

Crystal chemistry of the tsumcorite-group minerals. New data on ferrilotharmeyerite, tsumcorite, thometzekite, mounanaite, helmutwinklerite, and a redefinition of gartrellite

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Abstract: The general formula for the tsumcorite-group minerals is $\text{Me}(1)\text{Me}(2)_2(\text{XO}_4)_2(\text{OH},\text{H}_2\text{O})_2$; $\text{Me}(1) = \text{Pb}, \text{Ca}, \text{Na}$, and partly Bi ; $\text{Me}(2) = \text{Fe}, \text{Mn}, \text{Cu}, \text{Zn}, \text{Co}, \text{Ni}$, and partly Al ; $\text{X} = \text{P}, \text{As}, \text{V}, \text{S}$. Out of this group the minerals ferrilotharmeyerite, tsumcorite, thometzekite (sulfatian), mounanaite, helmutwinklerite, gartrellite and zincian gartrellite were investigated regarding optical properties, morphology, chemical composition, infrared and Mössbauer spectroscopy, and crystal structure. Crystal symmetry is either (i) triclinic in the case of an ordered occupation of two $\text{Me}(2)$ sites, (ii) triclinic due to ordering of the hydrogen bonds in the case of species with 2 water molecules per formula unit or (iii) monoclinic in the other cases. Cell parameters were refined from X-ray powder data; powder patterns are given for thometzekite (sulfatian), mounanaite, helmutwinklerite, gartrellite and zincian gartrellite. Mössbauer measurements confirmed the iron in ferrilotharmeyerite, tsumcorite, gartrellite and zincian gartrellite to be completely *trivalent*. Electron microprobe analyses showed that at least partial solid solution is common for the $\text{Me}(2)$ and less frequent for the X and $\text{Me}(1)$ site. In addition to homovalent substitutions [*e.g.* $\text{Zn}^{2+} \leftrightarrow \text{Cu}^{2+}$ or $(\text{AsO}_4)^{3-} \leftrightarrow (\text{PO}_4)^{3-}$] there are 3 heterovalent exchange mechanisms with a coupled substitution involving $\text{OH}/\text{H}_2\text{O}$ groups: (i) on the $\text{Me}(1)$ site, *e.g.* $[(\text{Ca})^{2+}(\text{H}_2\text{O})]^{2+} \leftrightarrow [(\text{Bi})^{3+}(\text{OH})]^{2+}$, (ii) on the $\text{Me}(2)$ site, *e.g.* $[(\text{Zn},\text{Cu},\text{Co},\text{Ni})^{2+}(\text{H}_2\text{O})]^{2+} \leftrightarrow [(\text{Fe},\text{Al},\text{Mn})^{3+}(\text{OH})]^{2+}$, and (iii) on the X site, *e.g.* $[(\text{AsO}_4)^{3-}(\text{H}_2\text{O})]^{3-} \leftrightarrow [(\text{SO}_4)^{2-}(\text{OH})]^{3-}$.

Crystals of ferrilotharmeyerite, tsumcorite, thometzekite (sulfatian), and mounanaite have monoclinic symmetry, space group $C2/m$. The crystal structures were investigated by single-crystal X-ray diffraction. The structural data for tsumcorite given by Tillmanns & Gebert (1973) were confirmed, for the other minerals isotopy is proved. Infrared absorption spectra indicate two independent and strong hydrogen bonds. In particular, there is no evidence for protonated arsenate groups. The chemical formulas of ferrilotharmeyerite and lotharmeyerite (for analogy reasons) have to be revised on a 10 oxygen basis to $\text{Ca}(\text{Fe}^{3+},\text{Zn})_2(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})_2$, and $\text{Ca}(\text{Mn}^{3+},\text{Zn})_2(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})_2$, respectively.

The triclinic members of the tsumcorite group are gartrellite, zincian gartrellite, phosphogartrellite, helmutwinklerite, and probably (sulfate-free) thometzekite; the space group is $P\bar{1}$, with a pronounced monoclinic C-centered *pseudocell*. A redefinition based on type material was performed for gartrellite; it has the ideal formula $\text{PbCuFe}^{3+}(\text{AsO}_4)_2(\text{OH})(\text{H}_2\text{O})$, but it frequently contains substantial amounts of Zn (at least up to 12.6 wt.% ZnO), whereas the ratio Cu:Fe is close to 1:1. The triclinic distortion is caused by an ordered arrangement of Fe^{6+}O_6 octahedra and tetragonal bi-pyramidal $\text{Cu}^{4+2}\text{O}_6$ polyhedra, as shown by Rietveld refinement of powder data. The weak *superstructure* reflections of helmutwinklerite observed by single-crystal X-ray investigations are obviously caused by an ordering of the hydrogen bonds.

Key-words: ferrilotharmeyerite, tsumcorite, thometzekite (sulfatian), mounanaite, helmutwinklerite, gartrellite, zincian gartrellite, redefinition, crystal chemistry, Mössbauer study, infrared spectra, crystal structure.

Introduction

Tsumcorite, a hydroxoarsenate of lead, zinc and iron, was originally found at the Tsumeb mine, Namibia, and named after the Tsumeb Corporation (Geier *et al.*, 1971). Since then a number of minerals have been discovered which show a strong relation with tsumcorite concerning their chemistry, their mineralogical and physical data, and their crystal structure (Table 1). The general formula $\text{Me}(1)\text{Me}(2)_2(\text{XO}_4)_2(\text{OH},\text{H}_2\text{O})_2$ may be assigned to these minerals; Me(1) = Pb, Ca, Na, and partly Bi; Me(2) = Fe^{3+} , Mn^{3+} , Cu, Zn, Co,

Ni, and partly Al; X = P, As, V, S. These minerals may be classified as "tsumcorite group"; out of this group tsumcorite was the first species showing the substitution $\text{OH} \leftrightarrow \text{H}_2\text{O}$ whose crystal structure and correct formula have been reported (Tillmanns & Gebert, 1973). They discussed the hydrogen bonding scheme based on the assumption that the iron atoms are *trivalent* instead of *divalent*. Even after the discovery of additional members of the tsumcorite group some crystal-chemical and crystallographic questions remained unsolved, especially details on the chemical composition, the solid solution involv-

Table 1. Tsumcorite-group minerals; the general formula is $\text{Me}(1)\text{Me}(2)_2(\text{XO}_4)_2(\text{OH},\text{H}_2\text{O})_2$.

mineral	Me(1)	Me(2)	X	symmetry	references
tsumcorite	Pb	Zn,Fe	As	monoclinic	Geier <i>et al.</i> (1971); Tillmanns & Gebert (1973)
mawbyite	Pb	Fe,Zn	As	monoclinic	Pring <i>et al.</i> (1989)
unnamed mineral	Pb	Co,Fe,Ni	As	monoclinic?	Schlegel <i>et al.</i> (1996)
thometzekite (sulfatian)	Pb	Cu,Zn	As,S	monoclinic	Schmetzer <i>et al.</i> (1985); this work
mounanaite ¹	Pb	Fe	V	monoclinic	Cesbron & Fritsche (1969)
helmutwinklerite	Pb	Zn,Cu	As	triclinic	Süsse & Schnorrrer (1980); Schmetzer <i>et al.</i> (1985)
thometzekite	Pb	Cu,Zn	As	triclinic?	Schmetzer <i>et al.</i> (1985)
unnamed mineral	Pb	Co,Ni	As	triclinic	Martin & Schlegel (1992)
gartrellite	Pb	Cu,Fe	As	triclinic	Nickel <i>et al.</i> (1989)
gartrellite (zincian)	Pb	Zn,Fe,Cu	As	triclinic	this work
phosphogartrellite	Pb	Cu,Fe	P	triclinic	Krause <i>et al.</i> (submitted)
lotharmeyerite	Ca	Mn,Zn	As	monoclinic	Dunn (1983); Kampf <i>et al.</i> (1984)
ferrilotharmeyerite	Ca	Fe,Zn	As	monoclinic	Ansell <i>et al.</i> (1992)
cobaltlotharmeyerite	Ca	Co,Fe,Ni	As	monoclinic	Krause <i>et al.</i> (in prep.)
natrochalcite	Na	Cu	S	monoclinic	Rumanova <i>et al.</i> (1958); Giester (1989); Chevrier <i>et al.</i> (1993)

¹ OH is (partly) substituted by F, as indicated by structure refinement and crystal chemical considerations

For further synthetic compounds with tsumcorite-type structures *cf.* Giester & Zemann (1987), Giester (1989), Chevrier *et al.* (1993) and references therein.

ing *di*- and *trivalent* cations, the nature of the hydroxyl and water content, and the crystal symmetry, respectively.

The valence state of Fe was assumed to be *trivalent* in tsumcorite, but an experimental verification with modern methods was missing to support the wet chemical analysis and the crystal-chemical considerations of Tillmanns & Gebert (1973). In tsumcorite the Me(2) cations occupy only one crystallographic site; it remained unclear to what extent this would also be valid for the other members of the tsumcorite group. The solid solution effect involving *di*- and *trivalent* cations has not been specifically discussed so far. Since a solid solution involving Fe³⁺ and Cu is uncommon in crystal chemistry, Ansell *et al.* (1992) assumed an ordered arrangement of (Zn,Cu) and (Fe³⁺,Zn) in ferrilotharmeyerite. The substitution of H₂O by OH in combination with the replacement of an XO₄ group by a protonated XO₃OH group was discussed by Harlow *et al.* (1984) for brackebuschite. The same mechanism was proposed for lotharmeyerite on the basis of an IR spectrum by Kampf *et al.* (1984); by analogy Ansell *et al.* (1992) postulated without further experimental evidence a protonated arsenate group in ferrilotharmeyerite as well.

For the major part of the tsumcorite-group minerals the Laue symmetry *2/m* and a C-centered cell was assumed in accordance with the space group *C2/m* verified by Tillmanns & Gebert (1973) for tsumcorite. Mounanaite (Cesbron & Fritsche, 1969), helmutwinklerite (Süsse & Schnorrer, 1980), and gartrellite (Nickel *et al.*, 1989) were described as triclinic. For helmutwinklerite Schmetzer *et al.* (1985) mentioned a *pseudomonoclinic* subcell with cell dimensions similar to that of tsumcorite but a triclinic *super*cell with a sixteenfold cell volume indicated by very weak interlayer reflections. Concerns about the status of helmutwinklerite as an independent mineral were raised by Walenta (1981). For thometzekite Schmetzer *et al.* (1985) were not able to decide between triclinic or monoclinic symmetry because of the insufficient quality of the investigated material.

Gartrellite was described by Nickel *et al.* (1989) as a new secondary arsenate mineral from Ashburton Downs and from Broken Hill, Australia. The chemical formula was given on the basis of Pb+Cu+Fe = 3 as Pb_{1.04}Cu_{1.22}Fe_{0.74}(AsO₄)_{1.88}(SO₄)_{0.10}(CO₃)_{0.54}(H₂O)_{0.18}. It was not clear how this formula could be simplified, if

there were any hydroxyl content, and whether sulfate and/or carbonate were essential constituents. The relationship to tsumcorite, helmutwinklerite, and thometzekite was pointed out by Nickel *et al.* (1989), but a detailed discussion was not possible due to lack of structural data. At the same time a suite of minerals from the Odenwald area, Germany, was under investigation, resulting in the description of a probable new lead-copper-iron-arsenate; a discussion with the IMA commission on New Minerals and Mineral Names led to the conclusion that this mineral was virtually identical with gartrellite (pers. comm., Dr. Mandarino, 1993).

Mineral samples closely related to gartrellite had already been mentioned several years before its original description under the working names "mineral gamma" (Pb-Fe-Cu-arsenate) and "mineral TK" (Pb-Fe-Cu-Zn-arsenate), respectively (Pinch & Wilson, 1977; Keller, 1984). Later, a number of short references particularly in magazines for mineral collectors were made dealing with these minerals (Kokinos & Wise, 1993; Martin *et al.*, 1994; Walenta, 1988, 1989, 1993, 1995), however, without any comments regarding the relation to gartrellite. In most cases the samples were referred to as copper-bearing tsumcorite or as a variety of thometzekite, probably formed by solid solution involving thometzekite, tsumcorite, and mawbyite, respectively.

For further clarification within the tsumcorite group, investigations were performed regarding physical and chemical properties, including Mössbauer and IR measurements as well as crystal structure investigations (for a preliminary note see Krause *et al.*, 1997). With the exception of mounanaite and part of the gartrellite samples, all other samples used for the present study are from the Tsumeb mine, Namibia. Ferrilotharmeyerite is from samples found in 1993 from level 43 of the Tsumeb mine, thometzekite is from co-type material, and tsumcorite was taken from several specimens originating from different mining periods since 1970. The investigated mounanaite sample is part of the type material (mineral collection of the University Pierre and Marie Curie, catalogue no. 11647) which was collected in 1962 from Mounana, Gaboon. A few gartrellite samples (#016, #023) are from Reichenbach, Odenwald, Germany. Gartrellite type material from Ashburton Downs, W. A., Australia, was used for the redefinition; the redefinition was approved by the Commission on New Minerals and Mineral Names. Additional samples from

Table 2. Optical data for ferrilotharmeyerite, tsumcorite, thometzekite (sulfatian), mounanaite, gartrellite, and helmutwinklerite (investigated on an optical spindle stage, $\lambda = 589$ nm); the chemical composition is given in Table 3.

mineral	ferrilotharmeyerite	tsumcorite	tsumcorite	thometzekite (sulfatian)	mounanaite	gartrellite	helmutwinklerite
sample	#241	#017	#259	#132	#262	#023	#272
n_x	1.83(1)	1.91(calc)	1.87(calc)	1.85(calc)	2.19(calc)	1.94(1)	1.83(2)
n_y	1.835(calc)	1.93(1)	1.89(1)	1.87(2)	2.25(2) ²	1.98(calc)	1.87(calc)
n_z	1.87(1)	1.96(1)	1.92(1)	1.92(2)	2.27(calc)	2.06(2)	1.89(2)
opt. character	positive	positive	positive	positive	negative	positive	negative
2V	40(2)°	67(3)°	83(5)°	70(10)°	50(10)°	78(4)°	70(5)°
orientation	X b Y $\wedge c=22^{\circ 1}$ Z	$\wedge c=15^{\circ 1}$ b	$\wedge c=8^{\circ 1}$ b	\approx c b	$\wedge c=20^{\circ 1}$ b	45/-22 ³ 48/130 ³ 76/-127 ³	11/-145 ³ 82/-35 ³ 82/56 ³
pleochroism	strong X orange Y yellow Z colorless	weak pale yellow yellow pale yellow	weak pale yellow yellow pale yellow	none	strong pale yellow brown pale yellow	weak pale yellow pale yellow yellow	none
dispersion	r>v strong	r>v weak	r>v weak	n.d.	r>v strong	n.d.	r>v strong

¹ in the acute of β
² from samples in sulfur/selenium melts
³ ρ/φ angles based on (010) = 90°/0° and (100) = 90°/90° (cf. Fig. 2c,d)

Tsumeb and Reichenbach were also investigated, but as the corresponding data reveal no extra information, they are not reported in the present paper.

Physical properties

Most of the investigated crystals seemed to be twinned or intergrowths of several individuals. Therefore only a very limited number of crystals were suitable for single-crystal investigations by means of an optical spindle stage, optical two-circle goniometer, or X-ray measurements. The optical data are mainly based on spindle-stage measurements and are summarized in Table 2 and Fig. 1a-d. Because of the high refractive indices, the undulatory extinction behaviour ("rolling extinction", probably due to solid-solution effects), and the decomposition of some samples in the immersion media, the data should serve only as a rough indication about the optical behaviour of the tsumcorite-group minerals. Tsum-

corite samples with high zinc contents as well as thometzekite (sulfatian) and helmutwinklerite were rapidly attacked by higher-refractive-index liquids; only gartrellite, mounanaite, and tsumcorite with Fe:Zn \approx 1:1 showed a sufficient stability. Therefore part of the refractive indices had to be estimated by using additional data like 2V and birefringence. The optical behaviour for most of the monoclinic tsumcorite-group minerals is similar: the optical character is positive (except for mounanaite and mawbyite¹ and the orientation of Y is parallel to [010] (except for ferrilotharmeyerite).

It has to be stated that the orientation of the indicatrix of ferrilotharmeyerite differs markedly from that given by Ansell *et al.* (1992); also the data of helmutwinklerite, in particular the refractive indices, are distinctly different from the data given by Süsse & Schnorrer (1980). This may be due to the fact that the refractive indices were calculated by Süsse & Schnorrer using reflectivity data, which may be inaccurate in consideration of the relatively low refractive indices. Some gartrellite crystals exhibit perfectly shaped reflec-

¹A comparative investigation of mawbyite (sample M39065, Museum of Victoria, Melbourne, Australia) gave $2V_x = 80^{\circ}(5)$, $n_x = 1.95(2)$, $n_y = 2.00(2)$, $n_z = 2.04(2)$, X approximately || [001], Y || [010], pleochroism is moderate with Y = brownish, X = Z = pale yellow; unit cell parameters: $a = 9.079(2)$, $b = 6.297(2)$, $c = 7.565(2)$ Å, $\beta = 115.05(2)^{\circ}$, $V = 391.8(1)$ Å³; morphology: prismatic parallel to [001] with {110}, { $\bar{1}01$ }, {001}; Fe:Zn ratio according to microprobe analyses is 1.25:0.75.

