Co}_{1.04}\text{Ni}_{0.74}\text{Fe}^{3+}_{0.22}(\text{AsO}_4)_{2.00}(\text{H}_2\text{O})_{1.06}(\text{OH})_{0.94}$.

[§] type material; mean of 7 analyses; calculated for $\text{Bi}_{0.73}\text{Ca}_{0.27}\text{Ni}_{1.20}\text{Co}_{0.64}\text{Fe}^{3+}_{0.16}(\text{AsO}_4)_{2.00}(\text{H}_2\text{O})_{1.11}(\text{OH})_{0.89}$.

[‡] mean of 8 analyses; calculated for $\text{Bi}_{0.61}\text{Ca}_{0.39}\text{Ni}_{1.08}\text{Co}_{0.62}\text{Fe}^{3+}_{0.30}(\text{AsO}_4)_{2.00}(\text{H}_2\text{O})_{1.09}(\text{OH})_{0.91}$; sample used for single-crystal structure determination.

* TGA on cotype material for schneebergite; calculated values for nickelschneebergite.

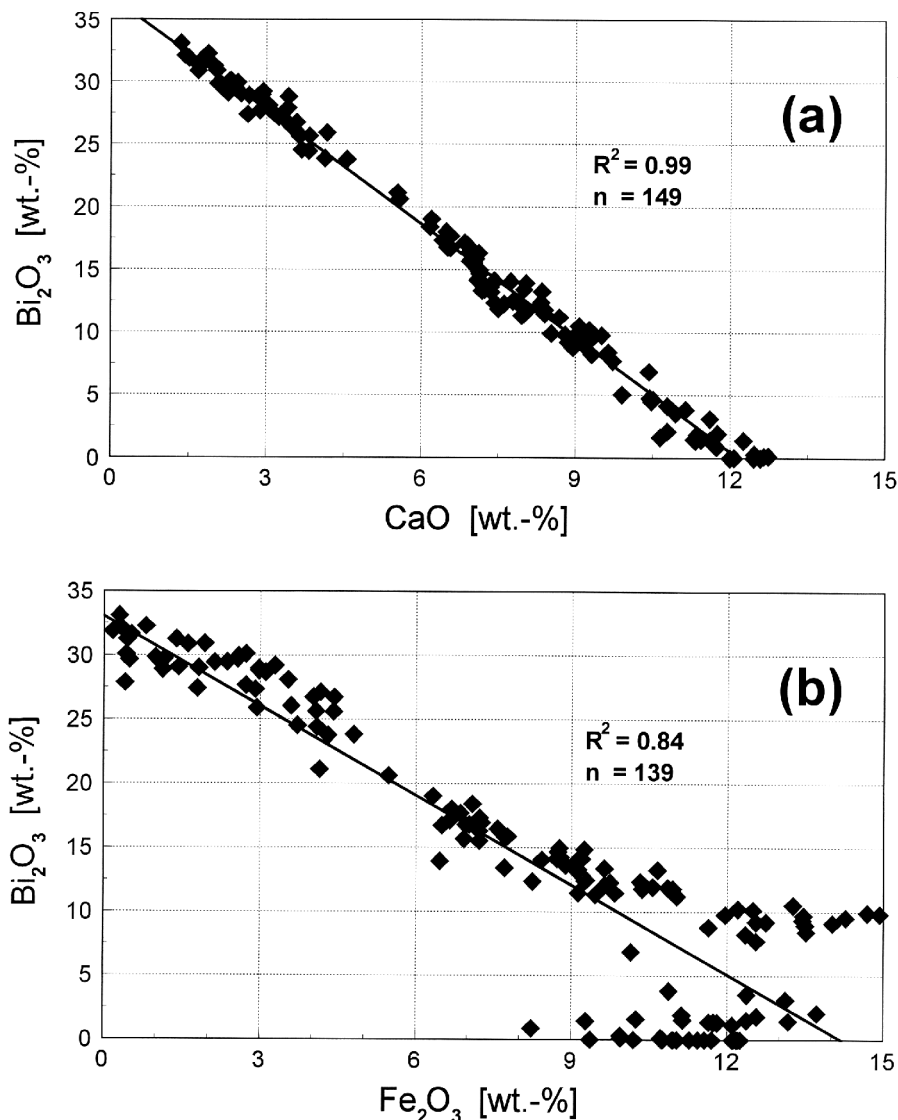


Fig. 4. Chemical variation in samples of schneebergite, nickelschneebergite, cobaltlotharmeyerite, and nickellotharmeyerite: (a) plot of Bi₂O₃ versus CaO contents; (b) plot of Bi₂O₃ versus Fe₂O₃ contents.

