

**GRAESERITE,  $\text{Fe}_4\text{Ti}_3\text{AsO}_{13}(\text{OH})$ ,  
A NEW MINERAL SPECIES OF THE DERBYLITE GROUP FROM THE  
MONTE LEONE NAPPE, BINNTAL REGION, WESTERN ALPS, SWITZERLAND**

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ABSTRACT

Graeserite, ideally  $\text{Fe}_4\text{Ti}_3\text{AsO}_{13}(\text{OH})$ , is a new mineral species of the derbylite group, which includes derbylite, tomichite, and hemloite. It is found in needle-shaped crystals, elongate along the *c* axis. Graeserite is monoclinic, space group *A2/m*, with the cell parameters *a* 7.184(2), *b* 14.289(6), *c* 5.006(2) Å,  $\beta$  105.17(2)°, *V* 495.9(2) Å<sup>3</sup>, *Z* = 2, *D*<sub>calc.</sub> = 4.56 g/cm<sup>3</sup>. The VHN<sub>25g</sub> is 521 (Mohs hardness ~5½). The strongest five lines of the X-ray powder-diffraction pattern [*d* in Å(*I*)(*hkl*)] are: 2.681(100)( $\bar{2}$ 31), 2.846(80)(131), 1.583(50)(351), 3.117 (30)(220), and 2.029(30)(122). Graeserite is black and metallic, with a black streak; it displays a conchoidal fracture. Pleochroism, bireflectance and internal reflections were not observed. The measured values of reflectance in air are compared with those of other members of the derbylite group. Electron-microprobe analyses gave TiO<sub>2</sub> 40.89, Fe<sub>2</sub>O<sub>3</sub> 33.64, FeO<sub>calc.</sub> 3.94, PbO 5.00, As<sub>2</sub>O<sub>3</sub> 13.51, Sb<sub>2</sub>O<sub>3</sub> 1.43, and H<sub>2</sub>O<sub>calc.</sub> 1.30, total 99.80 wt.%. The empirical formula, based on 13 atoms of oxygen and one hydroxyl group, is (Fe<sup>3+</sup><sub>2.91</sub>Fe<sup>2+</sup><sub>0.38</sub>Ti<sub>0.54</sub>Pb<sub>0.15</sub>) $\Sigma$ <sub>3.98</sub>Ti<sub>3</sub>(As<sup>3+</sup><sub>0.94</sub>Sb<sup>3+</sup><sub>0.07</sub>) $\Sigma$ <sub>1.01</sub>O<sub>13</sub>(OH). Graeserite occurs as a hydrothermal mineral in Alpine-type fissures in gneisses of the Monte Leone nappe at the locality Lärcheltini, in the Binntal region of Switzerland, in association with other rare arsenic oxides. With the name, we honor Stephan Graeser, University of Basel, Switzerland, for his fundamental studies of arsenic-bearing minerals.

*Keywords:* graeserite, new mineral species, derbylite group, Binntal region, Western Alps, Switzerland.