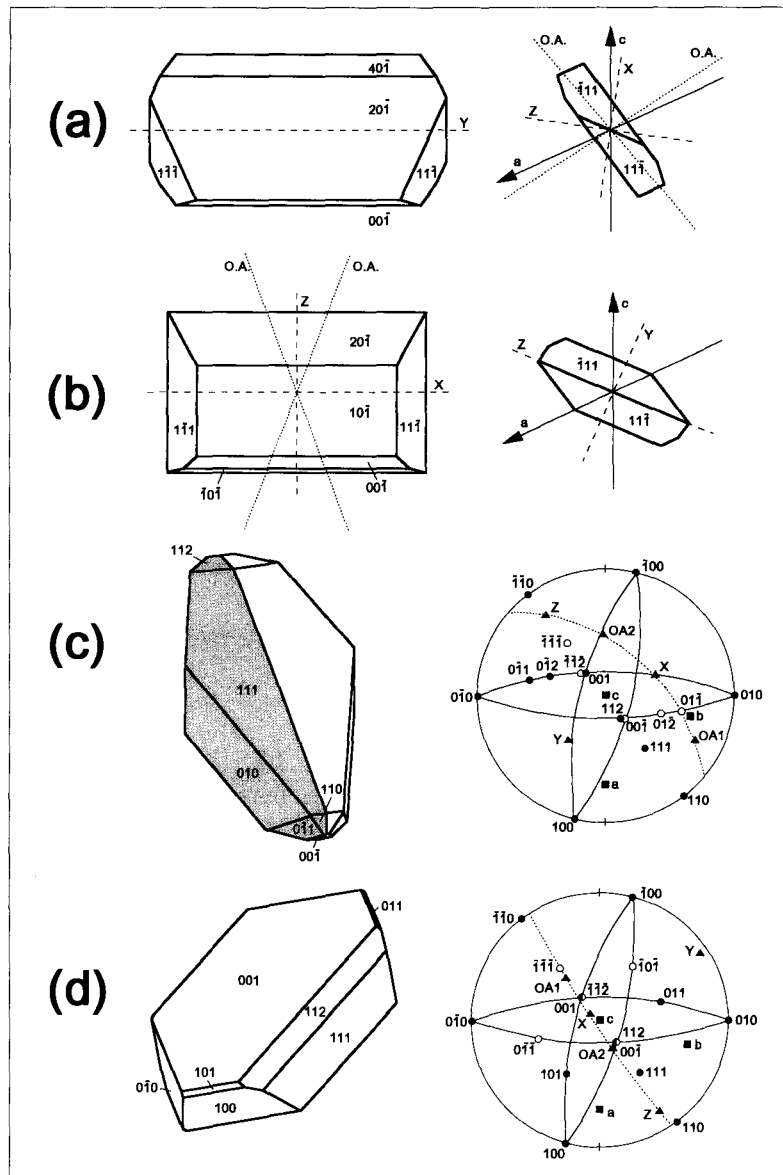


Fig. 1. Morphology and orientation of the optical indicatrix: (a) tsumcorite perpendicular and parallel to $[010]$; (b) ferrilotharmeyerite perpendicular and parallel to $[010]$; (c) gartrellite (morphology for a twinned crystal by reflection on $(1\bar{1}0)$); (d) helmutwinklerite.

tion twins (Fig. 2a,b), which could also be confirmed by extinction measurements. Crystal grains lying on (111) show an inclined extinction of $17(1)^\circ$ between Z' and the trace of the twin plane.

Morphological data were obtained by means of an optical two-circle goniometer, and the orien-

tation of some crystals was checked by single-crystal X-ray diffractometer studies. The monoclinic members of the tsumcorite group except mawbyite show a similar habit: tabular on monoclinic pinacoids parallel $[010]$ $\{ \{201\} \}$ (tsumcorite), $\{ \bar{1}01 \}$ (ferrilotharmeyerite), $\{001\}$ (mounanaite and sulfatian thometzkitite)], and

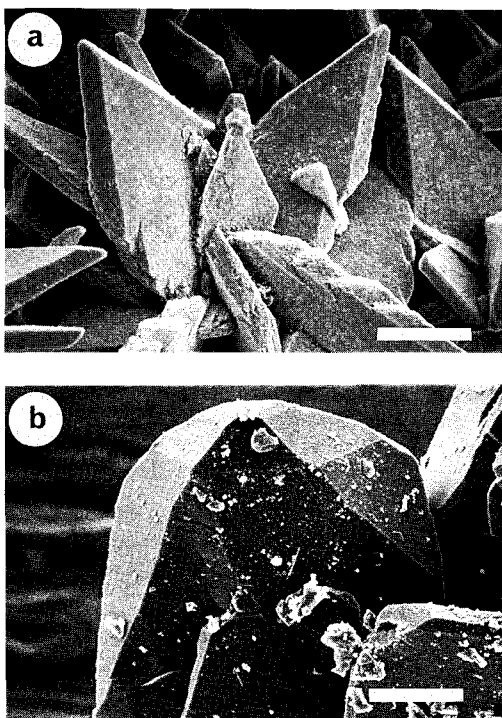


Fig. 2. SEM micrograph of gartrellite: (a) tabular aggregates from Reichenbach, Odenwald, Germany (sample #023, Cu:Fe = 1.0:1.0); (b) multifaceted crystal from Tsumeb, Namibia (sample #075, Cu:Fe:Zn = 0.90:0.94:0.16). The scale bar is 20 μm .

slightly elongated parallel [010]; terminating form in ferrilotharmeyerite and tsumcorite is $\{\bar{1}11\}$; additional forms are $\{101\}$, $\{100\}$, $\{010\}$, $\{221\}$ and $\{401\}$. Crystal drawings for ferrilotharmeyerite and tsumcorite including part of the optical data are shown in Fig. 1a,b. Triclinic gartrellite is tabular on $\{111\}$, additional forms are $\{010\}$, $\{001\}$, $\{01\bar{1}\}$, $\{01\bar{2}\}$, $\{110\}$, $\{112\}$, and probably $\{100\}$ (Fig. 1c). As far as the samples exhibit individual crystals, twinning can easily be observed (Fig. 2a,b). Twin plane is $\{1\bar{1}0\}$, showing a small characteristic angle of $4.0(5)^\circ$ (mean of 5 measurements; calculated angle: 4.4°) between the (111) faces of the two individuals. This is the same twin law found for mounanaite considering the different setting of mounanaite used by Cesbron & Fritsche (1969). Helmutwinklerite is tabular on $\{001\}$, additional forms are $\{100\}$, $\{010\}$, $\{011\}$, $\{101\}$, $\{111\}$ and $\{112\}$ (Fig. 1d). For an easier comparison of the morphological and optical data to those of

gartrellite, indexing is based on the triclinic *sub*-cell found for helmutwinklerite. This is also supported by the fact that it was impossible to derive a structure model for the *supercell*.

Other physical properties can be found in the first description of the individual species (Table 1). In the following only those data are reported which complete the original descriptions. Remarkable is the great colour variety of gartrellite and zincian gartrellite: there are yellow, brown, and green samples including various colour transitions; the streak of all these samples is bright yellow. There is a perfect cleavage parallel to $\{111\}$ for gartrellite, resulting in a pronounced texture effect of the powder diffraction patterns measured in reflection geometry. For the monoclinic minerals of the tsumcorite group a good cleavage parallel to (001) was observed (matching to both, the triclinic primitive and monoclinic C-centered cell choice); whereas for helmutwinklerite no distinct cleavage was found. The hardness values VHN_{25} determined with a Vickers microhardness tester vary from 350 kg/mm^2 for thometzekite (sulfatian), helmutwinklerite and mounanaite to approximately 500 kg/mm^2 for tsumcorite, ferrilotharmeyerite and gartrellite. All these values correspond to $4\frac{1}{2}$ on the Mohs' hardness scale. Due to lack of material the densities could not be determined experimentally; the X-ray densities were calculated according to Mandarino (1981) and gave the following data: 4.21 g/cm^3 for ferrilotharmeyerite (#241), 4.88 g/cm^3 for mounanaite (#262), 5.21 g/cm^3 for sulfatian thometzekite (#132), 5.29 g/cm^3 for helmutwinklerite (#272), and 5.43 g/cm^3 for gartrellite (#016).

Chemical composition

An electron microprobe was used for chemical analyses. The standards were mimetite (As, Pb), CuS (Cu), andradite (Fe, Ca), AlPO_4 (Al, P), SrSO_4 (S), vanadium metal (V), ZnO (Zn), NiO (Ni), Co metal (Co), Bi_2S_3 (Bi), and NaCl (Na). Investigations were performed on 10 different tsumcorite samples, 17 gartrellite samples, and single samples of ferrilotharmeyerite, thometzekite, mounanaite, and helmutwinklerite, respectively (Table 3a,b). Regarding tsumcorite and gartrellite, results are compiled only for those samples that were additionally checked by Mössbauer spectroscopy. The position of the

Table 3. Results (in wt.%) of electron-microprobe investigations (Cameca CAMEBAX, 20 kV, 6 nA, beam diameter 10 μm); H₂O contents were calculated from the idealized formulas. The number of ions were calculated on the basis of 10 oxygen atoms. (added in proof: read V₂O₅ instead of V₅O₅).

(a) ferrilotharmeyerite, tsumcorite, thometzekite (sulfatian) and mounanaite.

mineral		ferrilothar- meyerite		tsumcorite		tsumcorite		thometzekite (sulfatian)		thometzekite (sulfatian)		mounanaite	
sample		#241		#017		#091		#132		#120		#262	
oxide	ions	mean ¹		mean ²		mean ³		mean ⁴		mean ⁵		mean	
PbO	Pb ²⁺	0.14	-	33.39	0.95	35.30	1.02	36.10	0.99	35.72	0.99	38.47	1.02
CaO	Ca ²⁺	12.07	1.02	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-
Fe ₂ O ₃	Fe ³⁺	15.68	0.93	10.62	0.85	8.53	0.69	0.32	0.02	1.32	0.10	26.01	1.92
Al ₂ O ₃	Al ³⁺	<0.1	-	<0.1	-	<0.1	-	0.55	0.07	2.02	0.25	0.32	0.04
ZnO	Zn ²⁺	17.88	1.04	14.97	1.17	16.42	1.30	5.52	0.41	6.59	0.50	<0.1	-
CuO	Cu ²⁺	<0.1	-	0.15	-	<0.1	-	19.44	1.50	14.61	1.14	0.87	0.06
As ₂ O ₅	(AsO ₄) ³⁻	48.73	2.02	36.20	2.01	35.46	1.99	24.77	1.32	34.08	1.84	0.18	0.01
P ₂ O ₅	(PO ₄) ³⁻	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	0.81	0.07
V ₅ O ₅	(VO ₄) ³⁻	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	29.28	1.92
SO ₃	(SO ₄) ²⁻	<0.1	-	<0.1	-	<0.1	-	9.00	0.69	2.35	0.18	<0.1	-
H ₂ O _{calc}	(OH) ⁻	5.80	0.90	4.44	0.70	4.62	0.74	4.72	0.74	4.95	0.43	3.21	2.12
	H ₂ O		1.08		1.17		1.29		1.23		1.49		-
sum		100.31		99.76		100.33		100.42		101.65		99.15	

¹ mean of 20 analyses; ranges: Fe₂O₃ (14.53 - 16.43); ZnO (17.14 - 18.73)
² mean of 19 analyses; ranges: Fe₂O₃ (9.88 - 11.65); ZnO (14.58 - 15.45)
³ mean of 26 analyses; ranges: Fe₂O₃ (6.72 - 11.51); ZnO (12.79 - 18.39)
⁴ mean of 20 analyses; ranges: As₂O₅ (29.19 - 22.03); SO₃ (6.04 - 10.96); CuO (16.14 - 20.87); ZnO (4.12 - 8.63); Fe₂O₃ (0.00 - 0.66); Al₂O₃ (0.21 - 1.17)
⁵ mean of 8 analyses; ranges: As₂O₅ (31.32 - 37.34); SO₃ (0.25 - 4.47); CuO (11.55 - 18.48); ZnO (2.65 - 7.95); Al₂O₃ (1.00 - 3.33)

chemical composition of tsumcorite sample #259: Pb_{0.97}(Zn_{1.50}Fe_{0.50}Cu_{0.03})_{2.03}(AsO₄)_{2.01}(OH)_{0.49}(H₂O)_{1.51}

(b) helmutwinklerite, gartrellite, and zincian gartrellite.

mineral		helmut- winklerite		zincian gartrellite		zincian gartrellite		gartrellite		gartrellite		gartrellite	
sample		#272		#081		#080		type material		#016		#079	
oxide	ions	mean ¹		mean ²		mean ³		mean ⁴		mean ⁵		mean ⁶	
PbO	Pb ²⁺	34.20	0.98	33.49	0.97	35.13	1.03	36.53	1.04	35.40	1.01	34.45	0.98
CaO	Ca ²⁺	<0.05	-	0.35	0.04	0.07	-	<0.05	-	<0.05	-	<0.05	-
Fe ₂ O ₃	Fe ³⁺	<0.05	-	7.23	0.59	9.59	0.78	10.33	0.82	12.48	0.99	10.91	0.87
Al ₂ O ₃	Al ³⁺	<0.05	-	0.26	0.03	0.25	0.03	0.11	0.01	0.22	0.03	0.16	0.02
ZnO	Zn ²⁺	23.54	1.85	11.40	0.91	6.30	0.51	0.21	0.02	<0.05	-	<0.05	-
CuO	Cu ²⁺	1.62	0.13	6.26	0.51	8.36	0.69	14.02	1.12	12.25	0.98	13.78	1.10
As ₂ O ₅	(AsO ₄) ³⁻	36.42	2.03	34.72	1.96	34.52	1.96	33.11	1.83	35.50	1.97	34.67	1.92
P ₂ O ₅	(PO ₄) ³⁻	<0.05	-	<0.05	-	<0.05	-	<0.05	-	0.36	0.03	0.32	0.03
V ₅ O ₅	(VO ₄) ³⁻	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
SO ₃	(SO ₄) ²⁻	<0.05	-	0.13	0.01	0.13	0.01	1.68	0.13	<0.05	-	0.65	0.05
H ₂ O _{calc}	(OH) ⁻	5.53	-	4.80	0.83	4.48	1.00	4.47	1.10	4.21	1.05	4.40	0.90
	H ₂ O		2.00		1.31		1.12		1.03		0.96		1.10
sum		101.31		98.63		98.83		100.47		100.42		99.39	

¹ mean of 39 analyses; ranges: ZnO (21.83 - 24.77); CuO (0.94 - 3.72)
² mean of 16 analyses; ranges: Fe₂O₃ (6.59 - 7.68); ZnO (10.51 - 12.21); CuO (5.19 - 7.15)
³ mean of 15 analyses; ranges: Fe₂O₃ (8.78 - 10.37); ZnO (5.58 - 7.69); CuO (7.75 - 9.08)
⁴ mean of 15 analyses; ranges: Fe₂O₃ (7.81 - 12.08); CuO (12.69 - 16.86)
⁵ mean of 9 analyses; ranges: Fe₂O₃ (11.85 - 12.84); CuO (11.82 - 12.87)
⁶ mean of 12 analyses; ranges: Fe₂O₃ (10.37 - 11.39); CuO (13.09 - 14.68)

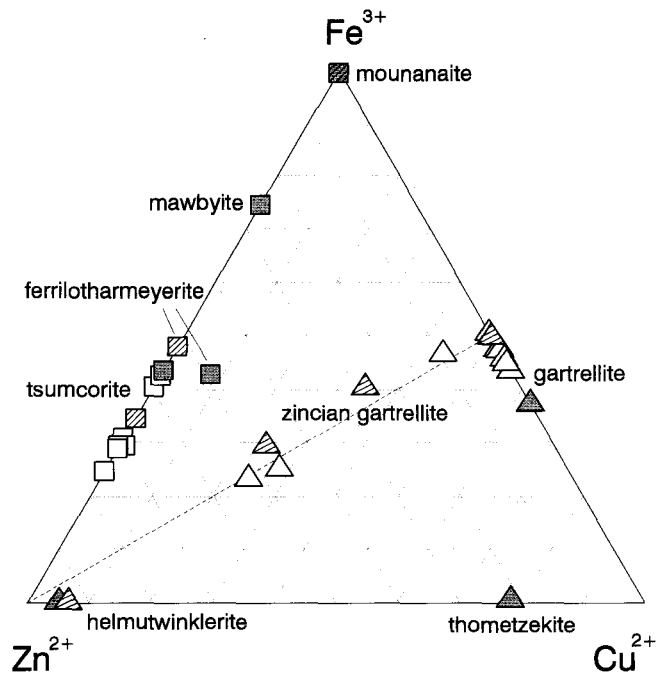


Fig. 3. Chemical composition of the tsumcorite-group minerals plotted in the triangle-diagram Zn^{2+} - Cu^{2+} - Fe^{3+} ; triclinic samples are plotted as triangles, monoclinic as squares. The compositions of the type material of the relevant minerals are shaded. The samples used for structural investigations are hatched. Thometzekite (sulfate-free) has been designated as triclinic by analogy with helmutwinklerite.