AlPO₄ (P), ZnO (Zn), and Bi₂S₃ (Bi). No other elements with atomic numbers greater than 8 were detected. H₂O was determined by thermogravimetric analysis on schneebergite co-type material (sample weight 1.32 mg; heating rate 10°C/min.; weight loss 4.4 % between 430 and 560°C in one step, loss of As₂O₃ at T > 900°C). A direct determination of water in nickelschneebergite was not possible because of the small amount of pure material available; H₂O was therefore calculated from the ideal formula. Microchemical tests confirmed that iron is trivalent; the test for divalent iron was negative. Schneebergite as well as nickelschneebergite are slowly soluble in warm dilute hydrochloric acid.

FT-IR spectra were taken on a Nicolet 5PC instrument equipped with a diamond microcell. The spectra are very similar to those of tsumcorite, ferrilotharmeyerite, gartrellite, and other tsumcorite-group minerals with the H₃O₂ hydrogen-bonding system (Krause *et al.*, 1998a).

Schneebergite and nickelschneebergite show very broad strong absorptions between 2600 and 3400, centered at about 3000 cm⁻¹ (O-H stretching vibration), and also strong absorptions between 1200 and 400 cm⁻¹ (due to arsenate).

The empirical formulas of schneebergite and nickelschneebergite calculated from the electron-microprobe data on the basis of 10 oxygen atoms are (Bi_{0.74}Ca_{0.29})_{Σ1.03}(Co_{1.06}Ni_{0.75}Fe_{0.22})_{Σ2.03}[(AsO₄)_{1.99}(SO₄)_{0.01}]_{Σ2.00}[(OH)_{1.09}(H₂O)_{0.91}]_{Σ2.00} and (Bi_{0.73}Ca_{0.28}Pb_{0.01})_{Σ1.02}(Ni_{1.18}Co_{0.64}Fe_{0.16})_{Σ1.98}(AsO₄)_{1.99}[(H₂O)_{1.10}(OH)_{0.93}]_{Σ2.03}, respectively. The ideal formulas are BiCo₂(AsO₄)₂(H₂O)(OH) (schneebergite) and BiNi₂(AsO₄)₂(H₂O)(OH) (nickelschneebergite). Schneebergite and nickelschneebergite represent the first examples out of the tsumcorite group with a dominant occupation of the Me(1) position by a trivalent cation (Bi³⁺). There is a nearly complete solid solution series between the Ca- and the Bi-dominant members (Fig. 4a). The microprobe data also confirm the

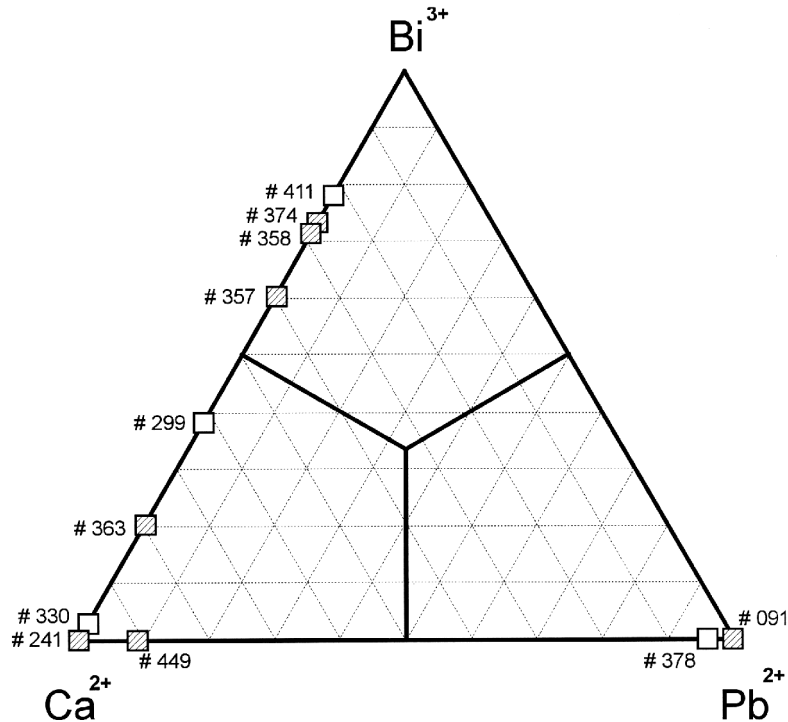


Fig. 5. Occupation of the *Me*(1) site plotted in the ternary diagram Bi^{3+} - Ca^{2+} - Pb^{2+} ; hatched squares refer to samples used for structural investigations. Relevant minerals (sample numbers): schneebergite (#358); nickelschneebergite (#357, #374, #411); cobaltlotharmeyerite (#299, #330); ferrillotharmeyerite (#241, #449), nickellotharmeyerite (#363); mawbyite (#378); tsumcorite (#091).

observations mentioned above that increasing Bi contents correlate with decreasing Fe^{3+} contents. This compensation for the increased charge on the *Me*(1) site results in a more or less unaffected OH: H_2O ratio of approximately 1:1. The relevant exchange mechanism is $[\text{Ca}^{2+}\text{Fe}^{3+}]^{5+} \leftrightarrow [\text{Bi}^{3+}(\text{Co},\text{Ni})^{2+}]^{5+}$.

