

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

WERNER KRAUSE<sup>1</sup>, KLAUS BELENDORFF<sup>2</sup>, HEINZ-JÜRGEN BERNHARDT<sup>3</sup>,  
CATHERINE McCAMMON<sup>4</sup>, HERTA EFFENBERGER<sup>5</sup>  
and WERNER MIKENDA<sup>6</sup>

<sup>1</sup>Henriette-Lott-Weg 8, D-50354 Hürth, Germany

<sup>2</sup>Albert-Einstein-Straße, D-64839 Münster, Germany

<sup>3</sup>Ruhr-Universität Bochum, Institut für Mineralogie, Universitätsstraße 150,  
D-44780 Bochum, Germany

<sup>4</sup>Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

<sup>5</sup>Institut für Mineralogie und Kristallographie, Universität Wien,  
Althanstraße 14, A-1090 Vienna, Austria

<sup>6</sup>Institut für Organische Chemie, Universität Wien,  
Währingerstraße 38, A-1090 Vienna, Austria

**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  $\text{Bi}$ ;  $\text{Me}(2) = \text{Fe}, \text{Mn}, \text{Cu}, \text{Zn}, \text{Co}, \text{Ni}$ , and partly  $\text{Al}$ ;  $\text{X} = \text{P}, \text{As}, \text{V}, \text{S}$ . 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  $\text{X}$  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  $\text{X}$  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  $PbCuFe^{3+}(AsO_4)_2(OH)(H_2O)$ , 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  $Fe^{6l}O_6$  octahedra and tetragonal bi-pyramidal  $Cu^{4+2l}O_6$  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  $Me(1)Me(2)_2(XO_4)_2(OH,H_2O)_2$  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  $OH \leftrightarrow H_2O$  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  $Me(1)Me(2)_2(XO_4)_2(OH,H_2O)_2$ .

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 <sup>1</sup>	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)

<sup>1</sup> 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 Fe<sup>3+</sup> and Cu is uncommon in crystal chemistry, Ansell *et al.* (1992) assumed an ordered arrangement of (Zn,Cu) and (Fe<sup>3+</sup>,Zn) in ferrilotharmeyerite. The substitution of H<sub>2</sub>O by OH in combination with the replacement of an XO<sub>4</sub> group by a protonated XO<sub>3</sub>OH 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<sub>1.04</sub>Cu<sub>1.22</sub>Fe<sub>0.74</sub>(AsO<sub>4</sub>)<sub>1.88</sub>(SO<sub>4</sub>)<sub>0.10</sub>(CO<sub>3</sub>)<sub>0.54</sub>(H<sub>2</sub>O)<sub>0.18</sub>. 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) <sup>2</sup>	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 <sup>3</sup> 48/130 <sup>3</sup> 76/-127 <sup>3</sup>	11/-145 <sup>3</sup> 82/-35 <sup>3</sup> 82/56 <sup>3</sup>
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

<sup>1</sup> in the acute of  $\beta$   
<sup>2</sup> from samples in sulfur/selenium melts  
<sup>3</sup>  $\rho/\varphi$  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 mawbyite<sup>1</sup> 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-

<sup>1</sup>A 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,  $\beta = 115.05(2)^{\circ}$ ,  $V = 391.8(1)$  Å<sup>3</sup>; morphology: prismatic parallel to [001] with {110}, { $\bar{1}01$ }, {001}; Fe:Zn ratio according to microprobe analyses is 1.25:0.75.

