

The crystal structure of Pb²⁺-bearing graeserite, Pb_{0,14}(Fe,Ti)₇AsO_{12+x}(OH)_{2-x}, a mineral of the derbylite group

Autor(en): **Berlepsch, Peter / Armbruster, Thomas**

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The crystal structure of Pb^{2+} -bearing graeserite, $\text{Pb}_{0.14}(\text{Fe},\text{Ti})_7\text{AsO}_{12+x}(\text{OH})_{2-x}$, a mineral of the derbylite group

by Peter Berlepsch¹ and Thomas Armbruster²

Abstract

Graeserite, ideally $\text{Fe}_4\text{Ti}_3\text{AsO}_{13}(\text{OH})$, is monoclinic, space group $C2/m$, $Z = 2$, with $a = 5.0053(4)$, $b = 14.272(1)$, $c = 7.1736(6)$ Å, and $\beta = 105.165(2)^\circ$. Its structure has been determined and refined to $R_1 = 2.92\%$ for 524 unique reflections with $F_o > 4\sigma(F_o)$, collected on a SIEMENS SMART CCD area-detector system using Mo K_α X-radiation. The structure is based on a closest-packed oxygen framework with a (chh) stacking sequence and is isotypic to barian tomichite and homeotypic to derbylite, tomichite, and hemloite. Small cations are ordered into 14 of the 30 octahedral sites per unit cell, forming α - PbO_2 - and V_3O_5 -type chains of edge-sharing octahedra along [100]. In the cubic-stacked oxygen layer-unit, two oxygen atoms per unit cell are missing, thus cuboctahedral cavities result. These cavities are either occupied by single ($\text{As}^{3+}, \text{Sb}^{3+}$) ions or ($\text{As}^{3+}, \text{Sb}^{3+}$)₂ pairs in pyramidal coordination, with the lone-electron pair directed towards the position of the missing anion, or by five-fold coordinated Pb^{2+} . The structure refinement was carried out for the average structure in which Pb and (As, Sb)₂ statistically occupy the same cavity. However, ordering of Pb and (As, Sb)₂ may be assumed since Pb and (As, Sb)₂ cannot occupy one cavity at the same time.

Keywords: graeserite, derbylite group, crystal structure, crystal chemistry.

Introduction

Graeserite with the empirical formula $(\text{Fe}_{2.91}^{3+}\text{Fe}_{0.38}^{2+}\text{Ti}_{0.54}\text{Pb}_{0.15}^{2+})\text{Ti}_3(\text{As}_{0.94}^{3+}\text{Sb}_{0.07}^{3+})\text{O}_{13}(\text{OH})$, has recently been described as a new mineral (KRZEMNICKI and REUSSER, in press) which occurs as a hydrothermal product in Alpine fissures and small related cavities within paragneisses of the Monte Leone nappe (Gorb, Binn valley, Western Alps, Switzerland). The mineral is associated with various other hydrothermal minerals (in alphabetical order) such as anatase, arsenopyrite, asbecasite [$\text{Ca}_3(\text{Ti}, \text{Sn})\text{As}_6\text{Si}_2\text{Be}_2\text{O}_{20}$], bournonite [PbCuSbS_3], cafarsite [$\text{Ca}_8(\text{Ti}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mn})_{6-7}(\text{As}^{3+}\text{O}_3)_{12} \cdot 4\text{H}_2\text{O}$], cervandonite-(Ce) [(Ce, Nd, La)(Fe³⁺, Fe²⁺, Ti, Al)₃(Si, As)₃O₁₃], chernovite-(Y) [YAsO₄], fetiasite [(Fe²⁺, Fe³⁺, Ti)₃O₂(As₂O₅)], native gold (traces), hematite, magnetite, monazite-(Ce) [(Ce, La, Nd, Th)PO₄], rutile, and tennantite [(Cu, Fe)₁₂As₄S₁₃].

Graeserite is a member of the derbylite group minerals (Tab. 1) consisting of derbylite [$\text{Fe}_4\text{Ti}_3\text{SbO}_{13}(\text{OH})$] (HUSSAK and PRIOR, 1987; MOORE and ARAKI, 1976), tomichite [(V, Fe)₄Ti₃AsO₁₃(OH)] (NICKEL and GREY, 1979; GREY et al., 1987), barian tomichite [$\text{Ba}_{0.5}(\text{As}_2)_{0.5}\text{Ti}_2(\text{V}, \text{Fe})_5\text{O}_{13}(\text{OH})$] (GREY et al., 1987), and hemloite [(As, Sb)₂(Ti, V, Fe, Al)₁₂O₂₃OH] (HARRIS et al., 1989). The four available crystal structure studies on members of the derbylite group yielded three different space group symmetries. Derbylite (MOORE and ARAKI, 1976) and tomichite (GREY et al., 1987) are monoclinic $P2_1/m$, barian tomichite has an average structure of $A2/m$ symmetry (GREY et al., 1987), and hemloite (HARRIS et al., 1989) is triclinic $P\bar{1}$. Common to all above structures is a close packed oxygen array with a (chh) stacking sequence. Furthermore, all structures display oxygen vacancies within the cubic close packed sequence giving rise to cuboctahedral cavities har-

¹ Mineralogisch-Petrographisches Institut, Universität Basel, Bernoullistrasse 30, CH-4056 Basel, Switzerland. <berlepsch@ubaclu.unibas.ch>

² Laboratorium für Chemische und Mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland. <armbruster@krist.unibe.ch>

Tab. 1 The five members of the derbylite group. Unit cell and other parameters were taken from the original publications. Graeserite: KRZEMNICKI and REUSSER (in press); tomichite: NICKEL and GREY (1979); barian tomichite: GREY et al. (1987); derbylite: MOORE and ARAKI (1976); hemloite: HARRIS et al. (1989).