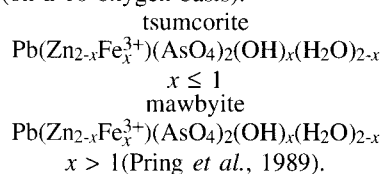
different samples out of the tsumcorite group with respect to their $\text{Cu}:\text{Zn}:\text{Fe}$ ratio is illustrated graphically (Fig. 3).

One of the results of the present study is the description of the tsumcorite-group minerals by the general formula $\text{Me}(1)\text{Me}(2)_2(\text{XO}_4)_2(\text{OH},\text{H}_2\text{O})_2$. Electron microprobe analyses showed that at least partial solid solution is common for the Me(2) and less frequent for the X and Me(1) site. In addition to the substitution involving homovalent ions [e.g. $\text{Zn}^{2+} \leftrightarrow \text{Cu}^{2+}$ or $(\text{AsO}_4)^{3-} \leftrightarrow (\text{PO}_4)^{3-}$] there are 3 heterovalent exchange mechanisms with a coupled substitution involving OH/H₂O groups: (i) on the Me(1) site, e.g. $[(\text{Ca})^{2+}(\text{H}_2\text{O})]^{2+} \leftrightarrow [(\text{Bi})^{3+}(\text{OH})]^{2+}$, (ii) on the Me(2) site, e.g. $[(\text{Zn},\text{Cu},\text{Co},\text{Ni})^{2+}(\text{H}_2\text{O})]^{2+} \leftrightarrow [(\text{Fe},\text{Al},\text{Mn})^{3+}(\text{OH})]^{2+}$, and (iii) on the X site, e.g. $[(\text{AsO}_4)^{3-}(\text{H}_2\text{O})]^{3-} \leftrightarrow [(\text{SO}_4)^{2-}(\text{OH})]^{3-}$. The Me(1) position is normally occupied by either Pb or Ca; at least partial solid solution is probable, but was not observed in the analyses of the present investigation. Only traces of calcium were detected which substitute for lead in the lead-

bearing minerals; the same applies for lead substituting for calcium in ferrilotharmeyerite. Bi-bearing samples with Bi_2O_3 up to 17 wt.% were found for cobaltlotharmeyerite (Krause *et al.*, in prep.). In the course of the investigation it became evident that natrochalcite is also a member of the tsumcorite group; therefore samples of ferrilotharmeyerite, tsumcorite, thometzekite (sulfatian), mounanaite, helmutwinklerite, and gartrellite were additionally examined for sodium and potassium, but all analytical results were below the detection limit. The Me(2) position is normally occupied by transition metal cations like Fe, Mn, Cu, Zn, Co, or Ni (and sometimes minor amounts of Al). Solid solution of the cations in the Me(2) position is common. Iron is always present as Fe^{3+} ; substantial amounts of Fe^{2+} could not be detected by microchemical tests and Mössbauer spectroscopy in any of the investigated samples. The X position is in most cases represented by As; currently only one phosphate (phosphogartrellite), one vanadate (mounanaite) and one sulfate (natrochalcite) are

known among minerals. Distinct solid solution involving AsO_4/SO_4 was found for thometzekite and to a small extent for gartrellite, but it is likely possible also for the other members of the tsumcorite group.

Tsumcorite shows distinct solid solution involving Zn and Fe^{3+} . Considering the variation of the $\text{Zn}^{2+}:\text{Fe}^{3+}$ ratio, charge balance can be achieved by adjusting the $\text{OH}:\text{H}_2\text{O}$ ratio. The structural formula of tsumcorite and consequently also of mawbyite can be written as follows (on a 10 oxygen basis):

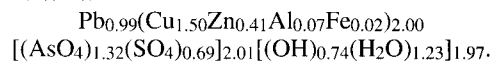


The distribution of the Zn:Fe ratio of 130 spot analyses of different tsumcorite samples has a maximum around $\text{Zn}_{1.20}\text{Fe}_{0.80}$ with a continuous range from $\text{Zn}_{1.60}\text{Fe}_{0.40}$ to $\text{Zn}_{1.05}\text{Fe}_{0.95}$, i.e. $0.40 \leq x \leq 0.95$. The tsumcorite analyses that have been reported in literature so far (Geier *et al.*, 1971; Tillmanns & Gebert, 1973; Elliott *et al.*, 1988) are also within this range. Only very small amounts of copper (mostly < 0.1 wt.%, maximum 0.6 wt.% CuO) were detected, although the association with copper-bearing minerals is common.

The Fe:Zn ratio of ferrilotharmeyerite is close to 1:1 and shows only minor variations. No copper could be detected in ferrilotharmeyerite, which is in contrast to the observations of Ansell *et al.* (1992) who found mean CuO values of 2.9 and 5.75 wt.%, respectively. According to the microprobe results and the crystal structure data (10 oxygen atoms), the structural formula of ferrilotharmeyerite has to be revised on a 10 oxygen basis to $\text{Ca}(\text{Fe}^{3+},\text{Zn})_2(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})_2$ (Fe:Zn \approx 1:1). For analogy reasons the formula of lotharmeyerite also should be revised to $\text{Ca}(\text{Mn}^{3+},\text{Zn})_2(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})_2$. For lotharmeyerite and ferrilotharmeyerite the compositions known so far centre around Mn:Zn = 1:1 and Fe:Zn = 1:1, respectively. The compositional range is small and there is no point in defining different species with cation ratios deviating only slightly from 1:1 (*cf.* Nickel, 1992). If species from these series with distinctly dominant Fe, Mn or Zn, or other cations are eventually found, separate mineral names should be assigned.

The investigated thometzekite sample consists of two generations: a coarse, dense, green mate-

rial, showing a distinct sulfur content (#132) which is overgrown by a second generation of very small, tabular, light-green crystals of substantially lower sulfur content (#120). It has to be noted that sulfate-free thometzekite and sulfate-bearing thometzekite might have different crystal symmetries. Structural studies on sulfate-free thometzekite were not possible due to lack of suitable material. The sample used for optical investigations and for the structure determination was a cleavage fragment of #132. Sulfur is present as sulfate anion, as proved by microchemical tests. The microprobe data clearly show that sulfate substitutes for arsenate up to a maximum SO_3 amount of 11.0 wt.%, which corresponds to an As:S ratio of 1.16:0.84. A partial substitution of AsO_4 by sulfate anions was already mentioned for gartrellite (Nickel *et al.*, 1989) and thometzekite (Gebhard & Schlüter, 1995). In addition to the substitution involving *di*- and *trivalent* cations like $[(\text{Cu},\text{Zn})^{2+}(\text{H}_2\text{O})]^{2+} \leftrightarrow [(\text{Fe},\text{Al})^{3+}(\text{OH})]^{2+}$, there is obviously a second mechanism involving *di*- and *trivalent* anions: $[(\text{AsO}_4)^{3-}(\text{H}_2\text{O})]^{3-} \leftrightarrow [(\text{SO}_4)^{2-}(\text{OH})]^{3-}$. A correlation between the $\text{Me}(2)^{2+}:\text{Me}(2)^{3+}$ and $(\text{AsO}_4)^{3-}:(\text{SO}_4)^{2-}$ ratios was observed; accordingly increasing $(\text{SO}_4)^{2-}$ contents result in decreasing $\text{Me}(2)^{3+}$ contents and *vice versa*. As a result there is only a slight variation of the $(\text{OH}):\text{H}_2\text{O}$ ratio, because the negative correlation between the $(\text{SO}_4)^{2-}$ and the $\text{Me}(2)^{3+}$ content keeps the charge nearly balanced. The general structural formula of sulfatian thometzekite can be written as $\text{Pb}(\text{Cu},\text{Zn})_x(\text{Al},\text{Fe})_{2x}(\text{AsO}_4)_2(\text{SO}_4)_y(\text{OH})_{2-x+y}(\text{H}_2\text{O})_{x-y}$, and based on the average microprobe analysis (#132) the empirical formula with $x = 1.91$ and $y = 0.69$ is:



The microprobe analysis of mounaite is the first complete analysis performed on natural material, because Cesbron & Fritsche (1969) were not able to isolate enough pure material to perform a wet-chemical analysis. Therefore a quantitative analysis was only available for synthetic material. The new analytical data indicate very small amounts of Cu and Al and confirm the chemical formula proposed by Cesbron & Fritsche (1969).

The composition of the helmutwinklerite sample is close to the ideal formula $\text{PbZn}_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$. The Fe content was below the limit of detection and a small amount of copper, ranging from 0.9 to 3.7 wt.% CuO, substitutes for

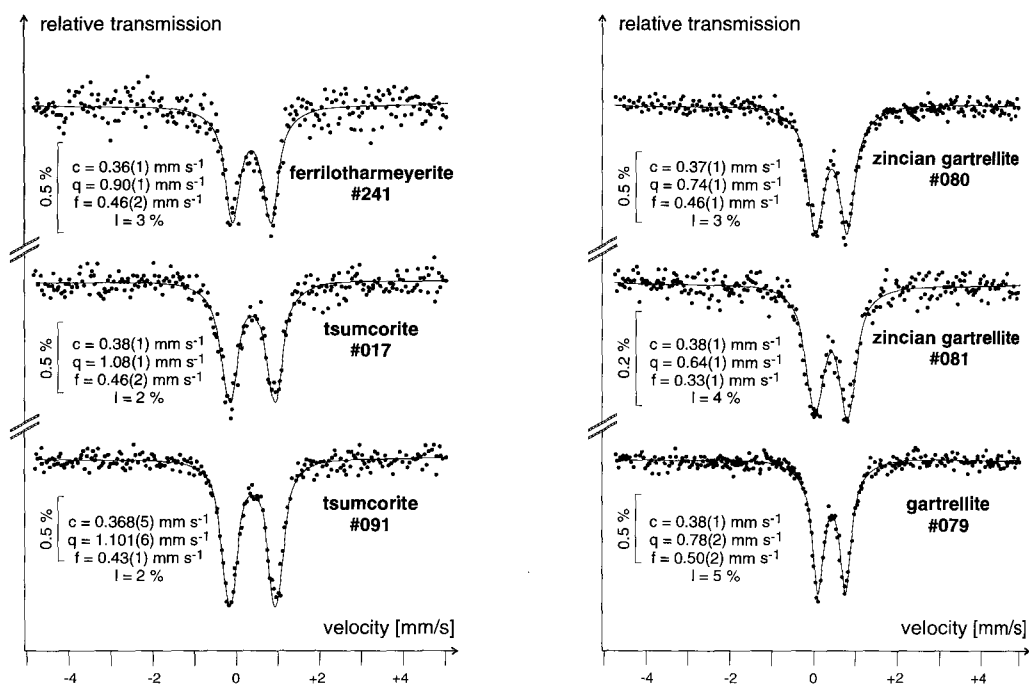


Fig. 4. Mössbauer spectra of ferrilotharmeyerite, tsumcorite, gartrellite and zincian gartrellite. For each spectrum are given: centre shift [mm s^{-1}] relative to $\alpha\text{-Fe}$ (c ; first line); quadrupolar splitting [mm s^{-1}] (q ; second line); full width at half maximum [mm s^{-1}] (f ; third line); detection limit for Fe^{2+} (% of the iron amount present) (l ; fourth line).

Zn which is in agreement with the data of the original description (Süsse & Schnorrer, 1980).

Based on the microprobe and structural data, the ideal formula of gartrellite is $\text{PbCuFe}^{3+}(\text{AsO}_4)_2(\text{OH})(\text{H}_2\text{O})$. No carbonate could be detected in any of the samples, either by microchemical tests or by infrared investigations; consequently gartrellite was redefined (see section 'redefinition of gartrellite'). According to results of chemical analyses currently available, up to 25 mol% of the iron may be substituted by copper; the sample with the highest copper content is the type material of gartrellite ($\text{Cu}:\text{Fe} = 1.25:0.75$; Nickel *et al.*, 1989). Thus an $\text{Fe}^{3+} \leftrightarrow \text{Cu}^{2+}$ substitution is obviously possible within narrow limits. Most samples are close to the ratio $\text{Cu}:\text{Fe} = 1:1$, which might be a barrier. Samples with an excess of iron have not been found so far, drawing attention to the possible excess of Cu as well as to the two crystallographically different Me(2) sites (see below), so the crystal chemical formula of gartrellite may be written as $\text{PbCu}(\text{Fe}^{3+}, \text{Cu})(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$. Gartrellite

samples from Tsumeb show intense solid-solution phenomena involving copper, zinc and trivalent iron; whereas the samples from the Odenwald area contain no zinc. The iron:copper ratio is in most cases very close to 1:1. Minor amounts of calcium may substitute for lead, and sulfate and/or phosphate may substitute for arsenate, respectively. Small amounts of aluminium (max. 2.3 wt.%, mostly < 1.0 wt.%) which substitute for iron are present in most of the samples. The incorporation of Ni (up to 4.5 wt.% NiO) and Co (up to 1.4 wt.% CoO) was confirmed for gartrellite samples from Pützbach, Bad Ems, Germany.

The variation of the chemical composition and of the unit-cell parameters (see section 'X-ray powder investigations') supports the assumption that gartrellite and zincian gartrellite are part of a solid solution series with the general formula $\text{Pb}(\text{Cu}, \text{Zn})(\text{Fe}^{3+}, \text{Zn}, \text{Cu})(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$. The series appear likely to be complete between pure gartrellite and zincian gartrellite with a $\text{Zn}:\text{Fe}:\text{Cu}$ ratio of $\approx 1.0:0.5:0.5$; the continuation

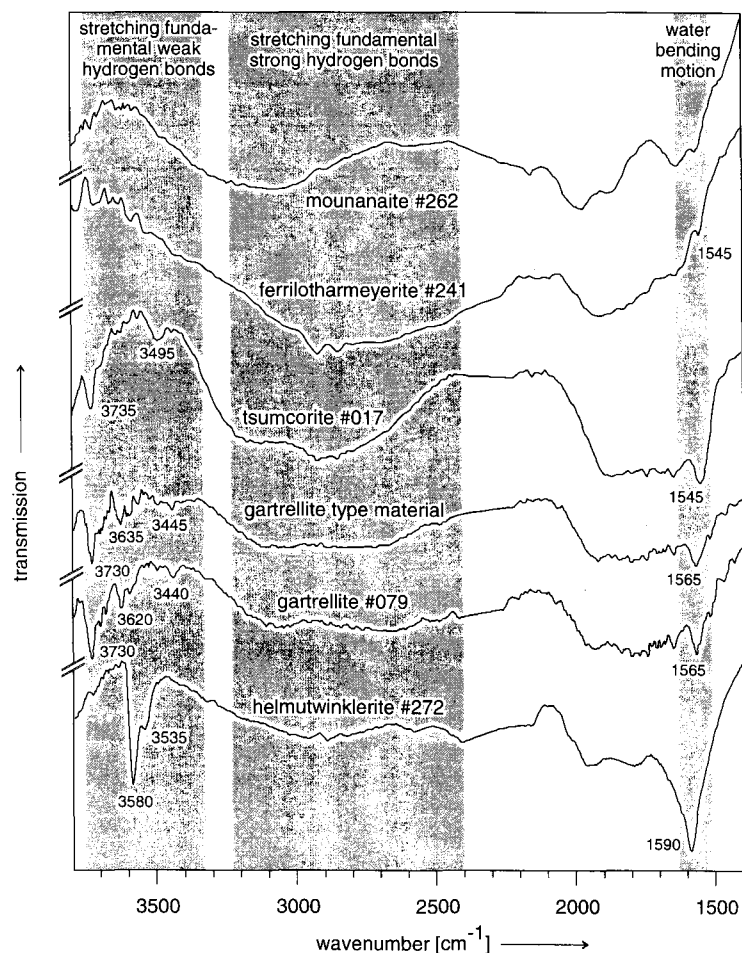


Fig. 5. Infrared spectra of mounanaite, ferrilotharmeyerite, tsumcorite, gartrellite and helmutwinklerite.

towards helmutwinklerite could not be proved during the present study. Additional investigations on (new) natural and/or synthetic material would be required to prove the limits of the solid-solution series. However, helmutwinklerite can not be regarded as a simple end-member because there are basic structural differences compared to gartrellite.