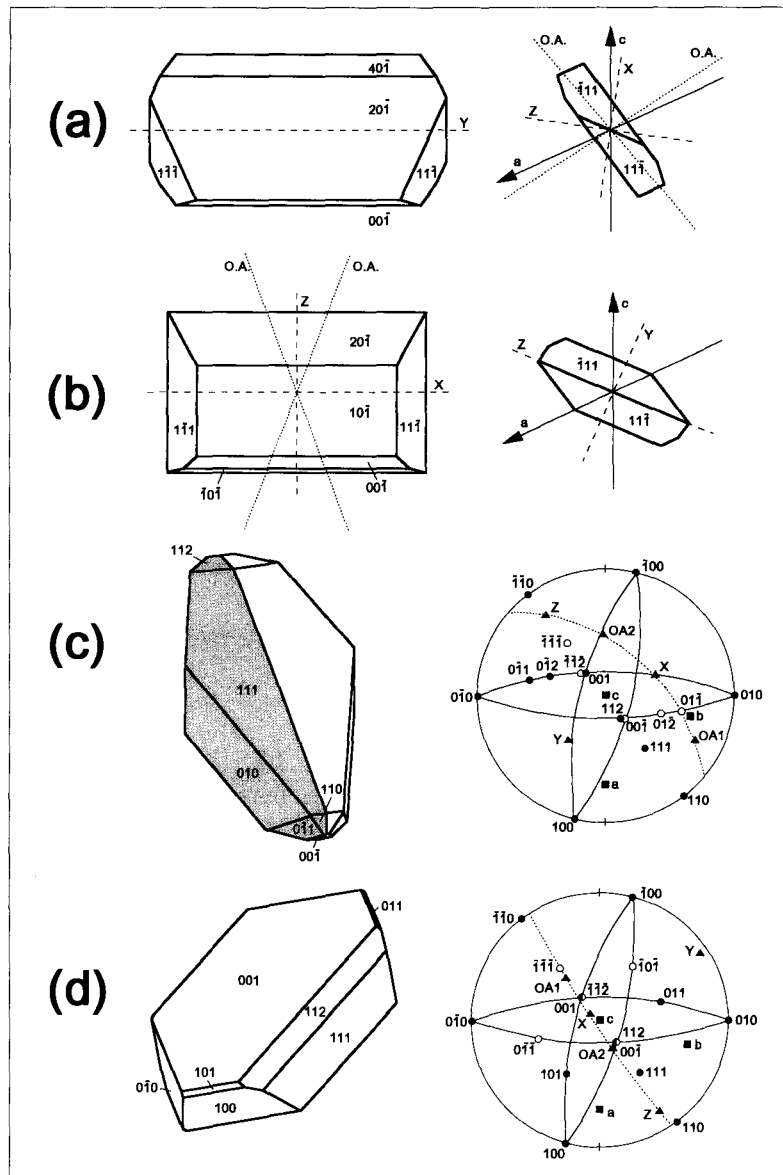


Fig. 1. Morphology and orientation of the optical indicatrix: (a) tsumcorite perpendicular and parallel to  $[010]$ ; (b) ferrilotharmeyerite perpendicular and parallel to  $[010]$ ; (c) gartrellite (morphology for a twinned crystal by reflection on  $(1\bar{1}0)$ ); (d) helmutwinklerite.

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

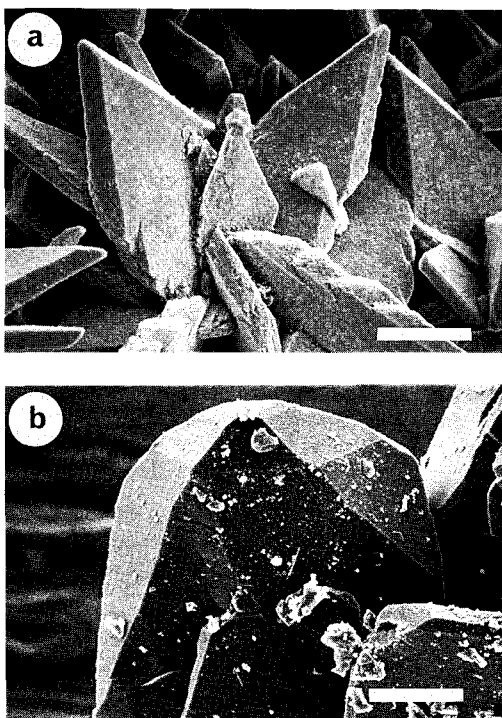


Fig. 2. SEM micrograph of gartrellite: (a) tabular aggregates from Reichenbach, Odenwald, Germany (sample #023, Cu:Fe = 1.0:1.0); (b) multifaceted crystal from Tsumeb, Namibia (sample #075, Cu:Fe:Zn = 0.90:0.94:0.16). The scale bar is 20  $\mu\text{m}$ .