A compilation of 139 spot analyses of different samples of schneebergite, nickelschneebergite, cobaltlotharmeyerite, and nickellotharmeyerite (Fig. 4b) clearly shows the negative correlation between bismuth and iron. The lowest Fe_2O_3 values are in the range of 0.2 to 0.5 wt.-%, corresponding to Bi_2O_3 contents of approximately 32 to 33 wt.-%, which is close to the Bi content of the ideal end member (36 wt.-% Bi_2O_3). It should be noted that the spots originating from samples with very low Fe and very high Bi contents still show significant Ca contents (about 1.5 wt.-% CaO), corresponding to a Bi:Ca ratio of approximately 0.85:0.15.

There is a general tendency for the species of the tsumcorite group to achieve a OH/ H_2O ratio of approximately 1.0; this is obviously related to the formation of the particularly stable H_3O_2 hydrogen-bonding system. Most of the analyses of the tsumcorite-group minerals known so far revealed a OH/ H_2O ratio within the range of 1.2 to 0.8. Coupled substitutions involving the crystallographic sites *Me*(1), *Me*(2), and X are responsible for the formation of a favorable OH/ H_2O ratio. Only few species are known to deviate distinctly from this ratio: helmutwinklerite, rappoldite (Effenberger *et al.*, 2000), mounanaite (Krause *et al.*, 1998a), mawbyite (Kharisun *et al.*, 1997), and krett-

nichite (Brugger *et al.*, 2001). It is worth mentioning that in these cases the OH/ H_2O ratio is either extremely large or extremely small, *i.e.* corresponding to approximately two OH groups or two H_2O molecules per formula unit (p.f.u.).

Occupation of the *Me*(1) site

A compilation of the chemical composition of the tsumcorite-group minerals known so far reveals that extensive solid solution is very common for the *Me*(2) site, less common for the X site, and very rare for the *Me*(1) site. Schneebergite and nickelschneebergite clearly show crystal-chemical features that were found for the first time in cobaltlotharmeyerite (Krause *et al.*, 1999): (i) trivalent cations *Me*(1); (ii) extensive solid solution at the *Me*(1) site; (iii) different valence states of the *Me*(1) cations. As shown in Fig. 4a and in the ternary diagram Bi^{3+} - Ca^{2+} - Pb^{2+} (Fig. 5), nearly complete solid solution Ca^{2+} - Bi^{3+} was verified within the series cobaltlotharmeyerite – schneebergite and in the corresponding Ni analogues. In contrast to this extensive solid solution, only few tsumcorite-group minerals exhibit minor substitution of Ca for Pb and *vice versa*; substitution involving Bi and Pb is unknown so far. The Ca content of Pb-bearing species is usually < 1 wt.-%, and the Pb content of Ca-bearing species is < 3 wt.-%. The degree of substitution is very small and amounts to usually less than 5 mole-%. Only in exceptional cases is the substitution in the range of 10 mole-%, as verified during the present investigation of a ferrillotharmeyerite sample (#449,

Table 4. Powder diffraction data of schneebergite and nickelschneebergite.