	Graeserite powder data	CCD data	Derbylite	Tomichite	Ba-Tomichite	Hemloite
system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$A 2/m$	$C 2/m$	$P 2_1/m$	$P 2_1/m$	$A 2/m$	$P\bar{1}$
a (Å)	7.184(2)	5.0053(4)	7.160(1)	7.119(3)	7.105(4)	7.158(1)
b (Å)	14.289(6)	14.272(1)	14.347(3)	14.176(5)	14.217(4)	7.552(1)
c (Å)	5.006(2)	7.1736(6)	4.970(1)	4.992(2)	5.043(2)	16.014(3)
α (°)						89.06(1)
β (°)	105.17(2)	105.165(2)	104.61(2)	105.05(1)	104.97(7)	104.32(2)
γ (°)						84.97(1)
V (Å ³)	495.5	494.6	494.0	486.5	492.1	834.8
Z	2	2	2	2	2	2
type locality	Gorb, Binntal Switzerland	Gorb, Binntal Switzerland	Tripuhy, Ouro Preto, Brazil	Kalgoorlie, W Australia	Hemlo, Ontario Canada	Hemlo, Ontario Canada

boring AsO_3 and/or SbO_3 pyramids. Mainly $\text{Fe}^{2+/3+}$, Ti^{4+} , and V^{3+} occupy octahedral interstices in the close oxygen packing. Derbylite, tomichite and barian tomichite exhibit the same arrangement of Fe, Ti, and V described as α - PbO_2 - and V_3O_5 -type chains of edge-sharing octahedra (MOORE and ARAKI, 1976) where Fe, Ti, and V occupy 14 out of 30 available octahedral interstices of the close packed oxygen array. Hemloite (HARRIS et al., 1989) has a different Fe, Ti, and V distribution and is regarded as an ordered intergrowth of a tomichite type structure and a new MO_2 structure type related to a stacking of rutile and goethite type units. The triclinic symmetry of hemloite is in accordance with this unique cation distribution. Due to this distinctive cation distribution the stoichiometry and symmetry of hemloite is different to the other derbylite minerals (Tab. 1).

From a chemical point of view, graeserite is directly related to derbylite with the difference that the cuboctahedral cavities in derbylite contain Sb^{3+} whereas graeserite has As^{3+} . The difference between tomichite and graeserite is the high octahedral vanadium concentration in tomichite. Thus, one should expect that graeserite is isotypic to derbylite and tomichite. Surprisingly, KRZEMNICKI and REUSSER (in press) reported for graeserite the higher symmetry $A2/m$ ($C2/m$ in standard setting) which is identical to the one observed for barian tomichite (GREY et al., 1987).

The aim of the present study is to provide a description of the crystal structure of graeserite and to show the relationship to known structures with similar chemical composition. In particular, the symmetry difference to derbylite and tomichite attracted our attention.

Single-crystal X-ray study

A small crystal of graeserite, $40 \cdot 70 \cdot < 5 \mu\text{m}^3$ in size, elongated parallel to b , was used for preliminary Weissenberg- and precession photographs as well as for X-ray data collection at 293 K. Cell parameters (Tab. 1) and intensities were collected on a SIEMENS SMART CCD system (graphite-monochromatized $\text{Mo } K_\alpha$ X-radiation). A half sphere in the reciprocal lattice was measured and a total of 4563 reflections from $2\theta = 0$ to 55.15° was collected with an exposure time of 60 seconds per frame. Table 2 contains a summary of the conditions of CCD data collection and the subsequent refinement parameters. All diffraction intensities were empirically corrected for absorption by using Ψ -scans. Data reduction including intensity integration, background, and Lorentz-polarization corrections, was carried out using the program SAINT (SIEMENS, 1996).

The space group of graeserite reported by KRZEMNICKI and REUSSER (in press) is monoclinic $A2/m$ which was confirmed by own single-crystal photographs. However, for data collection and structure solution the standard setting $C2/m$ was chosen. Test measurements on a conventional CAD4 diffractometer indicated additional reflections which could not be indexed with the C -centered monoclinic $5 \cdot 14 \cdot 7 \text{ \AA}$, $\beta = 105^\circ$ cell. Some of these reflections indicated a four-fold c -axis, other reflections could not be accommodated within a simple commensurate lattice. However, due to the small crystal size and the faint character of these superstructure reflections, data collection in the supercell had to be abandoned. Furthermore, the supercell reflections seemed to have the character of satellites similar to those ob-

Tab. 2 Summarized CCD data collection and refinement parameters of graeserite.