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:  $4.4^\circ$ ) 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<sub>25</sub> determined with a Vickers microhardness tester vary from 350 kg/mm<sup>2</sup> for thometzekite (sulfatian), helmutwinklerite and mounanaite to approximately 500 kg/mm<sup>2</sup> for tsumcorite, ferrilotharmeyerite and gartrellite. All these values correspond to 4½ 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<sup>3</sup> for ferrilotharmeyerite (#241), 4.88 g/cm<sup>3</sup> for mounanaite (#262), 5.21 g/cm<sup>3</sup> for sulfatian thometzekite (#132), 5.29 g/cm<sup>3</sup> for helmutwinklerite (#272), and 5.43 g/cm<sup>3</sup> 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<sub>4</sub> (Al, P), SrSO<sub>4</sub> (S), vanadium metal (V), ZnO (Zn), NiO (Ni), Co metal (Co), Bi<sub>2</sub>S<sub>3</sub> (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  $\mu\text{m}$ ); H<sub>2</sub>O contents were calculated from the idealized formulas. The number of ions were calculated on the basis of 10 oxygen atoms. (added in proof: read V<sub>2</sub>O<sub>5</sub> instead of V<sub>5</sub>O<sub>5</sub>).

(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 <sup>1</sup>		mean <sup>2</sup>		mean <sup>3</sup>		mean <sup>4</sup>		mean <sup>5</sup>		mean	
PbO	Pb <sup>2+</sup>	0.14	-	33.39	0.95	35.30	1.02	36.10	0.99	35.72	0.99	38.47	1.02
CaO	Ca <sup>2+</sup>	12.07	1.02	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-
Fe <sub>2</sub> O <sub>3</sub>	Fe <sup>3+</sup>	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 <sub>2</sub> O <sub>3</sub>	Al <sup>3+</sup>	<0.1	-	<0.1	-	<0.1	-	0.55	0.07	2.02	0.25	0.32	0.04
ZnO	Zn <sup>2+</sup>	17.88	1.04	14.97	1.17	16.42	1.30	5.52	0.41	6.59	0.50	<0.1	-
CuO	Cu <sup>2+</sup>	<0.1	-	0.15	-	<0.1	-	19.44	1.50	14.61	1.14	0.87	0.06
As <sub>2</sub> O <sub>5</sub>	(AsO <sub>4</sub> ) <sup>3-</sup>	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 <sub>2</sub> O <sub>5</sub>	(PO <sub>4</sub> ) <sup>3-</sup>	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	0.81	0.07
V <sub>5</sub> O <sub>5</sub>	(VO <sub>4</sub> ) <sup>3-</sup>	<0.1	-	<0.1	-	<0.1	-	<0.1	-	<0.1	-	29.28	1.92
SO <sub>3</sub>	(SO <sub>4</sub> ) <sup>2-</sup>	<0.1	-	<0.1	-	<0.1	-	9.00	0.69	2.35	0.18	<0.1	-
H <sub>2</sub> O <sub>calc</sub>	(OH) <sup>-</sup>	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 <sub>2</sub> O		1.08		1.17		1.29		1.23		1.49		-
sum		100.31		99.76		100.33		100.42		101.65		99.15	

<sup>1</sup> mean of 20 analyses; ranges: Fe<sub>2</sub>O<sub>3</sub> (14.53 - 16.43); ZnO (17.14 - 18.73)  
<sup>2</sup> mean of 19 analyses; ranges: Fe<sub>2</sub>O<sub>3</sub> (9.88 - 11.65); ZnO (14.58 - 15.45)  
<sup>3</sup> mean of 26 analyses; ranges: Fe<sub>2</sub>O<sub>3</sub> (6.72 - 11.51); ZnO (12.79 - 18.39)  
<sup>4</sup> mean of 20 analyses; ranges: As<sub>2</sub>O<sub>5</sub> (29.19 - 22.03); SO<sub>3</sub> (6.04 - 10.96); CuO (16.14 - 20.87); ZnO (4.12 - 8.63); Fe<sub>2</sub>O<sub>3</sub> (0.00 - 0.66); Al<sub>2</sub>O<sub>3</sub> (0.21 - 1.17)  
<sup>5</sup> mean of 8 analyses; ranges: As<sub>2</sub>O<sub>5</sub> (31.32 - 37.34); SO<sub>3</sub> (0.25 - 4.47); CuO (11.55 - 18.48); ZnO (2.65 - 7.95); Al<sub>2</sub>O<sub>3</sub> (1.00 - 3.33)

chemical composition of tsumcorite sample #259: Pb<sub>0.97</sub>(Zn<sub>1.50</sub>Fe<sub>0.50</sub>Cu<sub>0.03</sub>)<sub>2.03</sub>(AsO<sub>4</sub>)<sub>2.01</sub>(OH)<sub>0.49</sub>(H<sub>2</sub>O)<sub>1.51</sub>