Mössbauer study

Mössbauer measurements were performed for ferrilotharmeyerite (#241), tsumcorite (#017 and #091), gartrellite (#079), and zincian gartrellite

(#080 and #081); there was not enough material available to test also mounanaite. The samples of tsumcorite, gartrellite and zincian gartrellite were gently ground in an agate mortar with acetone to make a powder. This was evenly distributed over a circular area on cellophane foil using water-soluble glue. Crystals of ferrilotharmeyerite were used without grinding. Sample weights and diameter of the circular area were determined based on the chemical composition such that (i) an ideal sample thickness was achieved; and (ii) the sample diameter was maximised for the amount of sample available. The effective sample thickness (in mg Fe/cm²) was 3.0 for ferrilotharmeyerite, 1.0 for tsumcorite, and 0.6, 0.6, and 0.4 for the three samples of gartrellite, respectively;

Table 4. Powder diffraction data
(a) the monoclinic minerals thometzekite (sulfatian) and mounanaite.

thometzekite (sulfatian) #132							mounanaite #262						
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	6.837	13	6.837	11	0	0	1	6.949	8	6.954	15
1	1	0	4.980	11	4.980	14	1	1	0	4.967	18	4.961	23
1	1	-1	4.691	100	4.688	100	1	1	-1	4.640	100	4.640	100
2	0	-1	4.488	47	4.488	59	2	0	-1	4.566	52	4.562	49
2	0	0	4.057	10	4.062	8	2	0	0	4.193	13	4.190	10
1	1	1	3.582	8	3.580	6	1	1	1	3.626	14	3.625	14
2	0	-2	3.507	4	3.509	7	0	0	2	3.474	20	3.478	20
0	0	2	3.418	17	3.416	14	1	1	-2	3.266	87	3.264	92
1	1	-2	3.273	98	3.273	88	0	2	0	3.082	20	} 3.055 96	
0	2	0	3.156	21	3.155	24	2	0	1	3.054	61		
2	0	1	2.953	66	2.953	35	0	2	1	2.817	58	2.817	60
0	2	1	2.865	77	2.865	70	3	1	-1	2.767	57	7.766	72
3	1	-1	2.727	60	2.724	56	3	1	-2	2.597	32	2.596	35
3	1	-2	2.583	37	} 2.582 48		1	1	2	2.557	37	2.558	29
2	2	-1	2.581	3			3	1	0	2.546	17	} 2.543 35	
2	0	-3	2.534	17	} 2.512 41		2	0	-3	2.545	14		
1	1	2	2.513	37			2	2	0	2.483	25	2.484	24
2	2	0	2.491	30	} 2.491 30		1	1	-3	2.341	10	2.341	8
3	1	0	2.486	18			2	2	-2	2.320	34	} 2.320 59	
2	2	-2	2.346	35	2.344	47	0	2	2	2.306	4		
1	1	-3	2.331	9	2.330	8	4	0	-2	2.283	8	2.282	11
4	0	-2	2.244	8	2.244	6	3	1	-3	2.196	7	2.196	6
3	1	-3	2.192	9	2.191	7	2	2	1	2.170	18	2.169	14
2	2	1	2.156	16	2.152	9	3	1	1	2.135	6	2.133	5
3	1	1	2.076	5	2.076	6	4	0	0	2.097	12	2.097	12
4	0	-3	2.039	4	} 2.036 19		4	0	-3	2.057	6	2.058	4
1	3	0	2.036	5			1	3	0	1.996	4	1.995	4
4	0	0	2.028	12	2.015	9	1	3	-1	1.973	12	1.973	13
1	3	-1	2.015	12	1.913	6	2	0	-4	1.025	8	} 1.922 11	
2	0	-4	1.914	7	1.885	8	1	1	3	1.920	15		
1	1	3	1.884	21	1.885	8	0	2	3	1.852	17	} 1.851 15	
0	2	3	1.848	16	} 1.848 14		4	2	-1	1.844	11		
1	3	-2	1.844	14			2	2	2	1.813	10	} 1.813 13	
4	2	-1	1.826	11	1.821	11	1	3	-2	1.813	14		
2	2	2	1.791	16	1.791	5	3	1	-4	1.802	3	} 1.788 2	
4	0	-4	1.753	17	1.754	13	1	1	-4	1.788	3		
3	3	-1	1.727	20	1.728	23	5	1	-2	1.777	3	} 1.763 9	
4	2	-3	1.712	37	} 1.710 44		4	0	-4	1.762	13		
0	0	4	1.709	15			3	1	2	1.752	5	} 1.740 24	
5	1	-1	1.702	10	} 1.688 7		5	1	-1	1.745	10		
3	3	-2	1.689	4			0	0	4	1.737	15		
2	0	3	1.688	8	} 1.664 9		2	0	3	1.735	6		
1	3	2	1.669	8			3	3	-1	1.712	17	} 1.712 47	
3	3	0	1.661	9	} 1.635 7		4	2	-3	1.711	40		
2	2	-4	1.636	21			3	3	-2	1.669	7	1.670	5
1	3	-3	1.612	4	1.612	2	1	3	2	1.659	9	} 1.657 7	
0	4	0	1.578	19	} 1.575 13		3	3	0	1.656	7		
5	1	0	1.572	7			2	2	-4	1.633	19	1.633	10
3	3	-3	1.564	3	} 1.520 15		5	1	0	1.618	7	1.618	5
4	2	1	1.525	22			1	3	-3	1.595	4	1.595	2
2	0	-5	1.520	6	} 1.520 15		4	2	1	1.557	23	1.557	10

Philips PW1710 diffractometer, CuK α -radiation, internal standard: Si; the powder diffraction pattern with the program LAZY PULVERIX (Yvon *et al.*, 1977) was calculated according to the results of structure refinements; reflections with I_{calc} \geq 3 are listed; observed intensities are corrected for texture effects according to the March model (Deyu *et al.*, 1990).

the values are close to the ideal sample thicknesses for these compositions (Long *et al.*, 1983). Samples were run at room temperature (293 K) on a conventional transmission Mössbauer spectrometer. Results of the measurements are compiled in Fig. 4. Data were fitted to a single Lorentzian doublet (components were constrained to equal widths and areas) which was sufficient to account for all spectral absorption.

All of the iron in the investigated samples is Fe³⁺; no evidence for Fe²⁺ can be seen within experimental error. All spectra show only one component, which indicates that Fe³⁺ occupies predominantly one site in the structure. Comparison of the centre shift data with values from other minerals show unambiguously that it is the octahedral site. There is a slight difference between the (theoretically equal) areas of each component in each of the tsumcorite spectra resulting either

Table 5. Unit-cell parameters refined from powder-diffraction data (the chemical composition is given in Table 3).

monoclinic minerals	sample	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	V [Å ³]
ferrilotharmeyerite	#241	9.006(2)	6.238(1)	7.387(2)		115.54(2)		374.4
tsumcorite	#017	9.117(1)	6.323(1)	7.567(1)		115.25(1)		394.6
tsumcorite	#091	9.143(2)	6.335(1)	7.598(2)		115.07(2)		398.6
tsumcorite	#259	9.163(2)	6.347(2)	7.611(2)		115.09(2)		400.9
thomtezkite (sulfatian)	#132	9.088(2)	6.311(1)	7.656(2)		116.76(2)		392.0
thomtezkite (sulfatian)	#120	9.112(4)	6.331(4)	7.667(4)		116.74(5)		395.0
mounanaite	#262	9.294(2)	6.164(2)	7.703(2)		115.54(2)		398.1
triclinic minerals								
helmutwinklerite ¹	#272	5.606(2)	5.610(2)	7.617(1)	70.19(2)	69.91(2)	69.18(2)	203.7(1)
zincian gartrellite	#081	5.550(1)	5.620(1)	7.621(1)	68.59(1)	69.17(1)	69.51(1)	200.1(1)
zincian gartrellite	#080	5.516(1)	5.613(1)	7.599(1)	68.32(1)	69.17(1)	69.72(1)	198.0(1)
gartrellite	²	5.460(1)	5.653(1)	7.589(2)	67.68(1)	69.27(1)	70.04(1)	196.8(1)
gartrellite	#079a	5.431(1)	5.642(1)	7.573(1)	67.62(1)	69.57(1)	70.31(1)	195.4(1)
	#079b	5.454(1)	5.653(1)	7.579(1)	67.52(1)	69.27(1)	70.08(1)	196.1(1)
gartrellite	#016	5.452(1)	5.628(1)	7.565(1)	67.77(1)	69.34(1)	70.09(1)	195.2(1)
¹ Single-crystal X-ray film and diffractometer investigations showed weak <i>superstructure</i> reflections, which were not considered for calculation of cell parameters								
² type material								

Infrared absorption spectra

Powder IR spectra of samples of ferrilotharmeyerite (#241), tsumcorite (#017), and helmutwinklerite (#272) were obtained from nujol mulls on a Perkin Elmer FTIR 1740 spectrometer; the same samples, additional samples of gartrellite (#079 and type material from Ashburton Downs) and mounanaite were run on a Nicolet 5PC FTIR using a diamond microcell (Fig. 5). Thomtezkite or sulfatian thomtezkite could not be investigated due to lack of material. The samples of ferrilotharmeyerite, tsumcorite and gartrellite are close to a ratio $\text{Me}(2)^{2+}:\text{Me}(2)^{3+} = 1:1$, requiring one $(\text{OH})^-$ group and one H_2O molecule for charge balance, which consequently results in three hydrogen bonds p.f.u. (per formula unit). Helmutwinklerite was investigated because it has divalent $\text{Me}(2)$ atoms only: for charge balance two H_2O molecules are assumed in the chemical formula $\text{Pb}(\text{Zn,Cu})_2(\text{AsO}_4)_2(\text{H}_2\text{O})_2$, which causes four hydrogen bonds. The spectrum of ferrilotharmeyerite shows a broad absorption band ranging from approximately 3200 to 2300 cm^{-1} with the maximum at $\sim 2900 \text{ cm}^{-1}$ indicating strong to very strong hydrogen bonds. The spectrum of tsumcorite is similar to that of ferrilotharmeyerite with respect to this broad absorption band; in addition a weak absorption band at 3495 cm^{-1} as characteristic for a long hy-

drogen bond and a hint to a bending motion of H_2O is observed. The IR spectrum of helmutwinklerite is somewhat different. Although the broad absorption band at 2900 cm^{-1} is maintained, significant bands at 3580 and 3535 cm^{-1} were obtained indicating practically free hydrogen bonds; the bending motion of water is observed at 1590 cm^{-1} . The IR spectra of gartrellite from Tsumeb and of the type material from Ashburton Downs, Australia, are nearly identical with weak absorptions at 1565, 3440/3445, 3620/3635, and 3730 cm^{-1} , and a broad absorption band centered at about 2900 cm^{-1} . There is no indication for distinct absorptions due to carbonate in the range 1400 to 1500 cm^{-1} . From the spectra it can be expected that the hydrogen bonding scheme in the investigated samples is similar with respect to the short $\text{O}\cdots\text{H}\cdots\text{O}$ bonds. A suggestion of an additional weak or even free hydrogen bond is evident in tsumcorite and is obvious in gartrellite and helmutwinklerite. It should be mentioned that there are no cogent reasons for protonated anion groups in any of the compounds.

X-ray powder investigations

The X-ray powder-diffraction patterns of the investigated minerals are very similar, which is

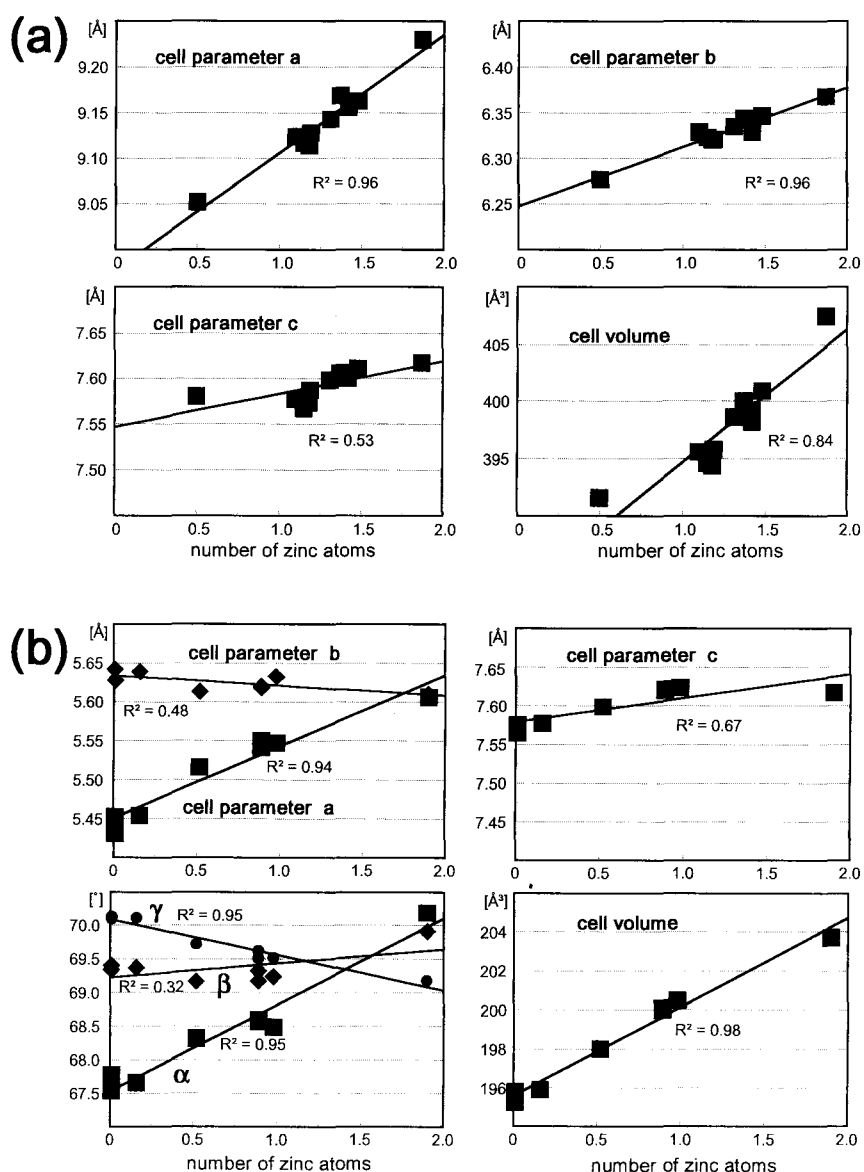


Fig. 6. Variation of cell parameters versus Zn content within the solid-solution series (a) mawbyite - tsumcorite (- helmutwinklerite) [i.e. $\text{PbFe}^+(\text{AsO}_4)_2(\text{OH})_2$ - $\text{PbFe}^{3+}\text{Zn}(\text{AsO}_4)_2(\text{OH})(\text{H}_2\text{O})$ - $\text{PbZn}_2(\text{AsO}_4)_2(\text{H}_2\text{O})_2$] and (b) gartrellite - zincian gartrellite (- helmutwinklerite) [i.e. $\text{PbFe}^{3+}\text{Cu}(\text{AsO}_4)_2(\text{OH})(\text{H}_2\text{O})$ - $\text{Pb}(\text{Fe}^{3+}\text{Zn})(\text{Cu,Zn})(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})_2$ - $\text{PbZn}_2(\text{AsO}_4)_2(\text{H}_2\text{O})_2$]. For helmutwinklerite the *superstructure* reflections are neglected, only the monoclinic / triclinic *pseudocell* is considered for comparison with the other cell parameters.

consistent with their similar compositions and strongly related crystal structures. Different unit-cell parameters and scattering factors result only in a small variability regarding d-values and intensities. Improved powder data are given in

Table 4; the patterns for ferrilotharmeyerite and tsumcorite were omitted because of the close similarity with the data given by Dunn (1983), and Geier *et al.* (1971), respectively. With the exception of helmutwinklerite the powder-

Table 6. Single-crystal X-ray data collection and structure refinements. A STOE AED 2 four-circle diffractometer (Mo tube, graphite monochromator) was used for data collection. Unit-cell parameters were obtained by least-square refinements of accurate 2θ values.