Diffractionmeter	SIEMENS SMART CCD system
X-ray radiation	sealed tube MoK _α (0.71073 Å)
X-ray power	50 kV, 40 mA
Temperature	293 K
Detector to sample distance	5.518 cm
Detector 2 θ angle	27°
Resolution	0.77 Å
Rotation axis	ω
Rotation width	0.3°
Total number of frames	1271
Frame size	512 * 512 pixels
Data collection time per frame	60 secs.
Collection mode	hemisphere
Reflections measured	4563
Max. 2 θ	55.15°
Index range	-6 ≤ h ≤ 6, -18 ≤ k ≤ 18, -9 ≤ l ≤ 9
Unique reflections	565
Reflections > 2σ(I)	524
R _{int} after empirical absorption correction	3.50%
R _σ	2.23%
Number of least squares parameters	99
Goof	1.312
R ₁ , F _o > 4σ(F _o)	2.92%
R ₁ , all data	3.22%
wR ₂ (on F ₂)	7.29%

$R_{\text{int}} = \frac{\sum F_o^2 - F_c^2(\text{mean}) }{\sum F_o^2}$	$R_{\sigma} = \frac{\sum \sigma(F_o^2)}{\sum F_o^2}$
$\text{Goof} = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{n - p}}$	$P = \frac{\text{Max}(F_o^2, 0) + 2 * F_c^2}{3}$
$R_1 = \frac{\sum F_o - F_c }{\sum F_o }$	$wR_2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$
$w = \frac{1}{(\sigma^2(F_o^2) + (0.0126 * P)^2 + 8.25 * P)}$	

served by GREY et al. (1987) for barian tomichite. The average structure was solved by direct methods and refined with the program package SHELX-93 (SHELDRICK, 1993). Based on varying scattering power, interatomic distances and angles, Fe/Ti, As, Pb, and O could be directly assigned from difference Fourier maps. The final refinement, applying neutral atom scattering factors, was performed with anisotropic displacement parameters for all positions and with an empirical extinction coefficient (SHELDRICK, 1993). To test variable occupancy on octahedral (Fe,Ti) sites, individual Fe/Ti populations were allowed to vary but the scattering curves of Fe and Ti are quite similar causing substantial correlation problems.

Results

The refined structure of graeserite (Figs 1, 2, and 3) is essentially isotopic to barian tomichite (GREY et al., 1987). However, the final difference

Tab. 3 Final fractional atomic position and isotropic displacement parameters, B_{eq}(Å²), with estimated standard deviations in parentheses, for graeserite from Gorb (Binn valley, Switzerland). Occ = occupancy.

Atom Occ	x/a	y/b	z/c	B _{eq} (Å ²)
M1	0	1/2	1/2	0.66(3)
M2	-1/2	0.62037(8)	1/2	0.65(2)
M3	-0.3756(2)	0.81093(6)	0.8136(1)	0.61(2)
As	0.493(6)	-0.2515(4)	1/2	0.9169(2)
Pb	0.072(2)	-0.456(1)	1/2	0.9367(8)
O1	-0.2702(8)	0.9016(3)	0.6626(5)	1.08(6)
O2	-0.2608(7)	0.7046(3)	0.6798(5)	0.94(6)
O3	-1/2	0.7139(3)	0	0.90(8)
O4	-1/2	0.9041(4)	0	1.17(9)
O5	-0.279(1)	1/2	0.6500(8)	1.02(9)

Satellite M and As sites				
M4	0.022(3)	-0.25(1)	1/2	0.504(6)
M5	0.022(3)	-1/2	0.880(2)	1/2
M6	0.020(4)	-1/2	1/2	1/2
M7	0.020(4)	-0.254(7)	0.619(3)	0.498(5)
M8	0.017(4)	-0.146(9)	0.810(3)	0.812(6)
M9	0.016(2)	-0.409(9)	0.689(3)	0.810(6)
As'	0.015(2)	-0.66(1)	1/2	0.925(7)
As''	0.013(2)	-0.08(1)	1/2	0.080(7)

$B_{\text{eq}} = 8/3 \pi^2 \sum_i (\sum_j [U_{ij} a_i^* \cdot a_j^* \cdot a_i a_j])$				
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Fourier map of graeserite exhibited nine positive peaks above 1.5 e/Å³ and flat minima of -0.6 e/Å³. Inspection of the positive residual peaks indicated they are all positioned in the cation layers of the close-packed oxygen array. In particular, seven peaks were caused by shifts of the three major M sites by x + 1/4, x + 1/2, and x + 3/4, where y and z remained uninfluenced. The two remaining peaks could be attributed to As positions shifted by x - 2/5 and x + 1/3. In a subsequent refinement Fe and As were assigned to these additional disordered M and As sites, the isotropic displacement parameters (U) were fixed at 0.01 Å², and the individual populations were allowed to vary. These refinements converged at R₁ = 2.92% yielding populations for the disordered M sites of about 2% and 1.3% for the additional As sites. Refinements without considering the low populated M and As sites converged at R₁ = 4.5%. It must be noted that these low-populated, disordered M sites, do not occupy interstices in the close packed oxygen arrangement. The additional O sites, coordinating the disordered M sites, cannot be resolved due to their low population. Thus it has to be assumed that the investigated crystal of graeserite is composed of non-commensurate stacks of close packed oxygen units piled along c. It cannot be decided whether the observed disorder is actually caused by complex twinning or is