schneebergite (sample #358)							nickelschneebergite (sample #374)						
h	k	l	d _{calc}	I _{calc}	d _{obs}	I _{obs}	h	k	l	d _{calc}	I _{calc}	d _{obs}	I _{obs}
0	0	1	6.732	15	6.744	9	0	0	1	6.763	16	6.759	29
1	1	0	4.940	1	4.948	3	1	1	0	4.939	1	4.937	3
1	1	$\bar{1}$	4.587	79	4.589	61	1	1	$\bar{1}$	4.587	79	4.586	40
2	0	$\bar{1}$	4.416	24	4.418	33	2	0	$\bar{1}$	4.411	24	4.411	24
2	0	0	4.074	11	4.075	9	2	0	0	4.076	11	4.075	6
2	0	$\bar{2}$	3.402	11	3.401	20	2	0	$\bar{2}$	3.404	11	3.401	22
0	0	2	3.366	8	3.370	13	0	0	2	3.381	8	3.382	13
1	1	$\bar{2}$	3.191	100	3.193	100	1	1	$\bar{2}$	3.198	100	3.196	100
0	2	0	3.105	25	3.107	27	0	2	0	3.104	25	3.102	23
2	0	1	2.970	77	2.971	92	2	0	1	2.979	77	2.980	72
0	2	1	2.820	59	2.820	61	0	2	1	2.821	59	2.821	44
3	1	$\bar{1}$	2.702	58	2.702	57	3	1	$\bar{1}$	2.699	57	2.700	24
2	2	$\bar{1}$	2.540	11	2.528	42	2	2	$\bar{1}$	2.538	11	2.538	17
3	1	$\bar{2}$	2.527	31			3	1	$\bar{2}$	2.525	31	2.525	17
1	1	2	2.498	36	2.498	62	1	1	2	2.507	36	2.507	47
3	1	0	2.489	11			3	1	0	2.489	11	2.490	9
2	2	0	2.470	24	2.469	23	2	2	0	2.469	24	2.471	19
2	0	$\bar{3}$	2.457	6			2	0	$\bar{3}$	2.462	6	2.462	7
2	2	$\bar{2}$	2.293	17	2.293	21	2	2	$\bar{2}$	2.293	17	2.293	15
1	1	$\bar{3}$	2.276	11	2.275	13	1	1	$\bar{3}$	2.283	11	2.284	6
4	0	$\bar{2}$	2.208	7	2.208	13	4	0	$\bar{2}$	2.206	7	2.206	9
2	2	1	2.146	17	2.146	15	2	2	1	2.149	17	2.149	18
3	1	$\bar{3}$	2.130	4			3	1	$\bar{3}$	2.131	4	2.127	8
4	0	0	2.037	8	2.037	9	4	0	0	2.038	8	2.038	8
4	0	$\bar{3}$	1.987	4	1.987	19	4	0	$\bar{3}$	1.986	4	1.986	17
1	3	$\bar{1}$	1.981	11			1	3	$\bar{1}$	1.980	11		
1	1	3	1.870	24	1.869	37	1	1	3	1.877	25	1.877	28
2	0	4	1.860	6			2	0	4	1.865	6	1.865	9
0	2	3	1.819	11	1.811	24	0	2	3	1.824	11	1.824	8
4	2	$\bar{1}$	1.812	6			4	2	$\bar{1}$	1.810	6	1.810	17
1	3	$\bar{2}$	1.809	15	1.783	13	1	3	$\bar{2}$	1.809	15		
2	2	2	1.784	13	1.783	13	2	2	2	1.788	13	1.788	16
3	3	$\bar{1}$	1.704	20	1.704	52	3	3	$\bar{1}$	1.703	20	1.702	57
4	0	4	1.701	15			4	0	4	1.702	15		
5	1	$\bar{1}$	1.698	11	1.674	51	5	1	$\bar{1}$	1.697	11	1.691	14
0	0	4	1.683	11			0	0	4	1.691	11		
4	2	$\bar{3}$	1.674	42	1.674	51	4	2	$\bar{3}$	1.673	41	1.673	30

Powder diffractometer Philips PW 1710, internal standard Si, CuK α radiation. Observed intensities are corrected for texture effects according to the March model (Deyu *et al.*, 1990). The powder-diffraction pattern were calculated with program LAZY PULVERIX (Yvon *et al.*, 1977); only reflections with I_{calc} \geq 3 were considered (except for 110).

see below). Additional analyses of further samples may presumably exceed this limit in future. Substantial solid solution simultaneously involving the three elements Ca, Pb and Bi are unknown for tsumcorite-group minerals up to now.

It has to be noted that in the case of rappoldite (Effenberger *et al.*, 2000) significant Ca contents up to 3 wt.-% were detected in some samples, suggesting a solid solution mechanism; however, this could be explained by means of X-ray powder diffraction analysis as a rappoldite-cobalttharmeyerite intergrowth.

Sample #449 (Fig. 5) from the Tsumeb mine has been investigated in detail and found to be a plumbian ferrilotharmeyerite. It is the sample with the largest substitution along the Ca-Pb path observed up to now. The small crystals are yellow, tabular on {201}, with additional forms {001} and {111}. The crystals are optically biaxial positive, 2V = 35°; pleochroism is weak to distinct with X = yellow and Y = Z = pale yellow; the orientation is X \wedge c 30°

(in the acute angle β) and Y = b, thus showing the “normal” optical orientation of the tsumcorite-group minerals (Krause *et al.*, 1998a). The empirical formula based on crystal structure investigations and supported by semi-quantitative EDX analyses is Ca_{0.91}Pb_{0.09}Zn_{1.08}Fe_{0.92}(AsO₄)_{2.00}(OH)_{1.08}(H₂O)_{0.92}.

X-ray investigation

The powder diffraction data of schneebergite and nickelschneebergite (Table 4) are virtually identical and a distinction of the two minerals by X-ray methods is not possible. This was expected due to isotopy and the similar atomic numbers of the chemical constituents. The different X-ray scattering power of Ca and Bi causes considerable intensity differences regarding certain X-ray reflections of schneebergite/nickelschneebergite on the one hand and the Ca-dominant analogues cobalt-

Table 5. Unit cell parameters, Bi/Ca ratios (in atoms p.f.u., derived from microprobe data) and calculated densities (g/cm³) for schneebergite, nickelschneebergite and related minerals.