(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 <sup>1</sup>		mean <sup>2</sup>		mean <sup>3</sup>		mean <sup>4</sup>		mean <sup>5</sup>		mean <sup>6</sup>	
PbO	Pb <sup>2+</sup>	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 <sup>2+</sup>	<0.05	-	0.35	0.04	0.07	-	<0.05	-	<0.05	-	<0.05	-
Fe <sub>2</sub> O <sub>3</sub>	Fe <sup>3+</sup>	<0.05	-	7.23	0.59	9.59	0.78	10.33	0.82	12.48	0.99	10.91	0.87
Al <sub>2</sub> O <sub>3</sub>	Al <sup>3+</sup>	<0.05	-	0.26	0.03	0.25	0.03	0.11	0.01	0.22	0.03	0.16	0.02
ZnO	Zn <sup>2+</sup>	23.54	1.85	11.40	0.91	6.30	0.51	0.21	0.02	<0.05	-	<0.05	-
CuO	Cu <sup>2+</sup>	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 <sub>2</sub> O <sub>5</sub>	(AsO <sub>4</sub> ) <sup>3-</sup>	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 <sub>2</sub> O <sub>5</sub>	(PO <sub>4</sub> ) <sup>3-</sup>	<0.05	-	<0.05	-	<0.05	-	<0.05	-	0.36	0.03	0.32	0.03
V <sub>5</sub> O <sub>5</sub>	(VO <sub>4</sub> ) <sup>3-</sup>	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
SO <sub>3</sub>	(SO <sub>4</sub> ) <sup>2-</sup>	<0.05	-	0.13	0.01	0.13	0.01	1.68	0.13	<0.05	-	0.65	0.05
H <sub>2</sub> O <sub>calc</sub>	(OH) <sup>-</sup>	5.53	-	4.80	0.83	4.48	1.00	4.47	1.10	4.21	1.05	4.40	0.90
	H <sub>2</sub> 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	

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

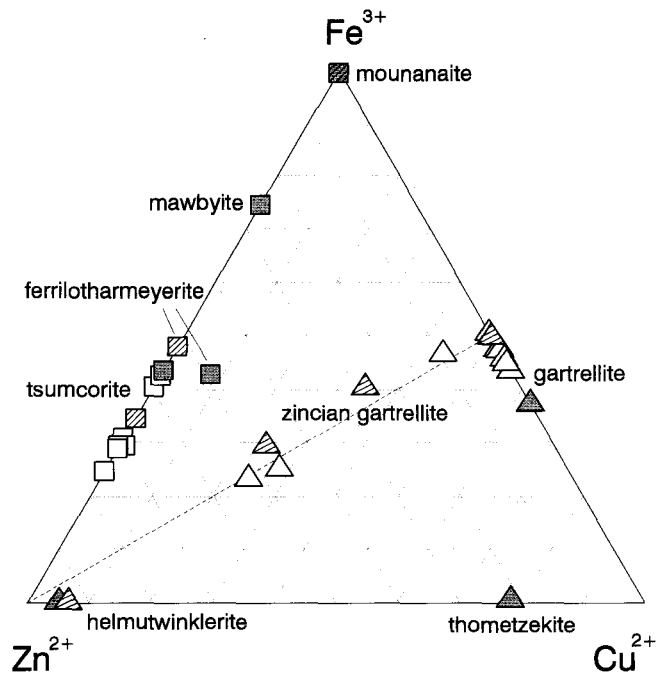


Fig. 3. Chemical composition of the tsumcorite-group minerals plotted in the triangle-diagram  $Zn^{2+} - Cu^{2+} - Fe^{3+}$ ; triclinic samples are plotted as triangles, monoclinic as squares. The compositions of the type material of the relevant minerals are shaded. The samples used for structural 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  $Cu:Zn:Fe$  ratio is illustrated graphically (Fig. 3).