Tab. 4 Anisotropic atomic displacement parameters for graeserite, with estimated standard deviations in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M1	0.0080(9)	0.0059(9)	0.0107(9)	0	0.0014(6)	0
M2	0.0086(6)	0.0074(6)	0.0088(6)	0	0.0024(4)	0
M3	0.0078(5)	0.0072(5)	0.0085(5)	0.0008(3)	0.0026(3)	0.0013(3)
As	0.022(1)	0.0052(8)	0.0079(8)	0	0.0003(6)	0
Pb	0.022(4)	0.018(2)	0.043(4)	0	-0.017(2)	0
O1	0.016(2)	0.012(2)	0.014(2)	-0.002(1)	0.006(1)	0.000(1)
O2	0.012(2)	0.013(2)	0.011(2)	-0.002(1)	0.004(1)	0.000(1)
O3	0.014(2)	0.009(2)	0.013(2)	0	0.005(2)	0
O4	0.020(3)	0.010(2)	0.016(3)	0	0.006(2)	0
O5	0.012(2)	0.012(2)	0.018(3)	0	0.010(2)	0

related to a true superstructure. The appearance of additional reflections which were ignored in the course of the data collection, coupled with the absence of diffuse diffraction streaks, indicates that at least some order exists among the close packed stacks. We do not believe that the additional low occupied M and As sites can be considered as artifacts (e.g., due to the effect of multiple diffraction). The investigated crystal exhibited only insignificant contributions of primary and secondary extinction which strongly reduces multiple diffraction phenomena.

The empirical formula ($\text{Fe}_{2.91}^{3+}\text{Fe}_{0.38}^{2+}\text{Ti}_{0.54}\text{Pb}_{0.15}$) $\text{Ti}_3(\text{As}_{0.94}^{3+}\text{Sb}_{0.07}^{3+})\text{O}_{13}(\text{OH})$, derived from the electron microprobe analyses of KRZEMNICKI and REUSSER (in press) is in good agreement with the composition $\text{Pb}_{0.14}(\text{Fe},\text{Ti})_7\text{AsO}_{14}$ obtained from the structure determination. In particular, the structure clearly indicates that Pb is two-valent occupying a position in the cuboctahedral cavities and is not replacing Fe/Ti. Similar to other lone electron pair ions like As^{3+} and Sb^{3+} , already established for derbylite minerals, Pb^{2+} prefers a one sided five-fold coordination where the lone electron pair may reach into the cuboctahedral cavity.

The unit cell parameters of graeserite and of the other members of the derbylite group are listed in table 1. The final fractional coordinates and isotropic displacement parameters of graeserite are given in table 3. Anisotropic displacement parameters are listed in table 4. Selected interatomic distances and angles are summarized in table 5.

The crystal structure of graeserite is isotopic with barian tomichite (GREY et al., 1987) with the difference that Ba in barian tomichite is twelve-fold coordinated and Ba partially fills the position of the missing oxygen in the center of the cuboctahedron (Fig. 4c). In graeserite Pb is displaced from the center of the cavity allowing for shorter Pb-O bonds (Fig. 4e). The three M sites in graeserite do not contain any V but mainly Fe and Ti. In both structures the M sites display a distorted

octahedral oxygen coordination and As forms the apex of a trigonal pyramid with three oxygen atoms at its base (Fig. 4d). The structure is visualized in terms of the MO_6 octahedra in figures 1, 2

Tab. 5 Selected interatomic distances (Å) and angles (°) for the (Fe,Ti), (As,Sb), and Pb sites in the crystal structure of graeserite.

M1 - O5	2	1.975(4)	O1 - M3 - O2	100.97(15)
- O1	4	1.989(4)	O1 - O2	95.14(15)
mean		1.984	O1 - O3	98.66(14)
			O1 - O4	96.22(16)
O5 - M1 - O5	180.00		O1 - O3	176.21(16)
O5 - O1	4	86.34(13)	O2 - O2	92.89(14)
O5 - O1	4	93.66(13)	O2 - O3	159.95(16)
O1 - O1	2	180.00	O2 - O4	88.00(11)
O1 - O1	2	90.11(14)	O2 - O3	79.57(11)
O1 - O1	2	89.89(14)	O2 - O3	81.26(14)
			O2 - O4	168.23(15)
			O2 - O3	88.58(15)
M2 - O2	2	1.933(3)	O3 - O4	93.95(10)
- O1	2	2.028(3)	O3 - O3	81.12(9)
- O5	2	2.170(3)	O4 - O3	80.04(15)
mean		2.044		
O2 - M2 - O2	103.07(15)		As - O4	2 1.850(4)
O2 - O1	2	95.17(13)	- O5	1.883(5)
O2 - O1	2	95.85(13)	mean	1.861
O2 - O5	2	165.87(16)		
O2 - O5	2	90.88(14)	O4 - As - O4	95.49(17)
O1 - O1	2	162.24(16)	O4 - O5	2 100.99(10)
O1 - O5	2	85.54(15)		
O1 - O5	2	80.41(16)		
O5 - O5	2	75.29(15)	Pb - O5	2.443(7)
			- O1	2 2.587(6)
			- O4	2 2.600(4)
M3 - O1	1.850(4)		mean	2.563
- O2	1.928(3)			
- O2	1.960(4)		O5 - Pb - O1	2 69.02(17)
- O3	2.033(1)		O5 - O4	2 69.59(14)
- O4	2.092(3)		O1 - O1	65.80(17)
- O3	2.128(3)		O1 - O4	2 100.24(14)
mean	1.999		O1 - O4	2 138.58(22)
			O4 - O4	63.57(17)