mineral	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	β [°]	<i>V</i> [Å ³]	<i>Z</i>	Bi	Ca	<i>D</i> _{calc}
schneebergite ¹⁾	9.005(1)	6.211(1)	7.440(1)	115.19(1)	376.5	2	0.72	0.28	5.28
nickelschneebergite ²⁾	8.995(1)	6.207(1)	7.462(1)	115.00(1)	377.6	2	0.73	0.27	5.23
nickelschneebergite ³⁾	9.007(1)	6.209(1)	7.447(1)	115.13(1)	377.1	2	0.61	0.39	5.08
cobaltlotharmeyerite ⁴⁾	9.026(1)	6.229(1)	7.448(1)	115.19(1)	378.9	2	0.38	0.62	4.69
nickellotharmeyerite ⁵⁾	9.005(1)	6.205(1)	7.411(1)	115.31(1)	374.4	2	0.20	0.80	4.44
cobaltlotharmeyerite ⁶⁾	9.024(1)	6.230(1)	7.421(1)	115.15(1)	377.1	2	0.00	1.00	4.13
lotharmeyerite ⁷⁾	9.066(4)	6.276(2)	7.408(2)	116.16(3)	378.3	2	0.00	1.00	4.13
ferrilotharmeyerite ⁸⁾	9.006(2)	6.238(1)	7.387(2)	115.54(2)	374.4	2	0.00	1.00	4.21

¹⁾ schneebergite type material (sample #358): this work
²⁾ nickelschneebergite type material (sample #374): this work
³⁾ nickelschneebergite (sample #357): this work
⁴⁾ cobaltlotharmeyerite (sample #299): Krause *et al.* (1999)
⁵⁾ nickellotharmeyerite type material (sample #363): Krause *et al.* (2001b)
⁶⁾ cobaltlotharmeyerite type material (sample #298): Krause *et al.* (1999)
⁷⁾ Kampf *et al.* (1984)
⁸⁾ Krause *et al.* (1998a)

Table 6. Single-crystal X-ray data collection and structure refinements.

	schneebergite (sample #358)	nickelschneebergite (sample #357)	ferrilotharmeyerite (sample #449)
crystal dimensions [μm]	20 x 30 x 80	10 x 20 x 120	30 x 80 x 170
range of data collection [°]	5° < 2θ < 60°	5° < 2θ < 60°	5° < 2θ < 70°
number of frames	495	374	450
scan time [s / °]	500	300	450
μ(MoKα) [mm ⁻¹]	28.6	30.0	16.6
$R_{int} = \Sigma F_o^2 - F_c^2(\text{mean}) / \Sigma F_o^2$	0.042	0.035	0.038
$R1 = \Sigma (F_o - F_c) / \Sigma F_o$	0.038	0.044	0.025
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$	0.082	0.113	0.058
extinction parameter	0.0028(6)	0.0060(10)	0.0065(8)
absorption correction	crystal shape	crystal shape	crystal shape
observed unique reflections (<i>n</i>)	604	605	896
reflections with $F_o > 4\sigma(F_o)$	585	596	850
variable parameters (<i>p</i>)	47	47	53
$\text{Goof} = \{\Sigma [w(F_o^2 - F_c^2)^2] / (n-p)\}^{0.5}$	1.38	1.47	1.20
<i>P</i> ₁	0.0	0.0	0.0197
<i>P</i> ₂	13.39	23.79	1.05
max Δ/σ	≤ 0.001	≤ 0.001	≤ 0.001
final difference Fourier map [eÅ ⁻³]	-1.66 to +2.22	-2.69 to +1.78	-0.96 to +0.86

NONIUS four-circle diffractometer equipped with a CCD detector and a fiber optics collimator, Mo tube, graphite monochromator, φ-scans for distinct ω-angles, Δφ = 2°/frame, frame size: binned mode, 621×576 pixels, detector-to-sample distance: 28 mm; range of data collection: ±h ±k ±l. Corrections for Lorentz and polarization effects and absorption effects; neutral-atomic complex scattering functions (Wilson, 1992), program SHELXS-97 (Sheldrick, 1997). $w = 1 / \{\sigma^2(F_o^2) + [P_1 * P]^2 + P_2 * P\}$; $P = [\max(0, F_o^2)] + 2 * F_c^2 / 3$.

lotharmeyerite and nickellotharmeyerite (Krause *et al.*, 1999, 2001b) on the other. Examples for schneebergite* (sample #358) and cobaltlotharmeyerite** (sample #298; Krause *et al.*, 1999) are [(hkl) $I_{\text{calc}}^*/I_{\text{calc}}^{**}$]: (110) 1/69; ($\bar{2}$ 01) 24/4; (200) 11/<1; (111) 1/16; ($\bar{2}$ 02) 11/83. Cell parameters refined from the powder data are compiled in Table 5. There are no significant differences between the cell parameters of schneeber-

Table 7. Structural parameters* (e.s.d.'s in parentheses) for schneebergite and nickelschneebergite.