SOMMAIRE

La graeserite, de composition idéale  $\text{Fe}_4\text{Ti}_3\text{AsO}_{13}(\text{OH})$ , est une nouvelle espèce minérale du groupe de la derbylite, qui inclut derbylite, tomichite, et hemloïte. Elle se présente en cristaux aciculaires allongés selon l'axe *c*. La graeserite est monoclinique, groupe spatial *A2/m*, paramètres réticulaires *a* 7.184(2), *b* 14.289(6), *c* 5.006(2) Å,  $\beta$  105.17(2)°, *V* 495.9(2) Å<sup>3</sup>, *Z* = 2, *D*<sub>calc.</sub> = 4.56 g/cm<sup>3</sup>. La dureté VHN<sub>25g</sub> est de 521 (~5½ sur l'échelle de Mohs). Les cinq raies les plus intenses du spectre de diffraction X (méthode des poudres) [*d* en Å(*I*)(*hkl*)] sont: 2.681(100)( $\bar{2}$ 31), 2.846(80)(131), 1.583(50)(351), 3.117 (30)(220), et 2.029(30)(122). La graeserite est noir métallique, avec une rayure noire; elle possède une fracture conchoïdale. Nous avons décelé ni pléochroïsme, ni biréflexion, ni réflexions internes. Les valeurs mesurées de réflectance dans l'air sont comparées avec celles d'autres membres du groupe de la derbylite. Les analyses obtenues par microsonde électronique ont donné TiO<sub>2</sub> 40.89, Fe<sub>2</sub>O<sub>3</sub> 33.64, FeO<sub>calc.</sub> 3.94, PbO 5.00, As<sub>2</sub>O<sub>3</sub> 13.51, Sb<sub>2</sub>O<sub>3</sub> 1.43, et H<sub>2</sub>O<sub>calc.</sub> 1.30, total 99.80% (par poids). La formule empirique, calculée sur une base de 13 atomes d'oxygène et un groupe d'hydroxyle, est (Fe<sup>3+</sup><sub>2.91</sub>Fe<sup>2+</sup><sub>0.38</sub>Ti<sub>0.54</sub>Pb<sub>0.15</sub>) $\Sigma$ <sub>3.98</sub>Ti<sub>3</sub>(As<sup>3+</sup><sub>0.94</sub>Sb<sup>3+</sup><sub>0.07</sub>) $\Sigma$ <sub>1.01</sub>O<sub>13</sub>(OH). La graeserite est le produit d'une cristallisation hydrothermale dans des fentes alpines dans des gneiss de la nappe de Monte Leone à Lärcheltini, dans la région de Binntal, en Suisse; elle y est associée à d'autres oxydes d'arsenic rares. Par le choix du nom, nous honorons Stefan Graeser, de l'Université de Bâle, en Suisse, qui a fait des études fondamentales des minéraux d'arsenic.

(Traduit par la Rédaction)

*Mots-clés:* graeserite, nouvelle espèce minérale, groupe de la derbylite, région de Binntal, Alpes occidentales, Suisse.

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## INTRODUCTION

Graeserite, ideally  $\text{Fe}_4\text{Ti}_3\text{AsO}_{13}(\text{OH})$ , is a new mineral species found in Alpine-type fissures in paragneisses of the Monte Leone nappe, Binntal region, Western Alps, Switzerland. It belongs to the derbylite group, which consists of the species derbylite, tomichite (including barian tomichite), and hemloite (Table 1). Except for hemloite, the minerals of this group exhibit the general formula  $M^{3+}_xM^{4+}_y\text{O}_{13}(\text{OH})$ . The cation site  $M^{3+}$  is occupied by  $\text{Fe}^{3+}$  and  $\text{V}^{3+}$  (with occasionally some  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ti}^{4+}$ ), and the  $M^{4+}$  site by  $\text{Ti}^{4+}$ . Both the  $M^{3+}$  and  $M^{4+}$  sites are octahedrally coordinated. The tetrahedrally coordinated  $T$  site is occupied by  $\text{Sb}^{3+}$ ,  $\text{As}^{3+}$ , and occasionally  $\text{Ba}^{2+}$  in barian tomichite. The values for the stoichiometric coefficients  $x:y$  are commonly 4:3 (derbylite, tomichite, and graeserite), but may also amount to 5:2 (barian tomichite).

Derbylite was discovered a century ago (Hussak & Prior 1897) in cinnabar-bearing gravels at Tripuhy, Minas Gerais, Brazil. Its close-packed oxide crystal structure was determined by Moore & Araki (1976) and refined by Mellini *et al.* (1983). Tomichite was first reported by Nickel & Grey (1979) from the Kalgoorlie gold deposit in Australia. The crystal structure of tomichite was determined by Grey *et al.* (1987), who further reported barian tomichite at the Hemlo gold deposit, Ontario. From the same deposit, Harris *et al.* (1989) described hemloite as a further member of the derbylite group.

In this study, we present mineralogical, chemical and preliminary structural data for graeserite. Graeserite is named in honor of Professor Stefan Graeser (b. 1935), of the Mineralogical–Petrographic Institute, University of Basel, Switzerland, who has been involved for years in research on oxides and sulfosalts of arsenic in the Binntal region of the Monte Leone nappe (Graeser 1966, Graeser & Roggiani 1976, Graeser *et al.* 1994, and references therein). Both the mineral and the name have been approved by the IMA Commission on New Minerals and Mineral Names (proposal 96–010). Specimens are held at the Natural History Museum in Basel, Switzerland.