and 3. The following structure description of graeserite is essentially based on an adapted version of the one published by GREY et al. (1987) for the isostructural mineral barian tomichite. In order to increase clarity of the description below, some introducing remarks are given first. Close packed anion layers can be labeled either with the "ABC..." or with the "ch" nomenclature. In the first case only the different types of shifts for the oxygen layers are considered whereas in the second case each layer is interpreted based on the neighboring layers above and below. The link between the two systems is as following: A in BAB or CAC corresponds to *h*, in all other cases to *c* (analogous for B and C). Since in graeserite the close packed oxygen layers are perpendicular to (001) we obtain repetition of the stacking sequence only after nine layers which can be labeled either ABABCBCAC or *chh...*, as used in this text. Due to the monoclinic symmetry of graeserite the nine layer stacking sequence is not apparent from the cell dimensions.

The structure is made up by stacking (001) layers of octahedra of two types, illustrated in figures 1 and 2. Between pairs of *h*-stacked anion layers, small cations occupy 6/10 of the octahedral interstices to form a layer resembling a V₃O₅-type structure (ÅSRINK et al., 1959). As shown in figure 1, this structural unit comprises [100] columns of edge-sharing octahedra, alternately one- and two-octahedra wide. Between pairs of *c*- and *h*-stacked anions layers, 4/10 of the octahedral sites are occupied by Fe and Ti, forming α-PbO₂-type units (ZASLAVSKY and TOLKACHEV, 1952) with zigzag chains of edge-sharing octahedra along [100]. The planes are in mirror-relation across

(010) at *y* = 0 and *y* = 1/2. These layers occur in pairs, *h*-M-*c*-M-*h*, above and below the *c*-stacked anion layer that contain Pb and As within the cuboctahedral cavity. The α-PbO₂-type chains in adjacent layers are linked by edge-sharing, as shown in figure 2.

A polyhedral representation of the structure of graeserite, viewed approximately along [100] in figure 3, portrays it as a tunnel structure, where the tunnels have α-PbO₂-type double chains as walls and V₃O₅-type columns at top and bottom, the different units being linked by corner sharing. The tunnel alternately constricts and expands along [100] as the width of the V₃O₅-type columns changes from one to two octahedra. The latter gives rise to cuboctahedral cavities, occupied by either (As,Sb) or Pb (Figs 4 e, d). The different cations cannot occupy the cavity simultaneously, and ordering is supposed which may be responsible for the observed additional satellite reflections.

Discussion

COMPARISON WITH DERBYLITE GROUP MINERALS

In the *P*2₁/*m* structures of derbylite (MOORE and ARAKI, 1976) and tomichite (GREY et al., 1987) only one AsO₃ or SbO₃ pyramidal unit per cuboctahedral cavity nests on a triangular oxygen face (Figs 4 a, b). For SbO₃ in derbylite this has steric reasons because the Sb–O distances of about 2.0 Å (MOORE and ARAKI, 1976) are too long to allow a second SbO₃ pyramid to be accommodated in the cuboctahedron (Fig. 4a). However, the short-

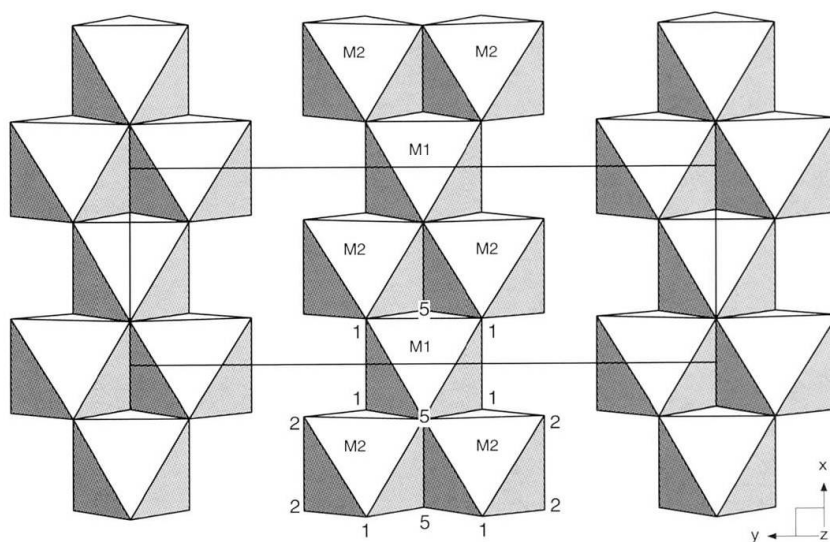


Fig. 1 V₃O₅-type columns of edge-sharing M1O₆ and M2O₆ octahedra extending in the [100] direction which are alternately one and two octahedra wide.

