

GANTERITE, A NEW BARIUM-DOMINANT ANALOGUE OF MUSCOVITE FROM THE BERISAL COMPLEX, SIMPLON REGION, SWITZERLAND

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ABSTRACT

Ganterite, $[\text{Ba}_{0.5}(\text{Na,K})_{0.5}]\text{Al}_2(\text{Si}_{2.5}\text{Al}_{1.5}\text{O}_{10})(\text{OH})_2$, the barium-dominant analogue of muscovite, was discovered in the crystalline basement rocks of the Berisal Complex, Simplon Region, Switzerland. Examples of this new rock-forming mica are found in bands and lenses of white-mica schist, and in a leucocratic zoisite–celsian gneiss. Samples of the schist, and especially of the celsian-bearing gneiss, are characterized by high whole-rock Ba contents of up to 15 wt.% BaO. The mineral paragenesis consists of zoisite, quartz, plagioclase, apatite, zircon and amphibole in the schist, and zoisite, celsian, quartz, margarite ± armenite in the gneiss. Ganterite is light grey to silver, has a vitreous luster, a perfect {001} cleavage, a laminated fracture, and a flexible tenacity. Mohs hardness, determined from micro-hardness indentations, is 4–4½. The mica is biaxial (–), α 1.600 (calc.), β 1.619, γ 1.622, and $2V$ (meas.) equal to $42.5 \pm 2^\circ$. The calculated density of the most Ba-rich ganterite is 3.11 g/cm^3 . Single crystals typically are 0.5 by 0.15 mm (or less), and occur in small bands, lenses or clusters 0.5 to 10 cm in thickness. Ganterite is monoclinic, space group $C2/c$, $Z = 4$, a 5.212(1), b 9.046(2), c 19.978(4) Å, β $95^\circ 48'$, V 937.6 Å³, corresponding to a $2M_1$ polytype. The strongest seven powder-diffraction lines [d in Å(I)(hkl)] are: 2.571(100)(131,202), 2.602(95)(130,131), 1.5054(91)(060,2010), 3.737(77)(023), 3.887(76)(113), 4.481(71)(110), and 3.495(71)(114). The new mineral species is named after the geographical region in which it was found.

Keywords: ganterite, barium, muscovite, new mineral species, Berisal Complex, Simplon, Switzerland.

SOMMAIRE

La gantérite $[\text{Ba}_{0.5}(\text{Na,K})_{0.5}]\text{Al}_2(\text{Si}_{2.5}\text{Al}_{1.5}\text{O}_{10})(\text{OH})_2$, un analogue de la muscovite à dominance de barium, a été découvert au sein du socle cristallin du complexe du Béréal, dans la région du Simplon, en Suisse. On trouve ce type de mica dans des couches et lentilles de schiste à mica blanc, et des lentilles de gneiss leucocrate à celsiane et zoïsite. Des échantillons de schiste et de gneiss possèdent jusqu'à 15% de BaO (poids). La gantérite coexiste avec zoïsite, celsiane, quartz, plagioclase, apatite, zircon et amphibole au sein du schiste, et zoïsite, celsiane, quartz, margarite ± arménite dans le gneiss. La gantérite est gris-pâle à argenté, elle possède un éclat vitreux, un clivage {001} parfait, une structure lamellaire et une ténacité élastique. La dureté de Mohs, déterminée à partir de micro-indentations de dureté, est de 4–4½. Les indices de réfraction sont α 1.600 (calc.), β 1.619 et γ 1.622, et la valeur mesurée de $2V$ (négatif) est de $42.5 \pm 2^\circ$. La densité calculée de la gantérite la plus riche en Ba est de 3.11 g/cm^3 . En général, les monocristaux font 0.5 par 0.15 mm (ou moins), et on les trouve au sein de petites couches, lentilles ou agrégats mesurant de 0.5 à 10 cm d'épaisseur. La gantérite est un minéral monoclinique, groupe spatial $C2/c$, $Z = 4$; a 5.212(1), b 9.046(4), c 19.978(4) Å, β $95^\circ 48'$, V 937.6 Å³; il s'agit du polytype $2M_1$. Les sept raies les plus intenses du spectre de diffraction X (méthode des poudres) [d en Å(I)(hkl)] sont: 2.571(100)(131,202), 2.602(95)(130,131), 1.5054(91)(060,2010), 3.737(77)(023), 3.887(76)(113), 4.481(71)(110), et 3.495(71)(114). Le nom de la nouvelle espèce minérale rappelle la région géographique de la localité-type.

Mots-clés: gantérite, barium, muscovite, nouvelle espèce minérale, complexe de Béréal, Simplon, Suisse.

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INTRODUCTION

Barium micas occur in metamorphic and igneous environments (Brigatti & Poppi 1993, Guggenheim 1984, and references therein). Metasomatic effects are also widely quoted as being of great importance in the formation of barium micas (Harlow 1995, and references therein), and there is evidence suggesting that elevated pressure may aid the accommodation of Ba in the interlayer site (Shmakin 1984, Massonne & Burchard 2000), here labeled *I* in accordance with the recommendation of Rieder *et al.* (1998).

In none of the numerous reported examples of barium-bearing muscovite (*i.e.*, Fortey & Beddoe-Stephens 1982, Pan & Fleet 1991, Tracy 1991, Harlow 1995 and Jiang *et al.* 1996) does the Ba content exceed 12 wt.% BaO. Moreover, occupancy of the *I* site is invariably dominated by potassium. Such white micas, where Ba occupies up to 20% of the interlayer site, have previously been referred to as "oellacherite" or "sandbergite" (Rieder *et al.* 1998).