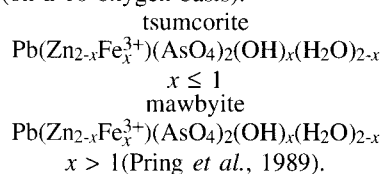
One of the results of the present study is the description of the tsumcorite-group minerals by the general formula  $Me(1)Me(2)_2(XO_4)_2(OH, H_2O)_2$ . Electron microprobe analyses showed that at least partial solid solution is common for the Me(2) and less frequent for the X and Me(1) site. In addition to the substitution involving homovalent ions [e.g.  $Zn^{2+} \leftrightarrow Cu^{2+}$  or  $(AsO_4)^{3-} \leftrightarrow (PO_4)^{3-}$ ] there are 3 heterovalent exchange mechanisms with a coupled substitution involving OH/H<sub>2</sub>O groups: (i) on the Me(1) site, e.g.  $[(Ca)^{2+}(H_2O)]^{2+} \leftrightarrow [(Bi)^{3+}(OH)]^{2+}$ , (ii) on the Me(2) site, e.g.  $[(Zn,Cu,Co,Ni)^{2+}(H_2O)]^{2+} \leftrightarrow [(Fe,Al,Mn)^{3+}(OH)]^{2+}$ , and (iii) on the X site, e.g.  $[(AsO_4)^{3-}(H_2O)]^{3-} \leftrightarrow [(SO_4)^{2-}(OH)]^{3-}$ . 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  $\text{AsO}_4/\text{SO}_4$  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  $\text{Fe}^{3+}$ . 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):

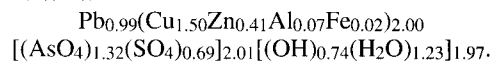


The distribution of the Zn:Fe ratio of 130 spot analyses of different tsumcorite samples has a maximum around  $\text{Zn}_{1.20}\text{Fe}_{0.80}$  with a continuous range from  $\text{Zn}_{1.60}\text{Fe}_{0.40}$  to  $\text{Zn}_{1.05}\text{Fe}_{0.95}$ , *i.e.*  $0.40 \leq x \leq 0.95$ . The tsumcorite 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  $\text{SO}_3$  amount of 11.0 wt.%, which corresponds to an As:S ratio of 1.16:0.84. A partial substitution of  $\text{AsO}_4$  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