	ferrilotharmeyerite #241	thometzekite (sulfatian) #132	mounanaite #262	helmutwinklerite #272
<i>a</i>	9.010(3) Å	9.077(8) Å	9.294(8) Å	5.606(2) Å †
<i>b</i>	6.246(2) Å	6.300(8) Å	6.166(7) Å	5.610(2) Å †
<i>c</i>	7.391(2) Å	7.661(8) Å	7.713(8) Å	7.617(1) Å †
α	-	-	-	70.19(2)° †
β	115.52(3)°	116.99(8)°	115.57(6)°	69.91(2)° †
γ	-	-	-	69.18(2)° †
V	375.4 Å ³	390.4 Å ³	398.7 Å ³	203.7 Å ³
space group	<i>C2/m</i>	<i>C2/m</i>	<i>C2/m</i>	<i>P1</i>
Z	2	2	2	1†
ρ_{calc} §	4.21 g cm ⁻³	5.21 g cm ⁻³	4.88 g cm ⁻³	5.29 g cm ⁻³
crystal dimensions	0.14x0.08x0.04 mm ³	0.10x0.08x0.03 mm ³	0.10x0.06x0.02 mm ³	0.07x0.09x0.22 mm ³
scan speed (2 θ / ω scan mode)	0.90 - 3.60°min ⁻¹	0.60 - 1.80°min ⁻¹	0.90 - 1.80°min ⁻¹	0.90 - 1.80°min ⁻¹
scan width (+ dispersion)	0.66°	1.38°	1.20°	1.50°
standards, intervall	3 standards, 2h	3 standards, 2h	3 standards, 2h	3 standards, 2h
maximal intensity variation	±1.77%	±3.38%	±1.51%	±2.94%
range of data collection [†]	6° < 2 θ < 70°	5° < 2 θ < 60°	5° < 2 θ < 60°	5° < 2 θ < 50°
$\mu(\text{MoK}\alpha)$	146 cm ⁻¹	319 cm ⁻¹	265 cm ⁻¹	374 cm ⁻¹
absorption correction	crystal shape	ψ -scans	crystal shape	ψ -scans
transmission factors	0.248 to 0.563	0.0257 to 0.0964	0.125 to 0.261	0.0301 to 0.0592
total measured reflection	2985	2326	2320	792† / 12626*
observed unique reflections	886	614	621	715†
reflections for refinements	833, $F_o > 3\sigma(F_o)$	544, $F_o > 3\sigma(F_o)$	493, $F_o > 3\sigma(F_o)$	662†, $F_o > 4\sigma(F_o)^2$
R_{int}	0.026	0.037	0.047	0.017
<i>R</i>	0.021	0.046	0.065	0.029
R_w (helmutwinklerite: $wR2$)	0.021	0.027	0.039	0.088
<i>w</i>	1.703 [$\sigma(F_o)$] ²	1.676 [$\sigma(F_o)$] ²	1.289 [$\sigma(F_o)$] ²	‡
variable parameters	46	46	45	74
max Δ/σ	≤ 0.003	≤ 0.001	≤ 0.001	≤ 0.001
final difference Fourier map	-1.25 to +1.25 eÅ ⁻³	-4.28 to +3.88 eÅ ⁻³	-3.65 to +5.68 eÅ ⁻³	-0.09 to +1.99 eÅ ⁻³

Data were corrected for Lorentz and polarization effects; neutral-atomic complex scattering functions (Wilson, 1992), programs SDP (Frenz & Associates, 1992), SHELX-76 and SHELXL-93 (Sheldrick, 1976, 1993) were used.
 $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$; $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$
§ ρ_{calc} calculated from the experimental chemical composition and the cell volume derived from powder data
‡ $w = 1 / \{ \sigma^2(F_o^2) + [0.01 * ([\max(0, F_o^2)] + 2 * F_c^2) / 3]^2 \}$; * including and † neglecting *superstructure* reflections

diffraction patterns of the tsumcorite-group minerals show a strong texture effect when measured in reflection geometry. The investigations of the powder patterns by applying the March model of preferred orientation (Deyu *et al.*, 1990) leads to March factors of about 0.5, assuming (001) and (111) to be the dominant faces for the monoclinic and triclinic samples, respectively. Unit-cell parameters refined from powder data are compiled in Table 5.

The variation of the cell parameters within the monoclinic series mawbyite - tsumcorite (- helmutwinklerite) is shown in Fig. 6a. A monoclinic setting (neglecting the small deviations of α and γ from rectangularity) was chosen for helmutwinklerite to illustrate the relation to tsumcorite. The unit-cell volumes slightly increase with increasing zinc content because of the larger ionic radius

of Zn²⁺ (0.740 Å; Shannon, 1976) compared to Fe³⁺ (0.645 Å), and the fact that Fe²⁺ is absent. In addition the influence of the increasing number of hydrogen bonds has to be considered, which also results in slightly larger cell volumes.

According to the previous investigations unit cells related to that of tsumcorite were expected for the triclinic minerals gartrellite and helmutwinklerite. With respect to the axial lengths and to the cell volume, the cell parameters given by Nickel *et al.* (1989) and Süsse & Schnorrer (1980) are similar to those determined in this work, but the unit-cell angles are approximately supplementary to the correct ones. The reduced triclinic cells used by Schmetzer *et al.* (1985) and in the present paper can be obtained from the monoclinic C-centered cell of tsumcorite

Table 7. Residuals of the Rietveld-powder refinements of gartrellite (STOE powder diffractometer, transmission geometry, Cu tube, monochromated by a curved Ge (111) monochromator, linear PSD detector, range of data collection $10^\circ < 2\theta < 120^\circ$, step width 0.01°).

	type material	#016	#079
weighted profile R_{wp} : $R_{wp} = [\sum_i w_i (y_{oi} - 1/C \cdot y_{ci})^2 / \sum_i w_i y_{oi}^2]^{1/2}$	0.076	0.071	0.053
theoretical minimum value for R_{wp} : $R_{exp} = ((N-P) / \sum_i w_i y_{oi})^{1/2}$	0.030	0.048	0.023
profile R_p : $R_p = \sum_i (y_{oi} - 1/C \cdot y_{ci}) / \sum_i y_{oi}$	0.053	0.054	0.039
background corrected R_p' : $R_p' = [\sum_i (y_{oi} - 1/C \cdot y_{ci}) / \sum_i y_{oi} \cdot y_{bi}]$	0.237	0.233	0.164
goodness-of-fit: s	6.53	2.18	5.46

Scale factor: C; observed, calculated, background profile intensities: y_{oi} , y_{ci} , y_{bi} ; numbers of statistically independent observations: N=11000, variable least-squares parameters: P=39; $w=1/y_{oi}$. Program "PC-Rietveld plus" (Fischer *et al.*, 1993), background points: $y_{bi} = \sum_{j=1}^4 B_j \cdot 2\theta_j^2$; corrections for standard deviations (Bérar & Lelann, 1991), for texture effects (Dollase, 1986) and for asymmetry effects if $2\theta < 30^\circ$ (Rietveld, 1969); simulation of the peak shape: pseudo-Voigt function (Young & Wiles, 1982); for diminishing the severe peak overlap: intensities within $4 \times \text{FWHM}$ (full width at half maximum) were considered; the angular dependence of FWHM (one free parameter) was refined (Caglioti *et al.*, 1958); X-ray scattering functions from Wilson (1992), for O^2 from Hovestreydt (1983).

(Tillmanns & Gebert, 1973) by a transformation according to $(\frac{1}{2} \ \frac{1}{2} \ 0 \ / \ \frac{1}{2} \ -\frac{1}{2} \ 0 \ / \ 0 \ 0 \ -1)$. The superstructure reflections of helmutwinklerite found by Schmetzer *et al.* (1985) and verified by single-crystal X-ray work during our investigation are not observable in the powder pattern due to very small intensities and frequent overlap with reflections of high intensity. The splitting of reflections caused by the lowering of symmetry from $C2/m$ to $P\bar{1}$ is clearly observable in the powder patterns of gartrellite. With increasing zinc content the splitting of the reflections becomes smaller, which finally leads to reflections that are only broadened. The variation of the cell parameters within the gartrellite - zincian gartrellite (- helmutwinklerite) series is shown in Fig. 6b.

X-ray structure investigation

For structure investigations single crystals of ferrilotharmeyerite, tsumcorite, sulfatian thometzekite, mounanaite, and helmutwinklerite were available; structural data for gartrellite were obtained from powder data. The crystals were selected for X-ray diffractometer measurements after checks by optical investigations and Weissenberg-film techniques. The atomic coordinates of tsumcorite given by Tillmanns & Gebert (1973) served as the starting set for structure re-

finements. Their labelling of the atoms has been maintained. Relevant data for structure refinements are summarized in Tables 6 and 7, structural parameters are given in Table 8 and interatomic distances and bond angles are listed in Table 9. The highest peaks found in the final difference Fourier summations are in the surrounding of the Pb atoms.

The monoclinic members of the tsumcorite group

A refinement of tsumcorite was performed to prove the structural identity of the material used for the recent investigations. All atomic parameters obtained by our refinement are equal within two standard deviations to those given by Tillmanns & Gebert (1973). Therefore our structural parameters are not given; data on tsumcorite refer to those of the first structure investigation.

Despite the fact that the symmetry of mounanaite was given as triclinic by Cesbron & Fritsche (1969), the recent refinement gave no evidence for a lower symmetry than $C2/m$. Data were collected in the full reciprocal sphere; merging according to Laue symmetry $\bar{1}$ instead of $2/m$ lowers R_{int} from 0.047 to 0.044 which does not justify the description of the structure based on lower symmetry. In addition the refinement of the cell parameters gave no evidence for

Table 8. Structural parameters (e.s.d.'s in parentheses), for B_{eq} see Fischer & Tillmanns (1988).

atom	Wyckoff letter	symmetry	x	y	z	occupation factor	B_{eq} / B_{iso}
ferrilotharmeyerite (#241)							
Ca	2(a)	2/m	0	0	0	1.0	0.92
Fe	4(f)	$\bar{1}$	0.25	0.25	0.5	$\left\{ \begin{array}{l} 0.497(11) \\ 0.503(11) \end{array} \right\}$	0.73
Zn							
As	4(i)	m	0.91466(4)	0.5	0.20451(5)	1.0	0.60
O(1)	4(i)	m	0.3439(3)	0.5	0.4083(3)	1.0	0.92
O(2)	4(i)	m	0.3183(3)	0	0.3621(4)	1.0	1.12
O(3)	8(j)	1	0.0339(2)	0.2798(2)	0.2453(3)	1.0	0.89
O(4)	4(i)	m	0.2429(3)	0.5	0.0206(4)	1.0	1.24
thomtezikite (sulfatian) (#132)							
Pb	2(a)	2/m	0	0	0	1.0	2.38
Cu	4(f)	$\bar{1}$	0.25	0.25	0.5	1.0	1.44
As	4(i)	m	0.9167(2)	0.5	0.2097(2)	$\left\{ \begin{array}{l} 0.617(8) \\ 0.383(8) \end{array} \right\}$	1.45
S							
O(1)	4(i)	m	0.3426(8)	0.5	0.4204(13)	1.0	1.91
O(2)	4(i)	m	0.3083(10)	0	0.3267(13)	1.0	2.31
O(3)	8(j)	1	0.0308(6)	0.2887(8)	0.2623(9)	1.0	1.83
O(4)	4(i)	m	0.2084(11)	0.5	0.0180(13)	1.0	2.82
mounanaite (#262)							
Pb	2(a)	2/m	0	0	0	1.0	1.82
Fe	4(f)	$\bar{1}$	0.25	0.25	0.5	1.0	1.51
V	4(i)	m	0.9228(4)	0.5	0.2256(5)	1.0	1.29
F	4(i)	m	0.3368(11)	0.5	0.4183(16)	1.0	1.43
O(2)	4(i)	m	0.3185(15)	0	0.3722(21)	1.0	2.00
O(3)	8(j)	1	0.0406(10)	0.2729(12)	0.2663(13)	1.0	1.40
O(4)	4(i)	m	0.2125(14)	0.5	-0.0053(19)	1.0	1.72
gartrellite (#079)							
Pb	1(a)	$\bar{1}$	0	0	0	1.0	0.07(3)
Fe	1(g)	$\bar{1}$	0	0.5	0.5	1.0	1.40(10) ¹
Cu	1(f)	$\bar{1}$	0.5	0	0.5	1.0	1.40(10) ¹
As	2(i)	1	0.4100(5)	0.4347(5)	0.7920(3)	1.0	1.00(8)
O(1)	2(i)	1	0.146(2)	0.171(2)	0.4198(15)	1.0	0.62(15) ²
O(2)	2(i)	1	0.284(2)	0.306(2)	0.6702(13)	1.0	0.62(15) ²
O(3a)	2(i)	1	0.251(2)	0.685(2)	0.2815(13)	1.0	0.62(15) ²
O(3b)	2(i)	1	0.686(2)	0.230(2)	0.2723(13)	1.0	0.62(15) ²
O(4)	2(i)	1	0.261(2)	0.275(2)	0.0366(14)	1.0	0.62(15) ²
helmutwinklerite (#272)							
Pb	1(a)	$\bar{1}$	0	0	0	1.0	2.72
Zn(1)	1(g)	$\bar{1}$	0	0.5	0.5	1.0	1.82
Zn(2)	1(f)	$\bar{1}$	0.5	0	0.5	1.0	1.84
As	2(i)	1	0.42101(16)	0.42320(16)	0.77763(13)	1.0	1.74
O(1)	2(i)	1	0.1554(14)	0.1572(14)	0.4059(13)	1.0	3.10
O(2)	2(i)	1	0.3131(11)	0.3093(11)	0.6509(10)	1.0	1.89
O(3a)	2(i)	1	0.2495(12)	0.6831(13)	0.2581(10)	1.0	2.56
O(3b)	2(i)	1	0.6842(12)	0.2471(12)	0.2610(10)	1.0	2.42
O(4)	2(i)	1	0.2786(19)	0.2874(21)	0.0085(11)	1.0	5.03

¹ and ²: these parameters are constrained

a deviation of the angles α and γ from 90° , the displacement parameters show no conspicuous anisotropy, and the powder data indicate no splitting or broadening of reflections even at high 2θ angles. Therefore, within the accuracy of the

structure investigation, the symmetry of mounanaite is $C2/m$.

During the first stage of structural refinement of mounanaite, negative displacement parameters were obtained for the atomic position O(1). After

Table 9. Interatomic distances (in Å), hydrogen bonds (bond angles in °) and bond valences ν (in valence units; calculated according to Brese & O'Keeffe, 1991).

monoclinic minerals	ferrilothar- meyerite	tsumcorite	thometzekite (sulfatian)	mounanaite
Me(1)—O(2), ν	2 \times 2.962(2) 0.07	2.955(6) 0.10	2.782(7) 0.16	3.109(13) 0.07
Me(1)—O(3), ν	4 \times 2.441(2) 0.28	2.597(6) 0.27	2.629(5) 0.25	2.554(8) 0.30
Me(1)—O(4), ν	2 \times 2.386(2) 0.32	2.591(6) 0.27	2.712(5) 0.20	2.654(7) 0.23
coordination, $\Sigma\nu$	[6(+2)] 1.90	[6+2] 1.82	[8] 1.72	[6+2] 1.80
Me(2)—O(1), ν	2 \times 2.027(1) 0.45	2.046(6) 0.43	2.006(3) 0.41	1.965(4) 0.45
Me(2)—O(2), ν	2 \times 2.097(1) 0.37	2.131(6) 0.34	2.272(5) 0.20	2.072(7) 0.43
Me(2)—O(3), ν	2 \times 2.052(1) 0.42	2.019(6) 0.46	2.012(5) 0.41	2.007(8) 0.51
<Me(2)—O>, $\Sigma\nu$	<2.059> 2.48	<2.065> 2.46	<2.097> 2.04	<2.015> 2.78
X—O(2), ν	1.726(2) 1.12	1.719(6) 1.14	1.604(6) 1.34	1.779(10) 1.07
X—O(3), ν	2 \times 1.692(1) 1.23	1.691(6) 1.23	1.621(5) 1.28	1.721(7) 1.25
X—O(4), ν	1.658(2) 1.34	1.663(6) 1.33	1.592(9) 1.39	1.620(13) 1.64
<X—O>, $\Sigma\nu$	<1.692> 4.92	<1.691> 4.93	<1.610> 5.29	<1.710> 5.21
O(1)···O(1)	2.543(2)	2.636(9)	2.548(7)	2.738(9)
O(1)···O(4)	2.607(3)	2.690(9)	2.753(13)	2.959(18)
O(1)···O(3)	2 \times 3.035(2)	3.013(6)	3.094(6)	3.117(8)
O(1)···O(1)···O(4)	111.58(8)	115.1(3)	111.5(3)	109.6(4)
triclinic minerals	gartrellite	helmutwinklerite		
Pb—O(2), ν	2 \times 2.72(1)	0.19	2.997(8)	0.09
Pb—O(3a), ν	2 \times 2.66(2)	0.23	2.600(9)	0.27
Pb—O(3b), ν	2 \times 2.63(2)	0.25	2.591(8)	0.27
Pb—O(4), ν	2 \times 2.57(1)	0.29	2.641(16)	0.24
coordination, $\Sigma\nu$	[8]	1.92	[6+2]	1.74
Me(2a)/(2b)—O(1), ν	2 \times 1.99(2) 2.03(1)	0.53 0.39	2.071(10) 2.085(13)	0.37 0.36
Me(2a)/(2b)—O(2), ν	2 \times 2.10(2) 2.30(2)	0.39 0.19	2.187(10) 2.160(7)	0.27 0.29
Me(2a)/(2b)—O(3a), ν	2 \times 1.94(1) —	0.61 —	2.090(9) —	0.35 —
Me(2a)/(2b)—O(3b), ν	2 \times — 1.91(1)	— 0.54	— 2.077(8)	— 0.36
<Me(2a)/(2b)—O>, $\Sigma\nu$	<2.01> <2.08>	3.06 2.24	<2.116> <2.107>	1.98 2.02
As—O(2), ν	1.77(2)	0.99	1.675(9)	1.28
As—O(3a), ν	1.70(1)	1.21	1.681(12)	1.26
As—O(3b), ν	1.70(1)	1.18	1.684(8)	1.25
As—O(4), ν	1.75(2)	1.04	1.694(9)	1.22
<As—O>, $\Sigma\nu$	<1.73>	4.42	<1.684>	5.01
O(1)···O(1)	2.58(2)		2.636(17)	
O(1)···O(4)	2.61(3)		2.758(12)	
O(1)···O(1)···O(4)	107.9(5)		117.8(6)	

Data on tsumcorite refer to Tillmanns & Gebert (1973). An occupation of the O(1) position by F atoms is assumed in mounanaite for bond valence calculations.

checks of the interatomic distances it was assumed that this atomic position might be occupied at least partly by fluorine atoms instead of hydroxyl groups. A trial to refine the structure with the scattering function for F instead of O for the O(1) position reduced R and R_w significantly from 0.068 and 0.043 to 0.065 and 0.039. The

displacement parameters of F(1) increased to values comparable to that of the other atoms.