atom	x	y	z	U _{equiv}		
schneebergite						
(sample #358)		<i>Me</i> (1)	Bi:Ca = 0.653(7):0.347(7)			
		<i>Me</i> (2)	Co:Ni:Fe = 1.04:0.60(15):0.36(15)			
<i>Me</i> (1) = Bi, Ca	0.0	0.0	0.0	0.0137(3)		
<i>Me</i> (2) = Co, Ni, Fe	0.25	0.25	0.5	0.0068(4)		
As	0.91418(11)	0.5	0.20607(15)	0.0075(4)		
O(1)	0.3485(9)	0.5	0.4138(11)	0.0119(15)		
O(2)	0.3186(9)	0.0	0.3599(12)	0.0117(15)		
O(3)	0.0336(6)	0.2799(8)	0.2421(7)	0.0094(10)		
O(4)	0.2425(10)	0.5	0.0198(12)	0.0172(16)		
nickelschneebergite						
(sample #357)		<i>Me</i> (1)	Bi:Ca = 0.551(9):0.449(9)			
		<i>Me</i> (2)	Ni:Co:Fe = 1.0(2):0.62:0.4(2)			
<i>Me</i> (1) = Bi, Ca	0.0	0.0	0.0	0.0154(4)		
<i>Me</i> (2) = Ni, Co, Fe	0.25	0.25	0.5	0.0086(5)		
As	0.91509(15)	0.5	0.20707(19)	0.0093(5)		
O(1)	0.3476(13)	0.5	0.4141(15)	0.017(2)		
O(2)	0.3203(11)	0.0	0.3658(14)	0.009(2)		
O(3)	0.0330(8)	0.2810(11)	0.2425(9)	0.012(1)		
O(4)	0.2424(14)	0.5	0.0204(14)	0.018(2)		
atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
schneebergite						
<i>Me</i> (1) = Bi, Ca	0.0160(4)	0.0111(4)	0.0156(4)	0.0	0.0081(3)	0.0
<i>Me</i> (2) = Co, Ni, Fe	0.0061(6)	0.0061(7)	0.0068(6)	-0.0004(5)	0.0013(4)	-0.0001(4)
As	0.0059(5)	0.0066(5)	0.0095(5)	0.0	0.0030(4)	0.0
O(1)	0.011(3)	0.015(4)	0.009(3)	0.0	0.004(3)	0.0
O(2)	0.011(3)	0.011(3)	0.024(4)	0.0	0.017(3)	0.0
O(3)	0.009(2)	0.006(2)	0.010(2)	-0.002(2)	0.000(2)	0.002(2)
O(4)	0.011(3)	0.027(4)	0.009(3)	0.0	0.000(3)	0.0
nickelschneebergite						
<i>Me</i> (1) = Bi, Ca	0.0184(6)	0.0126(6)	0.0168(6)	0.0	0.0091(5)	0.0
<i>Me</i> (2) = Ni, Co, Fe	0.0089(8)	0.0078(8)	0.0084(8)	0.0000(6)	0.0031(6)	0.0002(6)
As	0.0084(7)	0.0088(7)	0.0114(7)	0.0	0.0048(5)	0.0
O(1)	0.020(5)	0.017(5)	0.015(5)	0.0	0.008(4)	0.0
O(2)	0.011(4)	0.006(4)	0.019(5)	0.0	0.014(4)	0.0
O(3)	0.017(3)	0.009(3)	0.013(3)	0.000(2)	0.007(2)	0.004(3)
O(4)	0.022(5)	0.027(6)	0.004(4)	0.0	0.004(4)	0.0
* The anisotropic displacement parameters are defined as: $\exp [-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* h_i h_j]$, B _{cq} according to Fischer & Tillmanns (1988).						

gite and nickelschneebergite. Compared with cobaltlotharmeyerite there is a very small but significant increase of the cell parameter *c*.

Structure investigations were performed for schneebergite (#358) and two samples of nickelschneebergite (#357 and #374); in addition a ferrilotharmeyerite crystal with an unusually high Pb-content (sample #449) was studied. The results of the refinements for the nickelschneebergite samples were nearly identical; structural details are given only for sample #357 (Tables 6, 7 and 8) because of the higher accuracy of the corresponding structure refinement (*R*₁ = 0.044, *wR*₂ = 0.113) compared to that of sample #374 (*R*₁ = 0.077, *wR*₂ = 0.158). According to the microprobe analyses, sample #374 (Bi:Ca = 0.73:0.27) exhibits a higher Bi content than sample #357 (Bi:Ca = 0.61:0.39). The structural refinements yielded Bi:Ca = 0.752(13):0.248(13) for sample #374 and 0.551(9):0.449(9) for sample #357, which is in good accordance with the microprobe results. The occupation of the *Me*(2) position by Co, Ni and Fe atoms in sample #374 is indeterminable from the

structure refinement, while some clues were obtained for sample #357.