## OCCURRENCE

Graeserite was discovered 1995 in hydrothermal veins that occur in a two-mica paragneiss of the Monte Leone nappe, Binntal region, Western Alps, Switzerland, or in small cavities in proximity to such veins (wallrock alteration). Numerous specimens have been found at the locality Lärcheltini (Fig. 1), accompanied by a wide range of other hydrothermal minerals, including anatase, arsenopyrite, asbescasite, bournonite, cafarsite, cervandonite-(Ce), chernovite, fetiasite, gold (traces), hematite, magnetite, monazite-(Ce), rutile and tennantite.

The formation of graeserite is attributed to the hydrothermal activity associated with the Tertiary Alpine

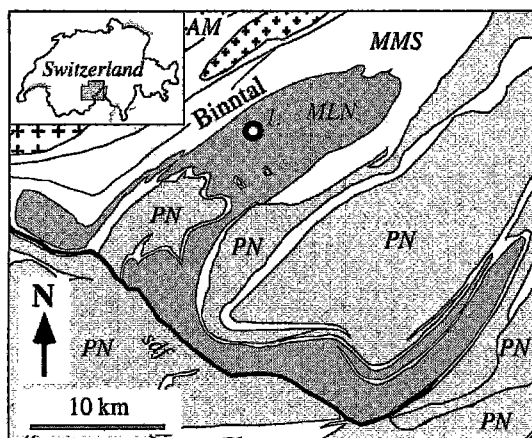


FIG. 1. General tectonic map of the Binntal region, Western Alps, Switzerland. Symbols: *l.* locality Lärcheltini, *MLN* Monte Leone nappe, *PN* Penninic nappes, *MMS* Mesozoic metasediments, *AM* Aar massif (granites), *sdf* Simplicon detachment fault.

orogeny, which affected the whole Alpine region by extensive ductile–brittle deformations and regional metamorphism reaching conditions of the lower amphibolite facies in the Monte Leone nappe. The regional geology is discussed in more detail by Streckeisen *et al.* (1974), Steck (1987), Hügi (1988), and Krzewnicky (1996). Several Prealpine ore concentrations (As–Fe–Cu–Pb sulfides) within this nappe were locally remobilized, thus generating some unique hydrothermal mineralizations (*e.g.*, Lengenbach, Pizzo Cervandone, Wannigletscher, Lärcheltini; *cf.* Graeser 1966, Graeser & Roggiani 1976, Krzewnicky 1996).

## PHYSICAL AND OPTICAL PROPERTIES

Table 2 presents a summary of the physical properties of graeserite compared with the other members of the derbylite group. Graeserite, monoclinic *A2/m*, is generally found in well-developed, euhedral crystals that are elongate along the *c* axis. Commonly, they are needle-shaped (<10  $\mu\text{m}$  thick, up to 5 mm long, Fig. 2). Lineations parallel to the *c* axis indicate extensive twinning. Occasionally, graeserite occurs in radial aggre-

TABLE 1. MINERALS OF THE DERBYLITE GROUP

Mineral	Chemical Formula	Space Group
Derbylite	$\text{Fe}_4\text{Ti}_3\text{SbO}_{13}(\text{OH})$	<i>P2<sub>1</sub>/m</i>
Tomichite	$(\text{V,Fe})_4\text{Ti}_3\text{AsO}_{13}(\text{OH})$	<i>P2<sub>1</sub>/m</i>
Barian Tomichite	$(\text{V,Fe})_4\text{Ti}_3\text{Ba}_{0.5}(\text{As})_{0.5}\text{O}_{13}(\text{OH})$	<i>A2/m</i>
Graeserite	$\text{Fe}_4\text{Ti}_3\text{AsO}_{13}(\text{OH})$	<i>A2/m</i>
Hemloite	$(\text{Ti,V,Fe,Al})_{12}(\text{As,Sb})_2\text{O}_{23}$	<i>PI</i>