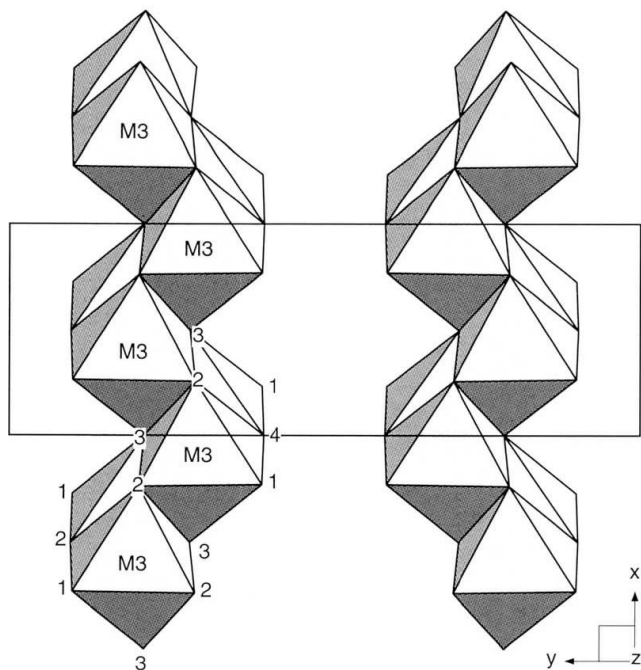


Fig. 2 α - PbO_2 -type zigzag double chains of edge-sharing M_3O_6 octahedra extending in the $[100]$ direction.

er As–O distances of about 1.8 \AA would theoretically also allow occupation of two adjacent AsO_3 pyramids per cavity (GREY et al., 1987) leading to an As–As separation of about 3.1 \AA . Nevertheless, the one sided occupation of As in tomichite seems

to be energetically favored in order to minimize structural strain (Fig. 4b) and to avoid close contacts of As lone electron pairs. In barian tomichite (space group $A2/m$) the center of the cuboctahedron is partially occupied by Ba (GREY et al., 1987) where Ba directly replaces the missing oxygen in the close packed oxygen array (Fig. 4c). In addition, the chemistry of barian tomichite with $(\text{As} + \text{Sb} + \text{Ba}) \gg 1$ p.f.u. indicates that also AsO_3 pairs must exist. The same is true for graeserite with $(\text{As} + \text{Sb} + \text{Pb}) \gg 1$ p.f.u. In case of barian tomichite one may assume that due to the local occupation of Ba in the center of the cage, the cooperative mechanism of strain reduction cannot operate thus pairs of AsO_3 pyramids become possible. In tomichite (GREY et al., 1987) the one sided arrangement of As leads to a characteristic distortion of the cuboctahedron whereas Ba in barian tomichite (GREY et al., 1987) makes the cuboctahedron more regular. In case of graeserite it could be argued that the strain reduction is disturbed by the presence of differently distorted Pb- and As-containing cuboctahedra. It must also be considered that the cuboctahedra form infinite chains parallel to \mathbf{a} with O4–O4 as common edge. Arsenic in barian tomichite and in Pb-bearing graeserite bonds to this common edge (Fig. 4d). Thus, if pairs of AsO_3 pyramids exist within one cuboctahedron the neighboring cuboctahedron cannot be occupied by AsO_3 pairs. Otherwise O4

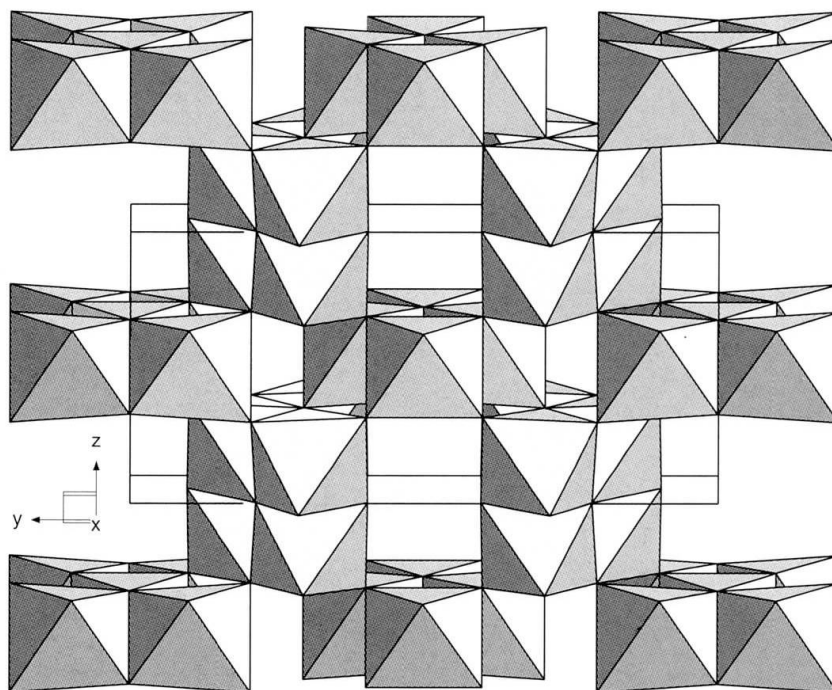


Fig. 3 The crystal structure of graeserite viewed approximately along $[001]$. The structure consists of layers of α - PbO_2 -type double chains and V_3O_5 -type columns, stacked in the $[001]$ direction, as shown in the figures 1 and 2. Channels of cuboctahedral cavities extend through the structure along $[100]$ containing (As,Sb) and Pb (cf. Fig. 4).