A check of the crystal qualities, symmetries, extinction rules and the data collections for structure refinements were performed with a single-crystal four-circle diffractometer. Experimental details are compiled in Table 6. For all samples monoclinic C-centered symmetry was found. The cell parameters corresponded to those obtained from refinements of the powder data; these were used for all further calculations. The atomic coordinates of ferrilotharmeyerite (Krause *et al.*, 1998a) were used in the starting set of structure refinements. In all cases the refinements contributed to the mixed occupation of the *Me*(1) and *Me*(2) sites. For *Me*(1) either the ratio Bi:Ca or Ca:Pb was allowed to vary. The large difference in the atomic numbers of the element pairs contributed to reasonable standard deviations of the refinements; good agreement with the chemical analyses were obtained. For the *Me*(2) position the results are less significant: In schneebergite and nickelschneebergite *Me*(2) exhibit a mixed occupation

by three chemical elements with succeeding atomic numbers. Consequently, it is impossible to refine their atomic ratios from the scattering power by conventional X-ray diffraction methods. The site occupation factor was fixed for Co to the analytically determined value. The ratio Fe:Ni was allowed to vary assuming a full occupation at the *Me*(2) site. Due to the difference of two electrons only, the estimated standard deviations of the occupation parameters are very large. However, the refined occupations of schneebergite / nickelschneebergite $\text{Co}_{1.04}\text{Ni}_{0.60}\text{Fe}_{0.36} / \text{Ni}_{1.0}\text{Co}_{0.62}\text{Fe}_{0.4}$ correspond reasonably to the analytically determined content of $\text{Co}_{1.04}\text{Ni}_{0.74}\text{Fe}_{0.22} / \text{Ni}_{1.08}\text{Co}_{0.62}\text{Fe}_{0.30}$. From structure investigations practically pure AsO_4 tetrahedra are expected, which corresponds to the absence of S, P and V confirmed by electron-microprobe analyses. Final structural parameters are compiled in Table 7.

Results and discussion

Interatomic bond distances and bond angles are compiled in Table 8. Due to their close chemical composition the results of the structure refinements of schneebergite and nickelschneebergite are nearly identical; moreover, the relations to cobaltlotharmeyerite and nickellotharmeyerite are close. All crystal-chemical data are in reasonable accordance with the results expected from the chemical composition. Crystal-chemical data of other tsumcorite-group minerals refer to Tillmanns & Gebert (1973), Krause *et al.* (1998a, 1999, 2001b) and Effenberger *et al.* (2000).

The positions *Me*(1) in schneebergite (#358) / nickelschneebergite (#357) are predominantly occupied by Bi atoms, and a partial substitution by Ca atoms is verified. The ratios Bi:Ca determined from structure refinements are 0.653(7):0.347(7) / 0.551(9):0.449(9). However, from chemical analyses somewhat larger ratios of 0.72:0.28 / 0.61:0.39 were expected for both minerals. The differences might indicate the chemical variability within one sample. But there is no doubt that the *Me*(1) positions are predominantly occupied by Bi atoms. The six nearest neighbours are in a [2+4] coordination. The average $\langle \text{Me}(1)\text{-O} \rangle$ bond distance in nickelschneebergite, cobaltlotharmeyerite, and nickellotharmeyerite (Krause *et al.*, 2001b) are identical within the error of the structure refinements (2.421 to 2.425 Å); in schneebergite the value is marginally smaller (2.414 Å). The gap between the two nearest and the four next-nearest neighbours is slightly larger in the Bi dominated compounds and in nickellotharmeyerite than in cobaltlotharmeyerite.

The site symmetry of the *Me*(1) position is $2/m$; therefore its occupation with Bi^{3+} atoms is peculiar: Usually Bi^{3+} atoms are one-sided surrounded by oxygen atoms as required by the steric active lone-pair electrons. Bi^{3+} atoms located on an inversion centre have been described occasionally *e.g.* for perovskite-related compounds which were investigated for high-temperature superconducting features (*e.g.* Luhrs *et al.*, 1998, or Kennedy, 1995, and references therein). In these cases partial and/or mixed occupations are common. The principal mean square atomic displace-

Table 8. Interatomic bond distances (in Å), bond angles (in °) and bond valences* v for schneebergite and nickelschneebergite.

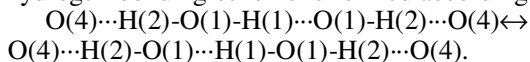
		schneebergite		nickelschneebergite	
<i>Me</i> (1)-O(4), v	2×	2.386(8)	0.82	2.386(11)	0.79
<i>Me</i> (1)-O(3), v	4×	2.428(5)	1.46	2.439(6)	1.37
<i>Me</i> (1)-O(2), v	2×	2.977(8)	0.17	3.017(10)	0.14
Σv			2.45		2.30
O(4)- <i>Me</i> (1)-O(3)	4×	76.8(2); 103.2(2)		76.7(2); 103.3(2)	
O(3)- <i>Me</i> (1)-O(3)	2×	88.6(2); 91.4(2)		88.7(3); 91.3(3)	
<i>Me</i> (2)-O(1), v	2×	2.023(5)	0.80	2.016(7)	0.79
<i>Me</i> (2)-O(3), v	2×	2.081(5)	0.69	2.090(7)	0.64
<i>Me</i> (2)-O(2), v	2×	2.104(5)	0.64	2.085(6)	0.65
Σv			2.13		2.08
O(1)- <i>Me</i> (2)-O(3)	2×	89.7(3); 90.3(3)		90.0(4); 90.0(4)	
O(1)- <i>Me</i> (2)-O(2)	2×	81.5(2); 98.5(2)		80.9(3); 99.1(3)	
O(3)- <i>Me</i> (2)-O(2)	2×	88.1(3); 91.9(3)		89.0(3); 91.0(3)	
As-O(4), v		1.672(8)	1.29	1.690(10)	1.23
As-O(3), v	2×	1.689(5)	2.47	1.675(7)	2.57
As-O(2), v		1.700(7)	1.20	1.727(9)	1.11
Σv			4.96		4.91
O(4)-As-O(3)	2×	111.6(2)		111.4(3)	
O(4)-As-O(2)		103.0(4)		104.0(5)	
O(3)-As-O(3)		108.1(3)		108.5(5)	
O(3)-As-O(2)	2×	111.3(2)		110.8(3)	
O(1)···O(1)		2.472(15)		2.488(21)	
O(1)···O(4)		2.669(11)		2.679(14)	
O(1) Σv		0.80		0.79	
O(2) Σv		1.93		1.82	
O(3) Σv		1.94		1.95	
O(4) Σv		1.70		1.63	
* in valence units (Bresle & O'Keeffe, 1991), without contribution of the hydrogen atoms.					