TABLE 2. COMPARISON OF THE DERBYLITE-GROUP MINERALS

	Graeserite	Tomichite	Barian tomichite	Derbylite
System	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>A2/m</i>	<i>P2<sub>1</sub>/m</i>	<i>A2/m</i>	<i>P2<sub>1</sub>/m</i>
<i>a</i> (Å)	7.184	7.119	7.105	7.16
<i>b</i> (Å)	14.289	14.176	14.21	14.347
<i>c</i> (Å)	5.006	4.992	5.043	4.97
$\beta$ (°)	105.17	105.05	104.97	104.61
<i>V</i> (Å <sup>3</sup> )	495.9			
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	4.56	4.42		4.76
microhardness				
VHN <sub>25</sub>	521	800		
color	opaque, black	opaque, black	opaque, black	resinous, black
color values	<i>R1 R2</i>	<i>R1 R2</i>		<i>R1 R2</i>
<i>x</i>	0.300 0.300	0.311 0.312		0.298 0.298
<i>y</i>	0.305 0.305	0.316 0.317		0.303 0.302
<i>Y</i> %	18.6 17.5	17.1 17.8		18 19.1
$\lambda$	476 476	504 589		476 475
<i>P e</i> %	5.2 5.2	0.3 0.7		5.9 6.2
type locality	Lärcheltini Binntal Switzerland	Kalgoorlie Western Australia	Hemlo deposit Ontario	Tripuhy Minas Gerais Brazil

TABLE 3. GRAESERITE: REFLECTED-LIGHT MICROSCOPY

$\lambda$	reflectance values			color values C illuminant	
	<i>R1</i>	<i>R2</i>		<i>R1</i>	<i>R2</i>
400 nm	22.6 %	23.5 %	<i>x</i>	0.2997	0.2998
420	21.7	22.5			
440	20.9	21.6	<i>y</i>	0.3049	0.3048
460	20.1	20.8			
480	19.6	20.3	<i>Y</i> %	18.6	17.5
500	19.3	19.9			
520	19.0	19.6			
540	18.7	19.3			
560	18.4	19.0	<i>1 d</i>	476.4	475.9
580	18.2	18.9			
600	18.1	18.6	<i>P e</i> %	5.2	5.2
620	17.9	18.5			
640	17.7	18.3			
660	17.5	18.1			
680	17.3	17.9			
700	17.3	17.9			

gates, which are attached to fetiasite and in some cases intergrown with feldspar crystals.

Graeserite displays a distinct ductile behavior; thus the crystals commonly are deformed and curved during sample preparation. Therefore, it is rather difficult to investigate the morphology by optical goniometer or to determine the crystal structure of graeserite by single-crystal X-ray methods. Graeserite exhibits a moderate cleavage along {100} and a conchoidal fracture. The density could not be measured directly by immersion in heavy liquids, as it is greater than that of Clerici solution, but was calculated on the basis of the empirical formula; *Dx* 4.56 g/cm<sup>3</sup>. The Vickers hardness was

measured with a load of 25 g on a polished section of a graeserite aggregate. The mean value of VHN<sub>25</sub>, 521, corresponds to a Mohs hardness of about 5½.

For reflectance measurements, we used a Leitz microscope with a Zeiss-SiC reference standard. Data measured in air only are listed in Table 3. A comparison of the data with values for derbylite and tomichite reveals a close similarity between graeserite and derbylite (Fig. 3). Pleochroism, bireflectance and internal reflections were not observed. The optical data are given in Table 2.

Raman spectra were obtained on a Renishaw Raman system 1000 (Swiss Gemmological Institute SSEF,

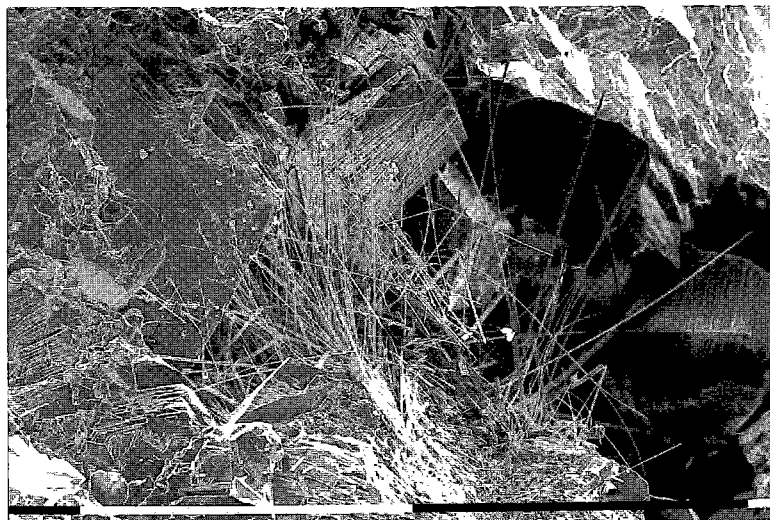


FIG. 2. SEM photomicrograph of an aggregate of graeserite crystals. Scale bar: 1 mm.