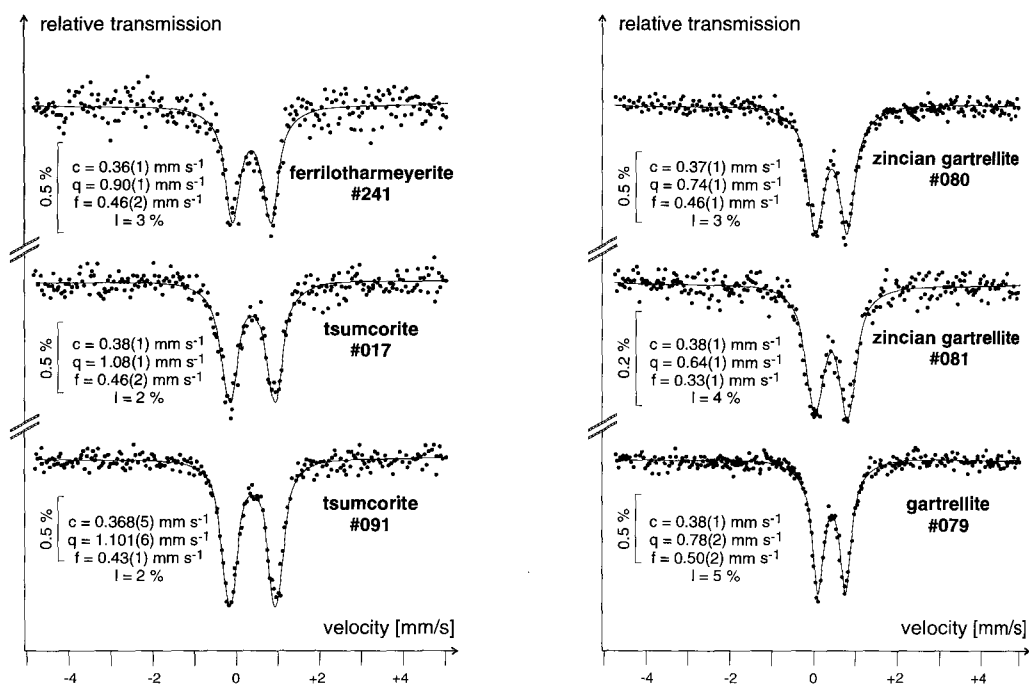


Fig. 4. Mössbauer spectra of ferrilotharmeyerite, tsumcorite, gartrellite and zincian gartrellite. For each spectrum are given: centre shift [ $\text{mm s}^{-1}$ ] relative to  $\alpha\text{-Fe}$  ( $c$ ; first line); quadrupolar splitting [ $\text{mm s}^{-1}$ ] ( $q$ ; second line); full width at half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

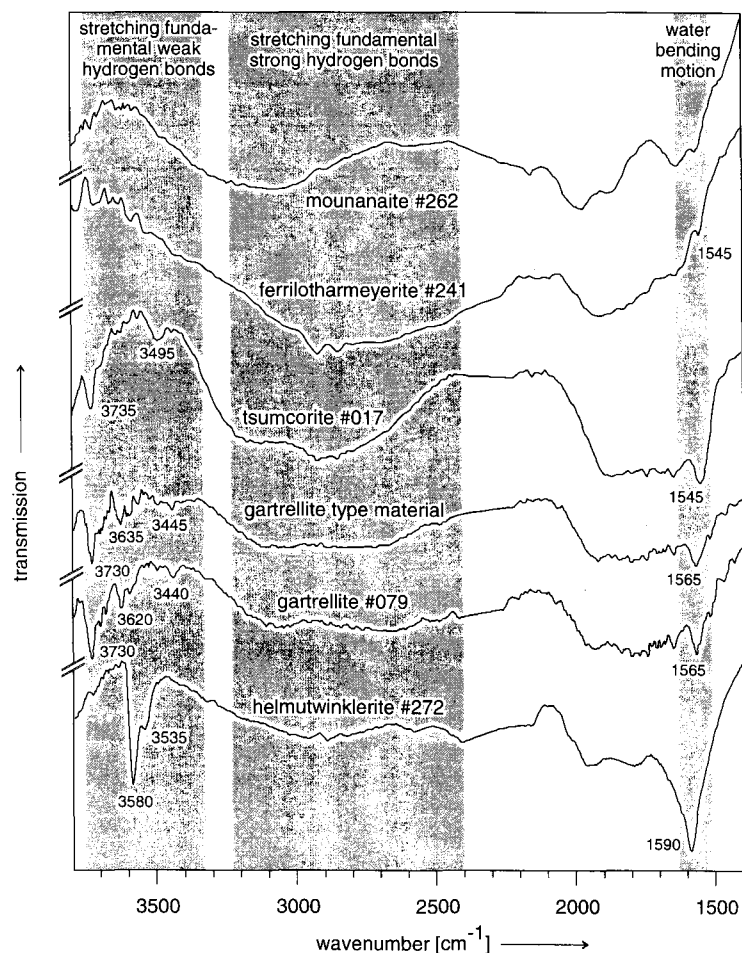


Fig. 5. Infrared spectra of mounanaite, ferrilotharmeyerite, tsumcorite, gartrellite and helmutwinklerite.

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/cm<sup>2</sup>) 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 <sub>calc</sub>	I <sub>calc</sub>	d <sub>obs</sub>	I <sub>obs</sub>	h	k	l	d <sub>calc</sub>	I <sub>calc</sub>	d <sub>obs</sub>	I <sub>obs</sub>
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 $\alpha$ -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<sub>calc</sub>  $\geq$  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 Fe<sup>3+</sup>; no evidence for Fe<sup>2+</sup> can be seen within experimental error. All spectra show only one component, which indicates that Fe<sup>3+</sup> 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