Despite careful X-ray investigations, no violations of the space-group symmetry $C2/m$ or a multiplication of the cell parameters could be detected for the monoclinic members of the tsumcorite-group minerals. A local site disorder

(statistically or dynamically) caused by the hydrogen-bonding schemes has to be assumed.

The triclinic members of the tsumcorite group

Schmetzer *et al.* (1985) found for helmutwinklerite a triclinic, but pronounced monoclinic C-centered tsumcorite-like *pseudocell*; additional weak *superstructure* reflections were responsible for a large triclinic cell: $a = 4 \times 5.600 = 22.400(4)$, $b = 4 \times 5.609 = 22.436(4)$, $c = 7.616(3)$ Å, $\alpha = 70.21(2)$, $\beta = 70.02(3)$, $\gamma = 69.24(2)^\circ$. These observations were confirmed during our investigations. The deviation from the monoclinic setting is very small but still significant. The distribution of the intensities shows that the reflections of the *pseudocell* adopts approximately the $C2/m$ symmetry; whereas the *superstructure* reflections show distinct violation of the Laue-symmetry $2/m$. However, at least the strongest of the weak *superstructure* reflections show a systematic non-space group extinction. Our investigations, which are based on data from a conventional scintillation detector, did not show whether the intensities of the reflections hkl : $h = 2n+1$ and $k = 2n+1$ or $h,k = 4n+2$ were not observed due to too weak intensities, or whether other structure models (twinning, stacking faults, or orientational disorder) have to be applied.

Unit-cell parameters of helmutwinklerite were obtained by least-square refinement of 152 accurate 2θ values (Table 6); the monoclinic *pseudocell* is obtained from the triclinic *pseudocell* by a transformation according to $(1\ 1\ 0 / 1\ -1\ 0 / 0\ 0\ 1)$: $a = 9.233$, $b = 6.367$, $c = 7.617$ Å, $\alpha = 90.22 \sim 90$, $\beta = 114.49$, $\gamma = 90.04 \sim 90^\circ$. The analysis of the measured reflections for total number $I_o > 3\ \sigma(I_o)$ / $I_o > 10\ \sigma(I_o)$ gave 792 / 734 / 667 reflections for the triclinic *pseudocell* and 11834 / 948 / 145 *superstructure* reflections. First, structure refinements on F^2 were performed in the monoclinic *pseudocell*, which resulted in $wR2 = 0.099$, $R1 = 0.028$ for 372 data with $F_o > 4\sigma(F_o)$, and $wR2 = 0.101$ and $R1 = 0.031$ for all 395 reflections and 43 variable parameters. The anisotropy of the displacement parameters was large for the O atoms; whereas that of the cations were reasonable. A transformation to the triclinic *pseudocell* changed the R values slightly: $wR2 = 0.088$, $R1 = 0.029$ for 662 data with $F_o > 4\sigma(F_o)$ and $wR2 = 0.092$ and $R1 = 0.033$ for all 715 data and 74 variable parameters. The anisotropy of the

displacement parameters is kept large especially for the atoms O(1) [principal mean square atomic displacements 0.068, 0.029 and 0.021 Å²] and O(4) [0.106, 0.065 and 0.020 Å²].

Single-crystal X-ray film investigations on well-shaped (twinned) gartrellite crystals were found to consist of an indefinite number of aggregates resulting in a broadening of the reflections in ω over some degrees; a single-crystal data collection for structural investigations was therefore impossible. Consequently, structure investigations were performed by Rietveld refinements of powder data. Tiny aggregates of 5 gartrellite samples (type material, #079, #016, #080 and #081) were hand-picked under the microscope and gently ground between two foils. After initial convergence, adjustment of the cell and profile parameters and interactive corrections with the background, all atomic coordinates and their isotropic displacement parameters (the displacement parameters for the O atoms were constrained to equal values) were refined as independent variables. Despite the fact that the samples were hand-picked with great care, the powder diagram of the type material was found to involve small amounts of quartz and mimetite, and sample #079 consists of two gartrellites in approximately equal amounts and slight different cell parameters (atomic parameters for the two phases were refined as constrained). Nevertheless, refinement of sample #079 gave a higher accuracy than that of sample #016 (obviously due to smaller texture effects and to higher count rates of the powder pattern). The samples #080 and #081 turned out to be mixtures of zincian gartrellite with duftite as well as a Ca-substituted duftite (Guillemin, 1956; Jambor *et al.*, 1980); accuracy of these refinements did not match expectations. It should be mentioned that all investigations gave no hint for the occurrence of *superstructure* reflections in the gartrellite samples under investigation.

Results and discussion

For discussion of the principles of the coordination polyhedra and the structure type of tsumcorite the reader is referred to Tillmanns & Gebert (1973). All crystal-chemical results were confirmed during the recent investigations: The $Me(2)O_6$ octahedra are edge-connected to chains in $[010]$ which are linked by the XO_4 tetrahedra

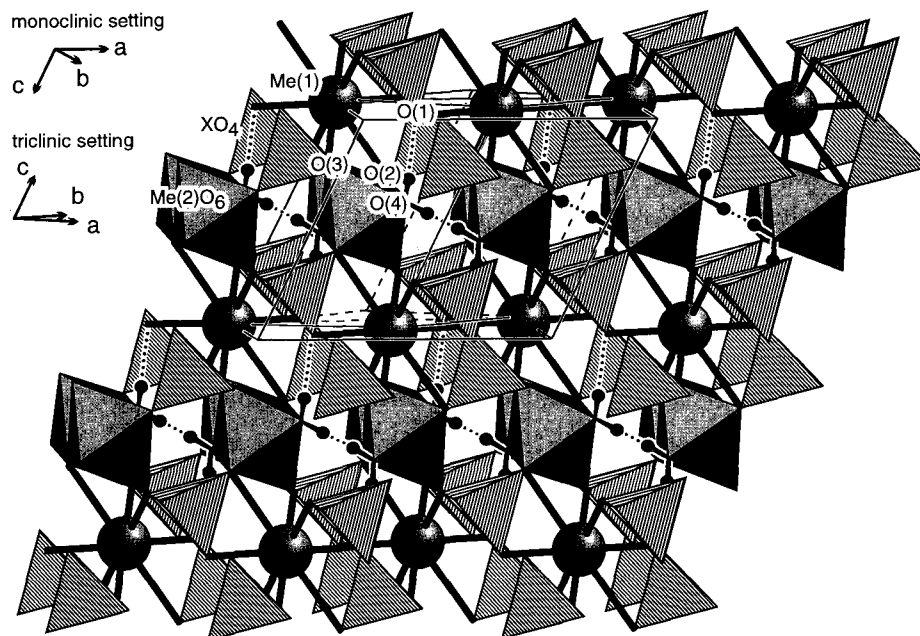


Fig. 7. The tsumcorite-type crystal structure. Within the H_3O_2 anion both formally half occupied sites of the H atoms of the symmetrically restricted hydrogen bond $O(1)\cdots O(1)$ are shown (program ATOMS, Dowty, 1995).

to form layers in (001), and the O atoms represent two layers out of a distorted close-packed arrangement. $Me(1)^{[6+2]}$ atoms link these layers. Obviously a hydrogen bond is between these layers, and a symmetrically restricted hydrogen bond is within the layer. The structure is depicted in Fig. 7.

The greater part of the tsumcorite-group minerals crystallizes with monoclinic symmetry. Although gartrellite and the average structure of helmutwinklerite show only moderate deviations from the monoclinic C -centered cell the assignment of the lower triclinic symmetry is not in doubt. The change of symmetry causes a lowering of the site symmetries of the atoms: Me(1) changes the site symmetry from $2/m$ to $\bar{1}$; X, O(1), O(2), and O(4) from m to 1; the Me(2) position splits into two positions Me(2a) and Me(2b) retaining the $\bar{1}$ symmetry, and the general position of the O(3) atom splits into two positions O(3a) and O(3b). Obviously two different reasons are responsible for the symmetry reduction: gartrellite exhibits an ordered occupation of the positions Me(2a) and Me(2b) by Fe^{3+} and Cu, respectively, and helmutwinklerite shows a particular arrangement of the hydrogen bonds.

Me(1) position

In ferrilotharmeyerite the Me(1) position is occupied by Ca atoms showing a distinct octahedral coordination with an average $\langle Ca-O \rangle$ bond length of 2.423 Å. Some interactions towards two additional ligands at opposite faces of the octahedra are evident. Despite the site symmetry $\bar{1}$, the Me(1) position is occupied by the lone-pair element Pb(II) in the other tsumcorite-type minerals under investigation. A tendency towards a larger coordination number is found for the Pb atoms as compared with the Ca atoms. The Pb atom is [6+2] coordinated in mounanaite, tsumcorite and helmutwinklerite, and essentially [8] coordinated in thometzekite (sulfatian) and gartrellite. The variation of the $O-Me(1)-O$ angles does not correlate with the difference between the six short and the two longer bonds.

Me(2) position

The Me(2) site is octahedrally coordinated, and the $O-Me(2)-O$ angles are close to 90° . For members of the solid solution series between Fe^{3+} and Zn^{2+} no deviation from $C2/m$ symmetry

was observed within accuracy of the structure refinement; the Me(2) site is statistically occupied by Fe and Zn atoms. The effective ionic radius of Zn (0.74 Å) is somewhat larger than that of Fe³⁺ (0.645 Å; Shannon, 1976). Consequently, the average <Me(2)—O> distance correlates with the Zn:Fe ratio; it is significantly larger in helmutwinklerite (2.116 and 2.107 Å) than in ferriotharmeyerite (2.059 Å) and tsumcorite (2.065 Å), and it is small in mounanaite (2.015 Å).

The ionic radius of Cu²⁺ (0.73 Å) compares with that of Zn (0.74 Å). The octahedral coordination polyhedron is avoided by the Cu atoms; instead a tetragonal bipyramidal [4+2] coordination is favoured due to the electron configuration d⁹ (Jahn-Teller effect). The positions Me(2) in thometzekite (sulfatian) and Me(2b) in gartrellite feature this distortion: Me(2)/Me(2b)—O(2) is extended to 2.272/2.30 Å. These distances are longer than the topologically equivalent bond distance within the Me(2)O₆ polyhedra of the compounds under discussion, although in general a slight lengthening of Me(2)—O(2) is observed.

Zn atoms can substitute for Fe³⁺, and a large number of minerals with a joint occupation of one position by both Cu and Zn are known, e.g. serpierite (Sabelli & Zanazzi, 1968), veszelyite (Ghose *et al.*, 1974), cuproan adamite (Toman, 1978), ktenasite (Mellini & Merlino, 1978), bayldonite (Ghose & Wan, 1979), kipushite (Piret *et al.*, 1985), ramsbeckite (Effenberger, 1988), aurichalcite (Harding *et al.*, 1994), namuwite (Groat, 1996), and bechererite (Hoffmann *et al.*, 1997). Obviously the different stereochemical behaviour of Fe³⁺ and Cu²⁺ results in the necessity of the formation of two different coordination polyhedra in gartrellite: the chain formed by the edge-connected Me(2)⁶ octahedra parallel to [010] in the monoclinic tsumcorite structures is substituted by Me(2a)O₆ = Fe⁶O₆ octahedra and Me(2b)O₆ = Cu^[4+2]O₆ tetragonal bipyramids which alternate within each chain (running parallel to [110] in the triclinic setting). Consequently the symmetry is reduced to *P*1, which is supported by the chemical analyses of gartrellite showing that the composition is close to PbCuFe(AsO₄)₂(OH)(H₂O). A similar stereochemical behaviour of Fe³⁺ and Cu²⁺ was found in medenbachite (Krause *et al.*, 1996). In zincian gartrellite the ratio Fe³⁺:Cu²⁺ is close to 1:1, and the Zn content shows a negative correlation with the deviation from monoclinic symmetry. The Zn atoms adopt the coordination polyhedra of both Fe and Cu; therefore triclinity of the gartrellites

is smaller for the zinc-rich members. In helmutwinklerite Me(2a)O₆ and Me(2b)O₆ are equal within the accuracy of structure refinements.

XO₄ group

The XO₄ groups form approximately regular tetrahedra; the average X—O bond lengths in ferriotharmeyerite, tsumcorite, gartrellite and helmutwinklerite correspond with an occupation by As atoms. The significant shortening of the <X—O> bond lengths in thometzekite (sulfatian) indicates a partial incorporation by P or S; electron-microprobe analyses show substantial amounts of S. In mounanaite an occupation of the X position by V is verified by the chemical analyses, by interatomic distances, and by scattering function refinements.

Protonated anion groups were postulated on the basis of an IR spectrum for lotharmeyerite (Kampf *et al.*, 1984) and by analogy also for ferriotharmeyerite (Ansell *et al.*, 1992). Therefore using the structure data, the geometry of the anion group was carefully examined for the presence of an XO₃OH group. Protonated anion groups generally show an elongated X—O_h distance (O_h = hydroxyl group) (Ferraris & Ivaldi, 1984). The individual X—O(2) distances within the XO₄ groups of ferriotharmeyerite, tsumcorite, mounanaite and gartrellite are slightly lengthened; in thometzekite (sulfatian) and helmutwinklerite the X—O(2) bond is shortened because of the extension of the Me(2)—O(2) bond, which is the elongated axis in the tetragonal bipyramid Cu^[4+2]O₆. However, the O(2) atoms cannot be considered as O_h atoms due to their [4] coordination by one Me(1) atom, two Me(2) atoms, and one X atom and due to their saturated bond valences (Table 10). In addition protonated anion groups as a rule show a decrease of the O_h—X—O angles and an increase of the O—X—O angles which could not be verified for the tsumcorite-group minerals; Baur (1974) reported for the relevant angles in protonated phosphates average values of 106.9° and 111.9°. Single-crystal X-ray investigations gave only decreased O(2)—X—O(4) angles (102.4° to 107.4°); the other O(2)—X—O angles are larger than 108.9°. Therefore the crystal-chemical considerations as well as the IR measurements allow the conclusion that the investigated compounds do not have protonated anion groups. As a result, the chemical formula of ferriotharmeyerite (based on 10

Table 10. Bond valences v (in valence units) for the oxygen atoms (O(1) = F in mounanaite) without contribution of the hydrogen atoms (according to Brese & O'Keeffe, 1991).

	ferrilothar- meyerite	tsumcorite	thometzekite (sulfatian)	mounanaite	gartrellite	helmut- winklerite
O(1)	0.90	0.86	0.83	0.90	0.92	0.73
O(2)	1.93	1.92	1.91	1.99	1.76	2.01
O(3),O(3a)	1.92	1.96	1.94	2.06	2.05	1.88
O(3b)					1.97	1.88
O(4)	1.67	1.60	1.58	1.87	1.33	1.46

oxygen atoms) has to be revised to $\text{Pb}(\text{Fe}^{3+}, \text{Zn})_2(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})$. Considering the cell metric, crystal chemistry and powder pattern, lotharmeyerite belongs to the tsumcorite group. Consequently the chemical formula of lotharmeyerite should be changed to $\text{Ca}(\text{Mn}^{3+}, \text{Zn})_2(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$ (based on 10 oxygen atoms) from that given by Dunn (1983), $\text{CaZnMn}^{3+}(\text{AsO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$, and by Kampf *et al.* (1984), $\text{CaZnMn}^{3+}(\text{AsO}_3\text{OH})_2(\text{OH})_3$.

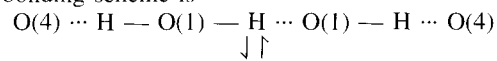
Charge balance and hydrogen bonding scheme

One of the most striking problems within the tsumcorite-group minerals is the charge balance involving $\text{Me}(2)^{2+}:\text{Me}(2)^{3+}$ and $\text{Me}(1)^{2+}:\text{Me}(1)^{3+}$ cations, $(\text{XO}_4)^{3-}:(\text{SO}_4)^{2-}$ anions and $(\text{OH})^{1-}:(\text{H}_2\text{O})^0$ groups. The relevant exchange mechanisms have already been mentioned in the section 'chemical composition'.