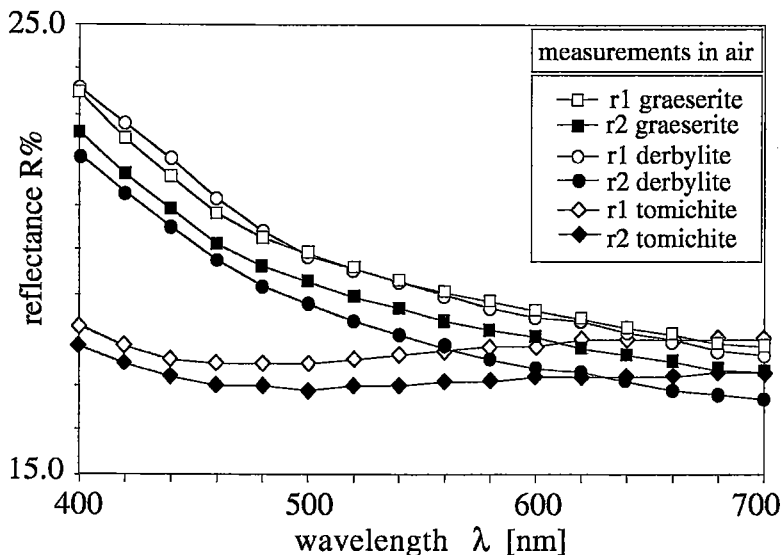


FIG. 3. Comparison of reflectance data for the derbylite-group minerals. The reflectance values  $R\%$  versus wavelength  $\lambda$  [nm] diagram (measured in air) reveals a close similarity between graeserite and derbylite.

Basel) with an argon laser (25 mW, omnichrome). A typical spectrum for graeserite is shown in Figure 4, as it may aid in identification.

#### X-RAY CRYSTALLOGRAPHY AND CHEMICAL COMPOSITION

X-ray-diffraction analyses by precession and Weissenberg techniques showed graeserite to be monoclinic  $A2/m$ . The cell parameters were refined from powder data and are compared with those of the other members of the derbylite group (Table 2). The indexed X-ray powder-diffraction data for graeserite are listed in Table 4. There are strong similarities between the powder pattern of graeserite and those of other derbylite-group minerals, which point to a close structural relationship among this group of minerals (Nickel & Grey 1979, Mellini *et al.* 1983, Grey *et al.* 1987, Berlepsch & Armbruster 1998).

All samples of graeserite were first analyzed qualitatively by energy-dispersion spectroscopy (ED-XRF) for element identification. These analyses and photographic documentation were carried out with a Philips 515 scanning electron microscope, equipped with an ED-XRF spectrometer (SEM Laboratory, University of Basel).

Six samples were analyzed quantitatively using a Cameca SX-50 electron microprobe with an acceleration voltage of 20 kV and a beam current of 10 nA. The following elements were measured (standards in parentheses): Fe (hematite), Ti (rutile), Mn (spessartine), Pb (galena), Si (quartz), As (synthetic GaAs), and Sb (syn-

thetic  $Sb_2O_3$ ). Vanadium and barium, which are important constituents of tomichite and barian tomichite, were found to be below the limit of detection. All data were corrected for matrix effects by a ZAF-type online procedure. The average composition determined from results of 39 analyses (6 samples) is shown in Table 5. The chemical composition of all the samples is rather uniform, although the concentrations of Fe, Ti, Pb and Sb show some variation from sample to sample. Back-scattered-electron images (BSE) revealed no compositional zoning within the analyzed samples.

The normalization of the graeserite formula (Table 5) is based on a total of 27 negative charges (*i.e.*,  $O^{2-}_{13} + OH^-$ ) and a sum of eight cations at the  $M^{3+}$ ,  $M^{4+}$ , and  $T$  sites, as first proposed by Moore & Araki (1976) for derbylite. The  $H_2O$  content was calculated assuming one hydroxyl group per formula unit (Moore & Araki 1976). According to Grey *et al.* (1987) and Mellini *et al.* (1983), charge balance is usually maintained by variation in the ratio of  $Fe^{2+}$  to  $Fe^{3+}$ . In graeserite, this ratio ( $\sim 0.130$ ) is comparable with the one found in derbylite ( $Fe^{2+}/Fe^{3+} \approx 0.155$ ; Mellini *et al.* 1983). The similarity in the values may be interpreted as a further indication of a close structural relationship between these two minerals.