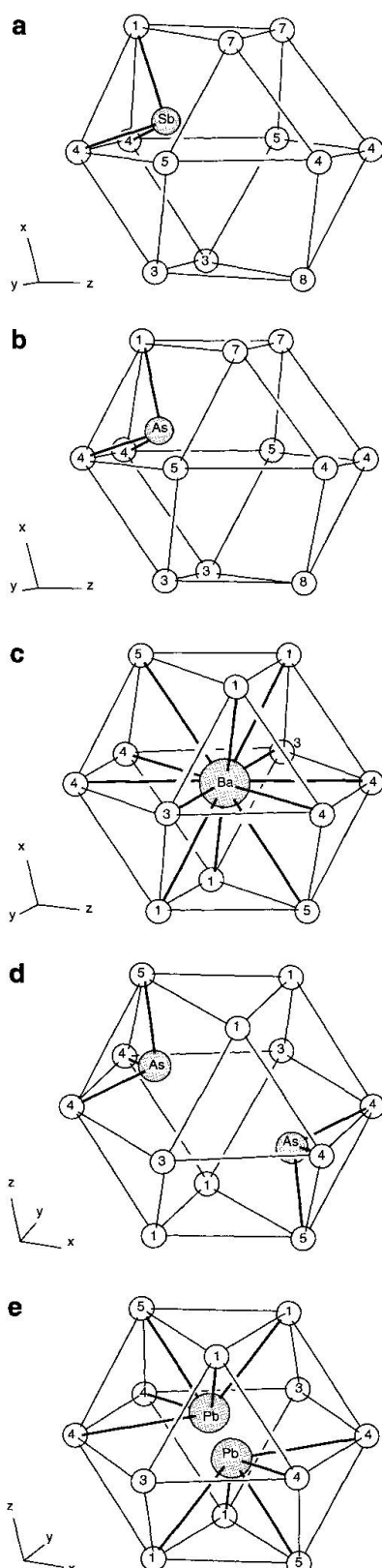


Fig. 4 A selection of visualized cuboctahedral cavities in the crystal structures of derbylite group minerals hosting various cations: a) Sb³⁺ in derbylite, b) As³⁺ in tomichite, c) Ba²⁺ in barian tomichite, d) (As³⁺, Sb³⁺)₂ in graeserite, e) Pb²⁺ in graeserite. Data from the original structure descriptions were used for generating (Figs 4 a–c).

Tab. 6 Bond valence estimation (BVE) for graeserite.

	O1	O2	O3	O4	O5	Sum
M1	0.59(4x)				0.61(2x)	3.58
M2	0.59(2x)	0.68(2x)			0.36(2x) ↓	3.14
M3	0.85	0.69 0.63	0.52(2x) ↓ 0.40	0.44(2x) ↓		3.53
As				0.86 ^{0.50} (2x) ↓	0.78 ^{0.50}	2.50
Pb	0.28 ^{0.07} (2x)			0.27 ^{0.07} (2x)	0.41 ^{0.50}	1.51
Sum	1.99	2.00	1.44	1.76	1.74	

Note: exponents refer to occupation; horizontal arrows indicate that multiple bond valences must be considered for the calculation of cation valence sums, vertical arrows indicate that multiple bond valences must be considered for the calculation of oxygen valence sums.

would be strongly overbonded and short As–As distances of 2.487 Å would result. This example indicates that a superstructure along *a* is very likely. The simplest superstructure model would require an alternation of paired AsO₃ units with empty or Pb filled cavities. However, any kind of alternation of AsO₃ pairs with single As occupied-, Pb occupied-, and empty cavities would be possible. An overlay of different ordering schemes could cause the observed satellite or superstructure reflections. Bond valence calculations (Tab. 6) indicate that if O5 is not locally bonded to either As or Pb it becomes strongly underbonded and is thus privileged to form an OH group (MOORE and ARAKI, 1976; GREY et al., 1987). Because the sum of (As + Sb + Pb) in Pb-bearing graeserite is 1.14 p.f.u. 0.86 OH p.f.u. must be expected. In analogy to barian tomichite with the assumed end-member composition Ba_{0.5}(As₂)_{0.5}M₇O₁₃OH (GREY et al., 1987), a plumbian graeserite can be predicted with the composition Pb_{0.5}(As₂)_{0.5}M₇O_{13.5}OH_{0.5}. Due to the lone electron pair character of Pb²⁺ the cation nests on one side of the cavity, five-fold coordinated by O, and prevents underbonding of O5 (Fig. 4e). Thus the OH contribution is reduced compared to barian tomichite. O5 contributes 20 p.f.u. thus in Pb-bearing graeserite the OH content is less than 50% at O5 which also explains why the proton could not be resolved in the structure refinement. An other candidate for OH or a hydrogen bond is O3 (Tab. 6) which is underbonded independent of the arrangement of As and Pb. One could argue that the low bond valence of 1.44 vu for O3 may be interpreted by about 50% OH on this site leading to the formula Pb_{0.14}(Fe, Ti)₇AsO_{12.14}OH_{1.86}. If we further consider 3.54 Ti p.f.u. with the remaining M sites occupied by Fe²⁺ and Fe³⁺, the above formula leads to a Fe²⁺/Fe³⁺ ratio of 1/1. Without knowing the exact

$\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and to allow for both mechanisms of OH substitution, the more general formula is $\text{Pb}_{0.14}(\text{Fe},\text{Ti})_7\text{AsO}_{12+x}(\text{OH})_{2-x}$.