In ferrilotharmeyerite, tsumcorite, sulfatian thometzekite, gartrellite and helmutwinklerite O(1)···O(1) contacts from 2.543 to 2.636 Å indicate strong hydrogen bonds which are among the longest symmetrically restricted bonds (Catti & Ferraris, 1976; Jessen & Küppers, 1991; Steiner & Sängler, 1994; and references therein). They are centered at the position (0 0 0.5) with site symmetry $2/m$ and $\bar{1}$ for the samples with space group $C2/m$ and $P\bar{1}$; a displacement of the H atom towards one of the two O(1) atoms is expected. In contrast O(1)···O(4) is 2.607 to 2.758 Å, which is characteristic for a strong, but asymmetric hydrogen bond. This hydrogen-bonding scheme was already given by Tillmanns & Gebert (1973), and is in accordance with the IR spectra. It is also supported by the bond valences (Table 10): the sum of bond valences indicate that hydrogen atoms are covalently bound to the O(1) atoms and that the O(4)^[2] atoms are acceptors of hydrogen bonds. Bond valences are satisfactory for the atoms O(2) and O(3).

In mounanaite the interatomic distances corresponding to the hydrogen bonds within the other compounds change significantly. The O(1)···O(1) distance increases to 2.738 Å and could be interpreted as an interatomic but not bound contact. O(1)···O(4) is increased nearly to 3 Å, and the O(1)···O(3) contacts are longer. The bond distances to the atoms O(1) and O(4) within the $\text{Me}(1)\text{O}_8$, $\text{Me}(2)\text{O}_6$, and XO_4 polyhedra are shortened as compared with the other title minerals; consequently the bond valence at O(4) is increased to 1.87 v.u. and need not be interpreted as the acceptor of a hydrogen bond. From these crystal-chemical considerations and from structure refinement a (partial) occupation of the O(1) position by fluorine instead of oxygen is evident. These findings could not be verified by electron-microprobe analyses, although these investigations were performed with great care. This might be caused by absorption phenomena due to the high absorption coefficient and a poor polish of the surface.

A composition of ferrilotharmeyerite and tsumcorite according to a ratio $\text{Me}(2)^{2+}:\text{Me}(2)^{3+} = 1:1$ requires one H_2O molecule and one OH group p.f.u. assuming pure $(\text{XO}_4)^{3-}$ anions. In accordance with Tillmanns & Gebert (1973) it has to be expected that the atomic position O(1) is occupied by O atoms belonging half to H_2O molecules and half to OH groups. The hydrogen bonding scheme is



O(4) ··· H — O(1) ··· H — O(1) — H ··· O(4)
Formally such a formation can be characterized as an $(\text{H}_3\text{O}_2)^-$ anion. The $(\text{H}_3\text{O}_2)^-$ anion was described in natrochalcite and in some organic and inorganic compounds (Clearfield *et al.*, 1976; Abu-Dari *et al.*, 1979; Bino & Gibson, 1981, 1982, 1984; Giester & Zemann, 1987; Giester, 1989; Chevrier *et al.*, 1990, 1993). The local site symmetry of the central O(1)···O(1) bond is vio-

lated. The formula for the tsumcorite-group minerals with $\text{Me}(2)^{2+}:\text{Me}(2)^{3+} = 1:1$ and $(\text{XO}_4)^{3-}$ is therefore $\text{Me}(1)^{2+}\text{Me}(2)^{2+}\text{Me}(2)^{3+}(\text{XO}_4)_2(\text{OH})(\text{H}_2\text{O})$ or possibly $\text{Me}(1)^{2+}\text{Me}(2)^{2+}\text{Me}(2)^{3+}(\text{XO}_4)_2(\text{H}_3\text{O}_2)$.

An exclusive occupation of the Me(2) site with trivalent cations causes the O(1) sites to be fully occupied by hydroxyl groups; consequently only two of the three hydrogen bonds discussed above are formed. An exclusive occupation of the Me(2) site with divalent cations causes a complete occupation of the O(1) sites by water molecules. The three short O...O bonds are essentially maintained. An additional fourth H atom forms essentially a free hydrogen bond: only two O(3) atoms form O(1)...O contacts below 3.5 Å which do not represent an edge in the $\text{Me}(1)^{6+2}\text{O}_8$, $\text{Me}(2)^{6}\text{O}_6$ or XO_4 polyhedra. Exchange mechanisms like $[(\text{OH})_2]^{2-} \leftrightarrow (\text{H}_3\text{O}_2)^-$ (for an excess of trivalent cations) or $(\text{H}_3\text{O}_2)^- \leftrightarrow \text{H}_2\text{O}_2^0$ (for an excess of divalent cations) are necessary for charge balance; consequently the general formula for the tsumcorite-group minerals (considering only the common solid solution on the Me(2) site) is $\text{Me}(1)^{2+}\text{Me}(2)_{2-x}^{2+}\text{Me}(2)_x^{3+}(\text{XO}_4)_2(\text{H}_2\text{O})_{2-x}(\text{OH})_x$, $0 \leq x \leq 2$.

In the monoclinic and triclinic pseudocell of helmutwinklerite a strong anisotropic displacement was found for the O atoms, especially for O(1) and O(4). By chemical analyses, infrared measurements and structure investigations helmutwinklerite requires two H_2O molecules p.f.u.; consequently both O(1) atoms are donors of two hydrogen bonds. Besides the contact from O(1) to another O(1) atom and to O(4), there are only two O(1)...O contacts below 3.5 Å that are no edges in the $\text{Me}(3a)\text{O}_6$ or $\text{Me}(2b)\text{O}_6$ polyhedron: one to the O(3a) atom and one to the O(3b) atom with 3.042(13) and 3.026(17) Å, respectively. It is assumed that the hydrogen bonds in helmutwinklerite are ordered resulting in a complex bonding scheme which causes the weak superstructure reflections and the triclinic symmetry.

Thometzekite is the second mineral out of the tsumcorite group with an exclusive occupation of the Me(2) position by Me^{2+} atoms (Cu, Zn). Among the material available only sulfate-bearing thometzekite was found to be suitable for structural studies. Superstructure reflections were not observed by long-exposed single-crystal X-ray film investigations, but somewhat larger anisotropic displacement parameters have been observed during structure refinements. A trial to refine the unit-cell parameters according to triclinic symmetry gave no hint for a lowering of

symmetry: $\alpha = 90.001(32)^\circ$ and $\gamma = 89.997(35)^\circ$. For the investigated crystal approximately $\frac{1}{3}$ of the $(\text{AsO}_4)^{3-}$ anions are substituted by $(\text{SO}_4)^{2-}$ groups, which balances parts of the excess of divalent Me(2) atoms and obviously stabilizes monoclinic symmetry. By analogy with helmutwinklerite, triclinic symmetry seems to be likely for sulfate-free thometzekite, $\text{Pb}(\text{Cu,Zn})_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$.

Redefinition of gartrellite

In the course of the present study on the tsumcorite-group minerals it became evident that the general formula for these minerals $\text{Me}(1)\text{Me}(2)_2(\text{XO}_4)_2(\text{OH},\text{H}_2\text{O})_2$ does not fit with the formula for gartrellite proposed in the original description (Nickel *et al.*, 1989). Their empirical formula $\text{Pb}_{1.04}\text{Cu}_{1.22}\text{Fe}_{0.74}(\text{AsO}_4)_{1.88}(\text{SO}_4)_{0.10}(\text{CO}_3)_{0.54}(\text{H}_2\text{O})_{0.18}$ was based on $\text{Cu} + \text{Fe} + \text{Pb} = 3$ and it was simplified to $\text{Pb}(\text{Cu,Fe})_2(\text{AsO}_4,\text{SO}_4)_2(\text{CO}_3,\text{H}_2\text{O})_x$, where x is approximately 0.7. The main difference is the lack of substantial carbonate in the new chemical analyses of gartrellite (Table 3b). It was therefore decided to redefine gartrellite as suggested by E.H. Nickel. The redefinition was based on holotype material from Ashburton Downs, W.A., Australia, with a focus on the chemical composition (microprobe analyses, microchemical tests, IR spectra) and the crystallographic properties (X-ray diffraction and Rietveld refinement). For the general description and the physical and optical properties the reader is referred to the original description of gartrellite.

Chemical analyses by means of an electron microprobe (Table 3b) gave similar results to those reported by Nickel *et al.* (1989), except for CO_2 which could not be detected. Gartrellite is slowly soluble in warm dilute hydrochloric acid. Observing the dissolution process under the microscope, no indication for a formation of CO_2 gas was found; gartrellite samples from other localities show the same behaviour. Type material and gartrellite from Tsumeb gave very similar FT-IR spectra (Fig. 5); in particular, there was no distinct absorption in both samples due to carbonate (1400-1500 cm^{-1} region). Reference data of samples with admixed carbonate phases show that even amounts from 1 to 10 wt.% carbonate phase are clearly observable. The presence of substantial amounts of carbonate can therefore be

excluded. The powder diffraction pattern is close to the data of the original description of gartrellite. Refined unit-cell parameters are given in Table 5. Single-crystal X-ray investigations were impossible because of the small crystal size ($< 10 \mu\text{m}$); consequently structural information was performed by Rietveld refinement of the powder data. The residuals of samples from the type locality of gartrellite, from Tsumeb (#079), and from Reichenbach (#016) are given in Table 7. These values confirm the identity of the structural data of the investigated samples. It should be mentioned that the type structure does not allow the incorporation of additional carbonate groups. The proposal to redefine gartrellite as having a chemical composition corresponding to the formula $\text{PbCu}(\text{Fe,Cu})(\text{AsO}_4)_2(\text{OH,H}_2\text{O})_2$ and the crystallographic parameters given in Table 5 has been approved prior to publication.

Related structure types

Tsumcorite is isotypic with natrochalcite, $\text{NaCu}_2(\text{SO}_4)_2(\text{H}_3\text{O}_2)$. The crystal structure of natrochalcite was first determined by Rumanova & Volodina (1958). Subsequently natural natrochalcite and a number of synthetic compounds were investigated with $\text{Me}(1) = \text{Na, K, Rb, Ag, Tl, NH}_4$; $\text{Me}(2) = \text{Cu, Mn, Ni, Co, Zn}$; $\text{X} = \text{S, Se, Mo, Cr}$, and additional compounds with a PO_3F group instead of XO_4 (see Chevrier *et al.*, 1993, and references therein). In the natrochalcite-series compounds the $\text{Me}(1)$ and $\text{Me}(2)$ positions are occupied by *mono-* and *divalent* cations, respectively; together with the $(\text{XO}_4)^{2-}$ anion three hydrogen atoms are required for charge balance. The formation of an H_3O_2 configuration was proved by neutron diffraction studies (Chevrier *et al.*, 1993). Even in the natrochalcite-series the hydrogen-bond lengths vary on a wide scale. In general, within the natrochalcite-type series the $\text{O}\cdots\text{O}$ distances of the symmetrically restricted hydrogen bonds are shorter than in the tsumcorite-type compounds, but the length of the asymmetric hydrogen bonds tends to be longer: the former varies from 2.440 Å in $\text{NaCu}_2(\text{SO}_4)_2(\text{H}_3\text{O}_2)$ to 2.606 Å in $\text{TlCu}_2(\text{SeO}_4)_2(\text{H}_3\text{O}_2)$, the latter from 2.695 Å in $\text{NaCu}_2(\text{SO}_4)_2(\text{H}_3\text{O}_2)$ to 3.114 Å in $\text{RbCu}_2(\text{SO}_4)_2(\text{H}_3\text{O}_2)$ (Giester, 1989). Effenberger (1989) showed the structural similarities between natrochalcite, dolerophanite and synthetic $\text{KCu}^{2+4}\text{Cu}_2^{4+2}[(\text{AsO}_4)\text{H}(\text{AsO}_4)](\text{OH})_2$.

A number of minerals with the general formula $\text{Me}(1)\text{Me}(2)_2(\text{XO}_4)_2(\text{OH,H}_2\text{O})_2$ are known to form a variety of structure types in apparent response to the variation in size and coordination of the cations $\text{Me}(1)$ and $\text{Me}(2)$ and to the size of the XO_4 tetrahedron. Pring *et al.* (1989) mentioned the relation between the isochemical $\text{PbFe}_2(\text{AsO}_4)_2(\text{OH})_2$ minerals carminite and mawbyite. Carminite has FeO_6 octahedra alternately linked to each other by $\text{O}-\text{O}$ edges and an O vertex to chains which are interconnected by the AsO_4 tetrahedra to a network; large holes are occupied by the Pb atoms. Olmi & Sabelli (1995) discussed on the basis of structural refinements the hydrogen bonding schemes and found evidence for short and symmetrically restricted hydrogen bonds. Further minerals with a similar chemical composition but different structures are lipscombite, $\text{Fe}_3(\text{PO}_4)_2(\text{OH})_2$ (Vencato *et al.*, 1989), jagowerite, $\text{BaAl}_2(\text{PO}_4)_2(\text{OH})_2$ (Meagher, 1974), the lazulite group minerals $(\text{Mg,Fe})\text{Al}_2(\text{PO}_4)(\text{OH})_2$ (Giuseppetti & Tadini, 1983) and hentschelite, $\text{CuFe}_2(\text{OH})_2(\text{PO}_4)_2$ (Sieber *et al.*, 1987), kimrite, $\text{BaAl}_2(\text{SiO}_4)_2(\text{H}_2\text{O})_2$ (Bolotina *et al.* (1991), scholzite, $\text{CaZn}_2(\text{PO}_4)_2(\text{H}_2\text{O})_2$ (Taxer, 1975), collinsite, $\text{MgCa}_2(\text{PO}_4)_2(\text{H}_2\text{O})_2$ (Brotherton *et al.*, 1974), thalmessite, $(\text{Mg,Co})\text{Ca}_2(\text{AsO}_4)_2(\text{H}_2\text{O})_2$ (Catti *et al.*, 1977), the fairfieldite group, $\text{MnCa}_2(\text{PO}_4)(\text{H}_2\text{O})_2$ (Fanfani *et al.*, 1970), and the kroehnkite group, $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Hawthorne & Fergusson, 1975). Drugmannite, $\text{Pb}(\text{Fe,Al})_2[(\text{PO}_4)\text{H}(\text{PO}_4)](\text{OH})_2$ (King & Sengier-Roberts, 1988) forms a hydrogen bond between two phosphate tetrahedra.

The relation between the structure types of tsumcorite and brackebuschite, $\text{Pb}_2(\text{Mn,Fe})(\text{VO}_4)_2 \cdot \text{H}_2\text{O}$ has been mentioned in the literature: Geier *et al.* (1971) noticed similarities within the cell metric of the two minerals. For a detailed comparison of the crystal structures of tsumcorite and arsenbrackebuschite, $\text{Pb}_2(\text{Fe,Zn})(\text{AsO}_4)_2(\text{OH,H}_2\text{O})$, see Hofmeister & Tillmanns (1978). The relationship of bearthite, $\text{Ca}_2\text{Al}(\text{PO}_4)_2(\text{OH})$, to brackebuschite, tsumcorite and many other minerals was discussed by Chopin *et al.* (1993). It should be mentioned that the hydrogen bonding schemes in tsumcorite and brackebuschite or arsenbrackebuschite (and obviously in its zinc analogue feinglosite, $\text{Pb}_2(\text{Zn,Fe})[(\text{As,S})\text{O}_4]_2 \cdot \text{H}_2\text{O}$, Clark *et al.*, 1997) are basically different; in the latter two minerals one atomic site is statistically occupied by O atoms of OH groups and H_2O molecules, and the formation of a symmetrically restricted hydrogen bond is avoided.