The empirical formula for graeserite, derived from electron-microprobe data (based on the average results, Table 5), is  $(Fe^{3+}_{2.91}Fe^{2+}_{0.38}Ti_{0.54}Pb_{0.15})_{\Sigma 3.98}Ti_3(As^{3+}_{0.94}Sb^{3+}_{0.07})_{\Sigma 1.01}O_{13}(OH)$ , which is in good agreement with the composition  $Pb_{0.14}(Fe,Ti)_7AsO_{12+x}(OH)_{2-x}$  obtained from the structure determination (Berlepsch & Armbruster 1998) on material from the

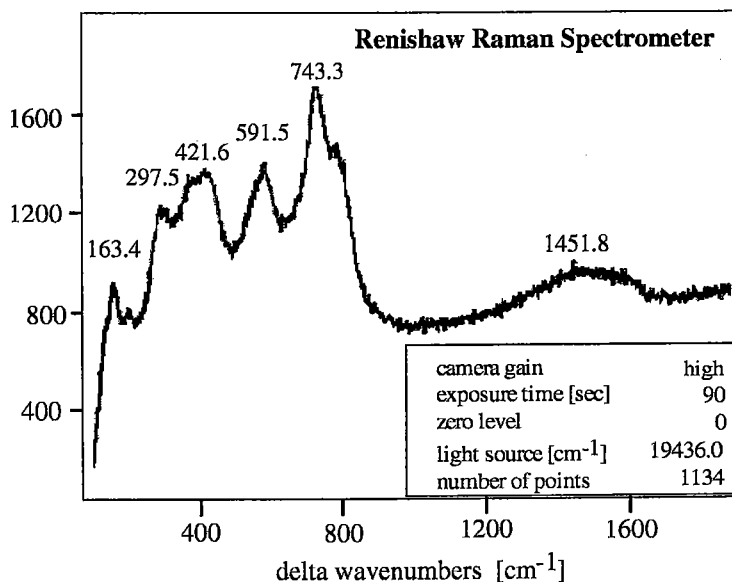


FIG. 4. Raman spectrum of graeserite, as obtained with a Renishaw Raman spectrometer.

same locality. The idealized formula of graeserite may be written as  $\text{Fe}_4\text{Ti}_3\text{AsO}_{13}(\text{OH})$ . The analyzed samples all contain some  $\text{Pb}^{2+}$  and  $\text{Fe}^{2+}$  (calculated on the basis of charge balance) and a small excess in  $\text{Ti}^{4+}$  with respect to the idealized stoichiometry. The incorporation of these substituting elements is probably due to the heterovalent substitution [i]  $(\text{Fe}, \text{Pb})^{2+}\text{Ti}^{4+}$  at the  $M^{3+}$  site. A plot (Fig. 5) of amount of  $\text{Fe}^{3+}$  versus  $\Sigma(\text{Fe}, \text{Pb})^{2+} + \text{Ti}^{4+}$  reveals a distinct negative correlation (slope:  $-1.043$ ,  $R^2 = 0.924$ ), which fits well with this mechanism of substitution. A bivariate plot for  $\text{As}^{3+}$  versus  $\text{Sb}^{3+}$  exhibits only a weak negative correlation, although the incorporation of minor Sb in graeserite is easily explained by a simple exchange substitution between  $\text{Sb}^{3+}$  and  $\text{As}^{3+}$  at the arsenic site.