COORDINATION POLYHEDRA

The coordinations around the three M sites in graeserite are distorted octahedral (Tab. 5). The mean M–O distances are 1.984 for M1–O, 2.044 for M2–O, and 1.999 Å for M3–O. These distances can be directly compared with those of barian tomichite which is isotypic to graeserite, but with V^{3+} replacing Fe^{3+} . The corresponding average M–O distances in barian tomichite are 1.981, 1.998, and 2.012. The mean M1–O distances for both minerals are very similar, whereas for the other two mean values significant differences are observed. A closer inspection of the cation-cation distances and angles in the two structures may provide an explanation. The 5 Å axis in graeserite is slightly shorter than the corresponding axis in barian tomichite. The compression of the $\alpha\text{-PbO}_2$ -type double chain in graeserite is obtained by reducing the M3–M3–M3 angles along [001] from 113.3° to 110.4° , i.e. the angles in the zigzag double chains are 2.9° smaller in graeserite than in barian tomichite (Fig. 2). Relative shortening/stretching of individual M–O distances within the octahedra match perfectly with the observed variation in angles which explains the differences in the mean M–O distances.

Similar observations can be made in the V_3O_5 -type layers in graeserite in which the M1–M2–M1 angles (111.1°) along [001] are reduced by two degrees compared to the corresponding angle in barian tomichite (113.1°) resulting in a slight compression as described above. Hand in hand with the compression along the 5 Å axis in graeserite goes the elongation along the 7 and 14 Å axes compared to barian tomichite (Tab. 1). Both, the substitution of Fe by V and different substituents in the cuboctahedral cavities may very well serve as explanations for the observed variations in bond lengths and angles.

In all derbylite group minerals As and/or Sb form the apices of trigonal pyramids each with three oxygen atoms at their bases (Figs 4 a, b, d). The mean (As,Sb)–O distances in graeserite are 1.857 Å compared to 1.826 Å in barian tomichite and 1.847 Å in tomichite. These average (As,Sb)–O distances are somewhat longer than values reported in the literature for pyramidal As^{3+} , e.g., in reinerite, $\text{Zn}_3(\text{AsO}_3)_2$, the average As–O bond length is 1.774 Å (GHOSE et al., 1977), and the observed elongation may reflect partial substitution of As by Sb. On the other hand, it has to be con-

sidered that Pb-bearing graeserite represents a strongly disordered average structure.

M CATION ORDER/DISORDER

To test Fe/Ti ratios on M sites, individual populations were allowed to vary during the structure refinement. However, the scattering curves of Fe and Ti are quite similar leading to substantial correlation of the refined values. The M population refinements yielded an average Ti/Fe ratio of about 2.8 whereas the Ti/Fe ratio determined by electron microprobe analyses is 1.02. This discrepancy can not be explained solely by correlation problems. On the other hand, KRZEMNICKI and REUSSER (in press) determined only 6.83 (Fe,Ti) p.f.u. compared with 7 (Fe,Ti) p.f.u. as expected for stoichiometry. It must be assumed that either octahedral vacancies exist or light octahedral elements such as Al, Mg, and/or Li were overlooked. Both possibilities would lead to an overestimation of Ti in the population refinements. The only conclusion so far from the population refinement is that M2 shows the highest and M3 the lowest average number of electrons. The multiplicity of M3 is 8, compared to 2 and 4 for the M1 and M2 sites, respectively. Thus, the distribution of Fe and Ti cannot be far away from complete disorder because the atomic proportion obtained from electron microprobe data is Fe : Ti = 3.29 : 3.54, which diverges less than 10% from the 1 : 1 ratio. Furthermore, ideal derbylite minerals have 3 Ti^{4+} + 4 M^{3+} p.f.u. in octahedral coordination. Increased Ti^{4+} concentrations, as observed for graeserite, are explained by the substitution $\text{Ti}^{4+} + \text{Fe}^{2+} \leftrightarrow 2 \text{Fe}^{3+}$ which additionally increases the disorder. Therefore, we propose that the populations of Fe and Ti in the M sites vary within the range $\text{Fe}_{1-x}\text{Ti}_x$ where $0.3 < x < 0.7$. This is in contrast to the findings of MOORE and ARAKI (1976), who found for stoichiometric derbylite, $\text{Fe}_4\text{Ti}_3\text{SbO}_{13}(\text{OH})$, pure Fe and Ti as well as mixed Fe/Ti M sites. Based on the values tabulated by ALTERMATT and BROWN (1985) ideal octahedral Ti^{4+} –O, Fe^{3+} –O, and Fe^{2+} –O distances are 1.965, 2.015, and 2.140 Å, respectively. If we ignore the possible effect of light elements or vacancies on M sites, these empirical bond lengths indicate by comparison with our observed distances, a preference of mainly Ti^{4+} and Fe^{3+} for M1 and M3 whereas the larger cations (e.g., Fe^{2+}) seem to be enriched on M2. This is the same trend as observed for derbylite (MOORE and ARAKI, 1976) and tomichite or barian tomichite (GREY et al., 1987).

The results of a bond-valence sum estimation are listed in table 6. The calculations were per-

formed for a hypothetical Fe³⁺:Ti⁴⁺ = 1 : 1 ratio on the M sites and either As³⁺ or Pb²⁺ in the cuboctahedron. The results for M1 and M3 are very close to the expected theoretical value (3.5). However, for M2 the estimated value is lower, eventually indicating that two- and three-valent elements may prefer the M2 site as already assumed from the M2–O distances.

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