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References

- Abu-Dari, K., Raymond, K.N., Freyberg, D.P. (1979): The bihydroxide (H_3O_2) anion. A very short symmetric hydrogen bond. *J. Amer. Chem. Soc.*, **101**, 3688-3689.
- Ansell, H.G., Roberts, A.C., Dunn, P.J., Birch, W.D., Ansell, V.E., Grice, J.D. (1992): Ferrilotharmeyerite, a new Ca-Zn-Fe³⁺ hydroxyl arsenate from Tsumeb, Namibia. *Can. Mineral.*, **30**, 215-217.
- Baur, W. (1974): The geometry of polyhedral distortions. Predictive relationships for the phosphate group. *Acta Cryst.*, **B30**, 1195-1215.
- Bérar, J.-F. & Lelann, P. (1991): E.S.D.'s and estimated probable errors obtained in Rietveld refinements with local correlations. *J. Appl. Cryst.*, **24**, 1-5.
- Bino, A. & Gibson, D. (1981): A new bridging ligand, the hydrogen oxide ion (H_3O_2). *J. Amer. Chem. Soc.*, **103**, 6741-6742.
- , — (1982): The hydrogen oxide bridging ligand (H_3O_2). 1. Dimerization and polymerization of hydrolyzed trinuclear metal cluster ions. *J. Amer. Chem. Soc.*, **104**, 4383-4388.
- , — (1984): The hydrogen oxide ligand (H_3O_2). 2. Effect of the hydrogen ion concentration. *Inorg. Chem.*, **23**, 109-115.
- Bolotina, N.B., Rastsvetaeva, R.K., Andrianov, V.I., Kashaev, A.A. (1991): Refinement of modulated crystals. Structure of kimrite. *Kristallografiya*, **36**, 361-368.
- Breese, N.E. & O'Keefe, M. (1991): Bond-valence parameters for solids. *Acta Cryst.*, **B47**, 192-197.
- Brotherton, P.D., Maslen, E.N., Pryce, M.W., White, A.H. (1974): Crystal structure of collinsite. *Austral. J. Chem.*, **27**, 653-656.
- Caglioti, G., Paoletti, A., Ricci, F.P. (1958): Choice of collimators for a crystal spectrometer for neutron diffraction. *Nucl. Inst.*, **3**, 223-228.
- Catti, M. & Ferraris, G. (1976): Very short hydrogen bonds and crystallographic symmetry. *Acta Cryst.*, **B32**, 2754-2756.
- Catti, M., Ferraris, G., Ivaldi, G. (1977): Hydrogen bonding in the crystalline state. Structure of talmesite, $\text{Ca}_2(\text{Mg},\text{Co})(\text{AsO}_4)_2(\text{H}_2\text{O})_2$, and crystal chemistry of related minerals. *Bull. Soc. fr. Minéral. Cristallogr.*, **100**, 230-236.
- Cesbron, F. & Fritsche, J. (1969): La mounanaïte, nouveau vanadate de fer et de plomb hydraté. *Bull. Soc. fr. Minéral. Cristallogr.*, **92**, 196-202.
- Chevrier, G., Giester, G., Jarosch, D., Zemann, J. (1990): Neutron diffraction study of the hydrogen bond system in $\text{Cu}_2\text{K}(\text{H}_3\text{O}_2)(\text{SO}_4)_2$. *Acta Cryst.*, **C46**, 175-177.
- Chevrier, G., Giester, G., Zemann, J. (1993): Neutron refinements of $\text{RbCu}_2(\text{H}_3\text{O}_2)(\text{SO}_4)_2$ and $\text{RbCu}_2(\text{H}_3\text{O}_2)(\text{SeO}_4)_2$: variation of the hydrogen bond system in the natrochalcite type series. *Z. Krist.*, **206**, 7-14.
- Chopin, Ch., Brunet, F., Gebert, W., Medenbach, O., Tillmanns, E. (1993): Bearthite, $\text{Ca}_2\text{Al}[\text{PO}_4]_2(\text{OH})$, a new mineral from high-pressure terranes of the western Alps. *Schweiz. mineral. petrogr. Mitt.*, **73**, 1-9.
- Clark, A.M., Criddle, A.J., Roberts, A.C., Bonardi, M., Moffatt, E.A. (1997): Feinglosite, a new mineral related to brackebuschite, from Tsumeb, Namibia. *Mineral. Mag.*, **61**, 285-289.
- Clearfield, A., Sims, M.J., Gopal, R. (1976): Studies of heavy-metal molybdates. I: Crystal structure of a basic zinc molybdate, $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$. *Inorg. Chem.*, **15**, 335-338.
- Deyu, L., O'Connor, B.H., Roach, G.I.D., Cornell, J.B. (1990): Use of X-ray powder diffraction Rietveld pattern-fitting for characterising preferred orientation in gibbsite. *Powder Diffraction*, **5**, 79-85.
- Dollase, W.A. (1986): Corrections of intensities for preferred orientation in powder diffractometry: application of the March model. *J. Appl. Cryst.*, **19**, 267-272.
- Dowty, E. (1995): ATOMS 3.2. A Computer Program for Displaying Atomic Structures, Kingsport, TN 37663.
- Dunn, P.J. (1983): Lotharmeyerite, a new mineral from Mapimi, Durango, Mexico. *Mineral. Rec.*, **14**, 35-36.
- Effenberger, H. (1988): Ramsbeckite, $(\text{Cu},\text{Zn})_{15}(\text{OH})_{22}(\text{SO}_4)_4 \cdot 6\text{H}_2\text{O}$: Revision of the chemical formula based on a structure determination. *N. Jb. Mineral. Mh.*, **1988**, 38-48.

- (1989): An uncommon $\text{Cu}^{2+4}\text{O}_6$ coordination polyhedron in the crystal structure of $\text{KCu}_3(\text{OH})_2[(\text{AsO}_4)\text{H}(\text{AsO}_4)]$ (with a comparison to related structure types). *Z. Krist.*, **188**, 43-56.
- Elliott, P., Pring, A., Birch, W.D. (1988): Tsumcorite from Puttapa, South Australia. *Austral. Mineral.*, **3**, 67-69.
- Fanfani, L., Nunzi, A., Zanazzi, P.F. (1970): The crystal structure of fairfieldite. *Acta Cryst.*, **26**, 640-645.
- Ferraris, G. & Ivaldi, G. (1984): X—OH and O—H···O bond lengths in protonated oxoanions. *Acta Cryst.*, **B40**, 1-6.
- Fischer, R.X. & Tillmanns, E. (1988): The equivalent isotropic displacement factor. *Acta Cryst.*, **C44**, 775-776.
- Fischer, R.X., Lengauer, C.L., Tillmanns, E., Ensink, R.J., Reiss, C.A., Fantner, E.J. (1993): PC-Rietveld plus, a comprehensive Rietveld analysis package for PC. *Mater. Sci. Forum*, **133-136**, 287-292.
- Frenz, B.A. & Associates (1992): Personal SDP, College Station, TX, USA.
- Gebhard, G. & Schlüter, J. (1995): Tsumeb, Namibia: Interessante Neufunde und Neubestimmungen. *Lapis*, **20 (10)**, 24-32.
- Geier, B.H., Kautz, K., Müller, G. (1971): Tsumcorit(e) $[\text{PbZnFe}(\text{AsO}_4)_2]\cdot\text{H}_2\text{O}$, ein neues Mineral aus den Oxidationszonen der Tsumeb-Mine, Südwestafrika. *N. Jb. Mineral. Mh.*, **1971**, 305-309.
- Ghose, S. & Wan, C. (1979): Structural chemistry of copper and zinc minerals. VI. Bayldonite, $(\text{Cu,Zn})_3\text{Pb}(\text{AsO}_4)_2(\text{OH})_2$: a complex layer structure. *Acta Cryst.*, **B35**, 819-823.
- Ghose, S., Leo, S.R., Wan, C. (1974): Structural chemistry of copper and zinc minerals. Part I. Veszelyite, $(\text{Cu,Zn})_2\text{ZnPO}_4(\text{OH})_3\cdot 2\text{H}_2\text{O}$: A novel type of sheet structure and crystal chemistry of copper-zinc substitution. *Am. Mineral.*, **59**, 573-581.
- Giester, G. (1989): The crystal structures of $\text{Ag}^+\text{Cu}_2(\text{OH})(\text{SO}_4)_2\cdot\text{H}_2\text{O}$ and $\text{Me}^+\text{Cu}_2(\text{OH})(\text{SeO}_4)_2\cdot\text{H}_2\text{O}$ [$\text{Me}^+ = \text{Ag}, \text{Tl}, \text{NH}_4$], four new representatives of the natrochalcite type, with a note on natural natrochalcite. *Z. Krist.*, **187**, 239-247.
- Giester, G. & Zemann, J. (1987): The crystal structure of the natrochalcite type compounds $\text{Me}^+\text{Cu}_2(\text{OH})(\text{zO}_4)_2\cdot 2\text{H}_2\text{O}$ [$\text{Me}^+ = \text{Na}, \text{K}, \text{Rb}; \text{z} = \text{S}, \text{Se}$], with special reference to the hydrogen bonds. *Z. Krist.*, **179**, 431-442.
- Giuseppetti, G. & Tadini, C. (1983): Lazulite, $(\text{Mg,Fe})\text{Al}_2(\text{OH})_2(\text{PO}_4)_2$: structure refinement and hydrogen bonding. *N. Jb. Mineral. Mh.*, **1983**, 410-416.
- Groat, L.A. (1996): The crystal structure of namuwite, a mineral with Zn in tetrahedral and octahedral coordination, and its relationship to the basic zinc sulfates. *Am. Mineral.*, **81**, 238-243.
- Guillemin, C. (1956): Contribution à la minéralogie des arsénates, phosphates et vanadates de cuivre: arsénates de cuivre. *Bull. Soc. franç. Minér. Crist.*, **79**, 7-95.
- Harding, M.M., Kariuki, B.M., Cernik, R., Cressey, G. (1994): The structure of aurichalcite, $(\text{Cu,Zn})_5(\text{OH})_6(\text{CO}_3)_2$, determination from a microcrystal. *Acta Cryst.*, **B50**, 673-676.
- Harlow, G.E., Dunn, P.J., Rossman, G.R. (1984): Gamaragite: a re-examination and comparison with brackebuschite-like minerals. *Am. Mineral.*, **69**, 803-806.
- Hawthorne, F.C. & Fergusson, R.B. (1975): Refinement of the crystal structure of kroehnkite. *Acta Cryst.*, **B31**, 1753-1755.
- Hoffmann, Ch., Armbruster, Th., Giester, G. (1997): The acentric structure (P3) of bechererite, $\text{Zn}_7\text{Cu}(\text{OH})_{13}[\text{SiO}(\text{OH})_3\text{SO}_4]$. *Am. Mineral.*, **82**, 1014-1018.
- Hofmeister, W. & Tillmanns, E. (1978): Strukturelle Untersuchungen an Arsenbrackebuschit. *Tschermaks mineral. petrogr. Mitt.*, **25**, 153-163.
- Hovestreydt, E. (1983): On the atomic scattering factor for O^{2-} . *Acta Cryst.*, **A39**, 268-269.
- Jambor, J.L., Owens, D.R., Dutrizac, J.E. (1980): Solid solution in the adelite group of arsenates. *Can. Mineral.*, **18**, 191-195.
- Jessen, S.M. & Küppers, H. (1991): Crystal and molecular structure and infrared spectra of tetraethylammonium hydrogen phthalate and tetrabutylammonium hydrogen phthalate. *J. Mol. Struct.*, **263**, 247-265.
- Kampf, A.R., Shigley, J.E., Rossman, G.R. (1984): New data on lotharmeyerite. *Mineral. Rec.*, **15**, 223-226.
- Keller, P. (1984): Tsumeb. *Lapis*, **9 (7/8)**, 13-63.
- King, G.S.D. & Sengier-Roberts, L. (1988): Drugmannite, $\text{Pb}_2(\text{Fe}_{0.78}\text{Al}_{0.22})\text{H}(\text{PO}_4)_2(\text{OH})_2$: its crystal structure and place in the datolite group. *Bull. Minéral.*, **111**, 431-437.
- Kokinos, M. & Wise, W.S. (1993): The Gold Hill Mine, Tooele County, Utah. *Mineral. Rec.*, **24**, 11-22.
- Krause, W., Belendorff, K., Bernhardt, H.-J., McCammon, C., Effenberger, H., Mikenda, W. (1997): New crystal chemical data for minerals of the tsumcorite-group. *Z. Kristallogr., Suppl. Issue*, **12**, 249.
- Krause, W., Bernhardt, H.-J., Gebert, W., Graetsch, H., Belendorff, K., Petitjean, K. (1996): Medenbachite, $\text{Bi}_2\text{Fe}(\text{Cu,Fe})(\text{O,OH})_2(\text{OH})_2(\text{AsO}_4)_2$, a new mineral species: its description and crystal structure. *Am. Mineral.*, **81**, 505-512.
- Long, G.J., Cranshaw, T.E., Longworth, G. (1983): The ideal Mössbauer effect absorber thickness. *Mössbauer Effect Reference and Data Journal*, **6**, 42-49.

- Mandarino, J.A. (1981): Comments on the calculation of the density of minerals. *Can. Mineral.*, **19**, 531-534.
- Martin, M. & Schlegel, F. (1992): Kobaltaustinit und Tsumcorit von der Rappold-Fundgrube in Schneeberg / Sachsen. *Lapis*, **17** (10), 28-29.
- Martin, M., Schlegel, F., Siemroth, J. (1994): Das Bergbaurevier Niederschlag bei Oberwiesenthal: Seltene Kupferarsenate aus dem Sächsischen Erzgebirge. *Lapis*, **19** (4), 13-22.
- Meagher, E.P. (1974): The crystal structure of jagowerite. *Am. Mineral.*, **59**, 291-295.
- Mellini, M. & Merlino, S. (1978): Ktenasite, another mineral with $\infty_2[(Cu,Zn)_2(OH)_3O]$ octahedral sheets. *Z. Krist.*, **147**, 129-140.
- Nickel, E.H. (1992): Solid solutions in mineral nomenclature. *Mineral. Mag.*, **56**, 127-130.
- Nickel, E.H., Robinson, B.W., Gerald, J.F., Birch, W.D. (1989): Gartrellite, a new secondary arsenate mineral from Ashburton Downs, W.A. and Broken Hill, N.S.W. *Austral. Mineral.*, **4**, 83-89.
- Olmi, F. & Sabelli, C. (1995): Carminite from three localities of Sardinia (Italy): crystal structure refinements. *N. Jb. Mineral. Mh.*, **1995**, 553-562.
- Pinch, W.W. & Wilson, W.E. (1977): Tsumeb minerals: a descriptive list. *Mineral. Rec.*, **8**, 17-37.
- Piret, P., Deliens, M., Piret-Meunier, J. (1985): Occurrence and crystal structure of kipushite, a new copper-zinc phosphate from Kipushi, Zaire. *Can. Mineral.*, **23**, 35-42.
- Pring, A., McBriar, E.M., Birch, W.D. (1989): Mawbyite, a new arsenate of lead and iron related to tsumcorite and carminite, from Broken Hill, New South Wales. *Am. Mineral.*, **74**, 1377-1381.
- Rietveld, H.M. (1969): A profile refinement method for nuclear and magnetic structures. *J. Appl. Cryst.*, **2**, 65-71.
- Rumanova, I.M. & Volodina, G.F. (1958): The crystal structure of natrochalcite $NaCu(OH)[SO_4] \cdot H_2O = Na[SO_4]_2[Cu_2(OH)_2O]$. *Dokl. Acad. Nauk. SSSR*, **123**, 78-81.
- Sabelli, C. & Zanazzi, P.F. (1968): The crystal structure of serpierite. *Acta Cryst.*, **B24**, 1214-1221.
- Schlegel, F., Kleeberg, R., Meissen, N. (1996): Sekundäre Wismutminerale und weitere Neufunde aus Schneeberg / Sachsen, 1992-1995. *Lapis*, **21** (9), 37-42.
- Schmetzer, K., Nuber, B., Medenbach, O. (1985): Thometzekite, a new mineral from Tsumeb, Namibia, and symmetry relations in the tsumcorite-helmutwinklerite family. *N. Jb. Mineral. Mh.*, **1985**, 446-452.
- Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.*, **A32**, 751-767.
- Sheldrick, G.M. (1976): SHELX-76 Programs for crystal structure determination, Univ. Cambridge, England.
- (1993): SHELXL-93 Program for crystal structure refinement, Univ. Göttingen, Germany.
- Sieber, N.W.H., Tillmanns, E., Hofmeister, W. (1987): Structure of hentschelite, $CuFe_2(PO_4)_2(OH)_2$, a new member of the lazulite group. *Acta Cryst.*, **C43**, 1855-1857.
- Steiner, Th. & Sängler, W. (1994): Lengthening of the covalent O—H and O—H...O hydrogen bonds re-examined from low-temperature neutron diffraction data of organic compounds. *Acta Cryst.*, **B50**, 348-357.
- Süsse, P. & Schnorrer, G. (1980): Helmutwinklerite, a new arsenate mineral from Tsumeb, S.W. Africa. *N. Jb. Mineral. Mh.*, **1980**, 118-124.
- Taxer, K.J. (1975): Structural investigation on scholzite. *Am. Mineral.*, **60**, 1019-1022.
- Tillmanns, E. & Gebert, W. (1973): The crystal structure of tsumcorite, a new mineral from the Tsumeb Mine, S.W. Africa. *Acta Cryst.*, **B29**, 2789-2794.
- Toman, K. (1978): Ordering in olivenite-adamite solid solutions. *Acta Cryst.*, **B34**, 715-721.
- Vencato, I., Mattievich, E., Mascarenhas, Y.P. (1989): Crystal structure of synthetic lipscombite: a re-determination. *Am. Mineral.*, **74**, 456-460.
- Walenta, K. (1981): Neue Mineralfunde aus der Grube Michael im Weiler bei Lahr. *Aufschluß*, **32**, 333-340.
- (1988): Neue Mineralfunde aus der Grube Clara. (3. Folge). *Lapis*, **13**(3), 11-22.
- (1989): Neufunde aus dem Schwarzwald. *Lapis*, **14**(5), 30-40.
- (1993): Neue Mineralfunde aus der Grube Clara. (5. Folge). *Lapis*, **18**(1), 16-23.
- (1995): Neue Mineralfunde aus der Grube Clara. (6. Folge, 1. Teil). *Lapis*, **20**(5), 22-38.
- Wilson, A.J.C. (ed.) (1992): International Tables for Crystallography, Vol. C, Kluwer, Dordrecht.
- Young, R.A. & Wiles, D.B. (1982): Profile shape functions in Rietveld refinement. *J. Appl. Cryst.*, **15**, 430-438.
- Yvon, K., Jeitschko, W., Parthé, E. (1977): LAZY PULVERIX, a computer program, for calculating X-ray and neutron powder patterns. *J. Appl. Cryst.*, **10**, 73-74.

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