TABLE 4. X-RAY-DIFFRACTION DATA FOR GRAESERITE

$I_{\text{rel}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	hkl	$I_{\text{rel}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	hkl
30	3.117	3.119	220	20	1.7234	1.7235	222
80	2.846	2.847	131	20	1.6218	1.6224	213
100	2.681	2.683	231			1.5834	422
20	2.495	2.493	102	50	1.5825	1.5824	351
20	2.225	2.226	151			1.5816	162
20	2.148	2.145	251	20	1.5150	1.5151	451
30	2.029	2.029	122			1.4405	153
20	1.8093	1.8088	351	10	1.4400	1.4400	431
20	1.7765	1.7760	202			1.3661	413
				20	1.3647	1.3648	182

Powder data with Debye-Scherrer camera,  $\text{FeK}\alpha$  radiation. Intensities  $I_{\text{rel}}$  by visual estimation;  $d_{\text{obs}}$  determined from the cell parameters  $a$  7.184,  $b$  14.289,  $c$  5.006 Å,  $\beta$  105.17°. Values of  $d_{\text{obs}}$  and  $d_{\text{calc}}$  are expressed in Å.

## DISCUSSION

Derbylite, tomichite, barian tomichite, hemloite, and graeserite are rare accessory phases known to date from only a few deposits worldwide: Tripuhy (Brazil), Kalgoorlie (Australia), Hemlo (Ontario, Canada), Buca della Vena (Italy), and Lärcheltini (Switzerland). The complex mineralizations of these deposits are commonly attributed to metasomatic and hydrothermal fluids (Mellini *et al.* 1983, Grey *et al.* 1987, Graeser & Roggiani 1976). Graeserite, as well as the other

TABLE 5. CHEMICAL COMPOSITION OF GRAESERITE

	mean wt%	range	1 $\sigma$	<i>apfu</i>	
$\text{TiO}_2$	40.89	(39.75–41.92)	0.46	$\text{Ti}^{4+}$	3.54
$\text{Fe}_2\text{O}_3$	33.64	(31.65–35.55)	0.85	$\text{Fe}^{3+}$	2.91*
FeO	3.94	(3.20–4.85)	0.43	$\text{Fe}^{2+}$	0.38*
PbO	5.00	(2.22–6.35)	1.05	Pb <sup>2+</sup>	0.15
MnO	0.06	(n.d.–0.13)	0.03	Mn <sup>2+</sup>	0.01
$\text{As}_2\text{O}_3$	13.51	(13.12–14.31)	0.30	$\text{As}^{3+}$	0.94
$\text{Sb}_2\text{O}_3$	1.43	(0.7–2.33)	0.45	$\text{Sb}^{3+}$	0.07
$\text{SiO}_2$	0.02	(n.d.–0.08)	0.02	$\text{Si}^{4+}$	0.00
$\text{H}_2\text{O}$	1.30	(1.28–1.34)	0.01	$\text{OH}^-$	1.00*
Total	99.79				

Electron-microprobe data, reported in wt%. The range of 39 analyses is reported. The normalization is based on 8 cations per formula unit and a total of 27 negative charges. The proportion of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  was calculated based on charge-balance constraints. The FeO and  $\text{Fe}_2\text{O}_3$  contents were recalculated, on the basis of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio. The proportion of  $\text{H}_2\text{O}$  was determined on the assumption of one hydroxyl group per formula unit (*cf.* Moore & Araki 1976, Grey *et al.* 1987, Mellini *et al.* 1983). n.d.: not detected (below the limit of detection limit); *apfu*: atoms per formula unit. The concentration of V and Ba are invariably below the limit of detection.

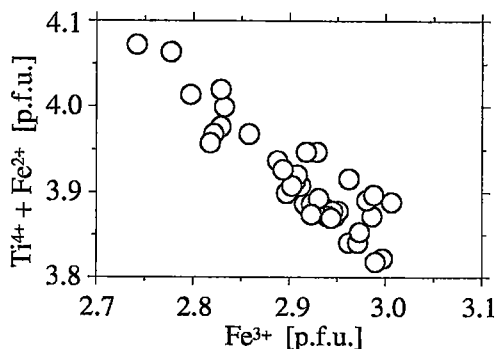


FIG. 5. A plot of the concentration of  $\text{Fe}^{3+}$  versus  $\Sigma(\text{Fe}, \text{Pb})^{2+} + \text{Ti}^{4+}$  reveals a distinct negative correlation, which fits very well the proposed mechanism of heterovalent substitution [i]  $(\text{Fe}, \text{Pb})^{2+}\text{Ti}^{4+}\text{Fe}^{3+}_{-2}$ . [p.f.u.]: per formula unit.

members of the derbylite group, seem to be related to the presence of Au mineralization (e.g., tomichite: Kalgoorlie gold deposit; barian tomichite: Hemlo gold deposit, hemloite: Hemlo gold deposit). At Lärcheltini, the occurrence of native gold (traces) close to graeserite has recently been confirmed (T. Mumenthaler, pers. commun.).