ments of U are for the Bi-dominant *Me*(1) positions in schneebergite and nickelschneebergite 0.017, 0.013, 0.011 and 0.019, 0.015, 0.013 Å², respectively. As a consequence, any statistical displacement (statically or dynamically) of the Bi atoms is excluded from discussion.

The *Me*(2)O₆ octahedra in schneebergite and nickelschneebergite have $\langle \text{Me}(2)\text{-O} \rangle$ bond distances of 2.069 / 2.064 Å. This corresponds with the expected values deduced from the ionic radii (Shannon, 1976) based on the ratio $\text{Co}^{2+}:\text{Ni}^{2+}:\text{Fe}^{3+}$ determined from the chemical analysis. $\langle \text{Me}(2)\text{-O} \rangle$ is slightly larger than in cobaltlotharmeyerite and cobalttsumcorite (Krause *et al.*, 2001b) (both 2.060 Å) which is due to the higher Ni:Fe ratio.

Charge balance requires approximately three hydrogen atoms p.f.u. in both title compounds. Consequently formally one hydroxyl group and one water molecule p.f.u. are necessary if all the oxygen positions are fully occupied; the oxygen atoms of these two different groups occupy statistically one atomic position. The O(1) atom is the donor of all the hydrogen bonds. This is in accordance with bond valence calculations (without contribution of the hydrogen atoms; Table 8) which are in the range of 1.6 to 2.0 v.u. (valence units) for O(2) and O(4), whereas O(1) has

0.8 v.u. and is coordinated only to *Me*(2). The main hydrogen bonding scheme is formed according to:



The H atoms were not localized experimentally in schneebergite and nickelschneebergite; in Pb-substituted ferrilotharmeyerite the H(2) atom was located in the difference Fourier map. As characteristic for the tsumcorite-group minerals with $\text{OH}:\text{H}_2\text{O} \approx 1:1$, the two hydrogen bond lengths are distinctly different. The symmetrically restricted hydrogen bond $\text{O}(1)\cdots\text{O}(1)$ scatters around 2.48 Å. $\text{O}(1)\cdots\text{O}(4)$ is definitely larger and amounts to 2.67 Å. For the excess of H_2O additional coordination, probably to two O(3) atoms, have to be assumed. The distances donor-H \cdots acceptor are responsible for only weak hydrogen bonds: $\text{O}(1)\cdots\text{O}(3)$ is in the range of 3 Å.

The result of the structure investigation of lead-bearing ferrilotharmeyerite (sample #449) is very close to that of lead-free ferrilotharmeyerite; the complete structural data are therefore not given. The ratio Ca:Pb determined from structure refinement is 0.911(2):0.089(2). Lengthening and shortening of bond distances point towards the respective values obtained for tsumcorite (Tillmanns & Gebert, 1973). The results for sample #449 are: *Me*(1)-O is 2.402(3) Å, 2 \times and 2.452(2) Å, 4 \times ; $\text{O}(1)\cdots\text{O}(1) = 2.570(5)$ Å, $\text{O}(1)\cdots\text{O}(4) = 2.620(4)$ Å, $\langle\text{Me}(2)-\text{O}\rangle = 2.0577$ Å. The location of the hydrogen bonds corresponds to that determined for other tsumcorite-type minerals (see e.g. Giester & Zemann, 1987; Chevrier *et al.*, 1993; Beran *et al.*, 1997, and references therein).

Due to the observed symmetry reduction of some tsumcorite-group minerals (gartrellite type, $Z = 1$, and helmutwinklerite type, $Z = 4$; see Effenberger *et al.*, 2000), the investigated samples were carefully checked for any symmetry violation and/or for superstructure reflections. As expected, these tests were negative. Consequently schneebergite and nickelschneebergite as well as Pb-substituted ferrilotharmeyerite belong to the monoclinic C-centered tsumcorite-type ($Z = 2$).

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