Finally, it seems likely that an isomorphic series (partial or even complete) exists between graeserite and both derbylite and tomichite. This conclusion is based on the proposed mechanism of substitution on various sites in graeserite, and in addition on structural and crystallographic analogies between these minerals (e.g., Tables 2, 3).

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#### REFERENCES

BERLEPSCH, P. & ARMBRUSTER, T. (1998): The crystal structure of  $\text{Pb}^{2+}$ -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. *Schweiz. Mineral. Petrogr. Mitt.* **78**, 1-9.

GRAESER, S. (1966): Asbecasit und Cafarsit, zwei neue Mineralien aus dem Binnatal (Kt. Wallis). *Schweiz. Mineral. Petrogr. Mitt.* **46**, 367-375.

\_\_\_\_\_, & ROGGIANI, A.G. (1976): Occurrence and genesis of rare arsenate and phosphate minerals around Pizzo Cervandone, Italy/Switzerland. *Rend. Soc. Ital. Mineral. Petrogr.* **32**, 279-288.

\_\_\_\_\_, SCHWANDER, H., DEMARTIN, F., GRAMACCIOLI, C.M., PILATI, T. & REUSSER, E. (1994): Fetiasite  $(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Ti})_3\text{O}_2[\text{As}_2\text{O}_5]$ , a new arsenite mineral: its description and structure determination. *Am. Mineral.* **79**, 996-1002.

GREY, I.E., MADSEN, I.C. & HARRIS, D.C. (1987): Barian tomichite,  $\text{Ba}_{0.5}(\text{As}_2)_{0.5}\text{Ti}_2(\text{V}, \text{Fe})_5\text{O}_{13}(\text{OH})$ , its crystal structure and relationship to derbylite and tomichite. *Am. Mineral.* **72**, 201-208.

HARRIS, D.C., HOSKINS, B.F., GREY, I.E., CRIDDLE, A.J. & STANLEY, C.J. (1989): Hemloite  $(\text{As}, \text{Sb})_2(\text{Ti}, \text{V}, \text{Fe}, \text{Al})_{12}\text{O}_{23}\text{OH}$ : a new mineral from the Hemlo gold deposit, Hemlo, Ontario, and its crystal structure. *Can. Mineral.* **27**, 427-440.

HÜGI, M. (1988): *Mineralogie und Petrographie der Lärcheltinzone (Monte Leone Decke, Binntal, VS)*. Diploma thesis, Mineral. Petrograph. Institute, Univ. of Bern, Bern, Switzerland.

HUSSAK, E. & PRIOR, G.T. (1897): On derbylite, a new antimonio-titanate of iron, from Tripuhy, Brazil. *Mineral. Mag.* **11**, 176-179.

KRZEMNICKI, M.S. (1996): *Mineralogical Investigations on Hydrothermal As- and REE-Bearing Minerals within the Gneisses of the Monte Leone Nappe (Binntal Region, Switzerland)*. Ph.D. thesis, Mineral. Petrograph. Institute, Univ. of Basel, Basel, Switzerland.

MELLINI, M., ORLANDI, P. & PERCHIAZZI, N. (1983): Derbylite from Buca della Vena mine, Apuan Alps, Italy. *Can. Mineral.* **21**, 513-516.

MOORE, P.B. & ARAKI, T. (1976): Derbylite,  $\text{Fe}^{3+}_4\text{Ti}^{4+}_3\text{Sb}^{3+}\text{O}_{13}(\text{OH})$ , a novel close-packed oxide structure. *Neues Jahrb. Mineral., Abh.* **126**, 292-303.

NICKEL, E.H. & GREY, I.E. (1979): Tomichite, a new oxide mineral from Western Australia. *Mineral. Mag.* **43**, 469-471.

STECK, A. (1987): Le massif du Simplon – réflexions sur la cinématique des nappes de gneiss. *Schweiz. Mineral. Petrogr. Mitt.* **67**, 27-45.

STRECKEISEN, A., WENK, E. & FREY, M. (1974): On steep isogradic surfaces in the Simplon area. *Contrib. Mineral. Petrol.* **47**, 81-95.

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