The dioctahedral Ba-analogue of muscovite from the Berisal Complex, Wasenhorn, Simplon, Switzerland, constitutes a new mineral and has been named ganterite after the Gantertal, a famous valley in the geographical region in which it was found. The mineral species and

its name were approved by the International Mineralogical Association, Commission on New Minerals and Mineral Names (IMA 2000-033). Type material is preserved in the Naturhistorisches Museum, Basel, and at the Mineralogical Institute, University of Basel, Switzerland. In this paper, we examine the crystallographic and chemical properties of ganterite and its relationships with other micas, particularly muscovite, paragonite and margarite.

BACKGROUND INFORMATION

One of the earliest recorded Ba-rich micas was found at the Franklin mine, New Jersey (Bauer & Berman 1933). Heinrich & Levinson (1955) studied the same material and made the first cell refinements based on X-ray powder data. They concluded that for muscovite to accommodate considerable quantities of barium, the structure had to revert from a *2M* to a *1M* polytype, and would show an increase in trioctahedral character. This observation was supported by results of their chemical analyses.

To date, the highest concentrations of Ba reported in the mica minerals (Table 1) are 25 wt.% BaO in biotite (Tracy 1991), and 29 wt.% BaO in the barium-dominant trioctahedral micas kinoshitalite and ferrokinoshitalite (*e.g.*, Gnos & Armbruster 2000). No structure refinements are available for these Ba-rich micas, but all members of the kinoshitalite-ferrokinoshitalite series are *1M* trioctahedral micas. The highest previously recorded BaO content in a muscovite other than in the Berisal Complex is 11.41 wt.% (Tracy 1991).

The brittle micas are characterized by a layer charge per formula unit of -2.0 due to the presence of a divalent cation in the *I* site. The most common brittle mica is margarite, which is dioctahedral, and contains Ca^{2+} in the *I* site. In the end member, Al_2O occupy the octahedrally coordinated *M* sites, with the excess charge being balanced by Al^{3+} for Si^{4+} substitution at the tetrahedral site (*T* site). In the case of the barium-dominant brittle micas, which are trioctahedral, the *M* site is filled with Mg^{2+} or Fe^{2+} with further substitution of Al^{3+} for Si^{4+} in the *T* site also possible, if required, to balance the overall charge of the silicate structure. The variations in composition between the dioctahedral and trioctahedral micas inevitably lead to differences in the structural and crystallographic properties of the minerals.

In the Berisal Complex, a strong positive Ba-anomaly was first recognized by Frank (1979); the existence of a Ba-dominant white mica was detected, but no detailed studies were made until that done by Senn (1989). Additional localities of Ba-enrichment, containing Ba-rich white micas, were reported by Köhn (1993). In most of these localities, only micas in which Ba was a minority component of the *I* site were found. The micas presented here typically have Ba concentrations around 15 wt.% BaO, and crystals with more than

TABLE 1. LOCALITIES FOR Ba-RICH WHITE MICA

Locality	BaO content wt. %	K/Ba ratio*	Assemblage
Aberfeldy, Scotland, U.K. Fortey & Beddoe-Stephens (1982)	8.25	2.96	Cln + Brt + Dol + Rt
West Greenland Dymek <i>et al.</i> (1983)	7.75	3.23	Pl + Or + Sil + Rt + Zrn ± Ms ± Bt ± Grt
Franklin, New Jersey Tracy (1991)	11.41	1.14	Ab + Flt + Py + Rt-(Cr)
Hemlo, Ontario Pan & Fleet (1991)	10.31	2.13	Ba-Or + Qtz + Rt + Chr + Ttn + Tur + Grt + Bt + Chl
Kipushi, Democratic Republic of Congo Chabu & Boulègue (1992)	7.51	3.54 [‡]	Brt + Chl + Ba-Or + Cal + Dol
Southern Alps, New Zealand Grapes (1993)	5.42	4.18	Qtz + Chl + Grt + Tur + Ap ± Pl
Motagua Fault Zone, Guatemala Harlow (1995)	7.26	3.18	Ab + Cln + Chl + Or ± Zo + Ap + Cal ± Qtz
Qinling, China Jiang <i>et al.</i> (1996)	8.77	2.66	Ab + Qtz + Cal + Dol + Bt

Notes: Mineral abbreviations according to Kretz (1983). Additional abbreviations: Cln: celsian, Ba-Or: Barium-rich orthoclase. * Ratio calculated with highest Ba *apfu* provided. [‡] H₂O content measured and the stoichiometry calculated on the basis of 12 atoms of oxygen; all other authors used an idealized anion group and calculated stoichiometry on the basis of 11 atoms of oxygen.

17 wt.% BaO are common. This results in Ba²⁺ being the dominant interlayer cation. The presence of Ba²⁺ in the interlayer site would result in an increase in charge of the unit cell. This is compensated for entirely by Al³⁺ for Si⁴⁺ exchange at the tetrahedral site, hence unit-cell charge neutrality is maintained. The elevated Ba concentrations are coupled with increases in the Na concentrations, but there is no increase in octahedrally coordinated Fe²⁺ or Mg²⁺ concentrations (*M* site); thus the micas are barium-dominant and dioctahedral.

OCCURRENCE

Ganterite is a rock-forming mineral in two different rock-types. It is found in bands and lenses of white-mica schists that occur throughout the Berisal Complex. Such schists are dominated by muscovite and ganterite (up to 90 vol.%), and they also contain some quartz and epidote-group minerals, and the accessory phases zircon and apatite. The whole-rock chemical composition at some of these localities is characterized by unusually high concentrations of Ba (>8 wt.% BaO). In the white-mica schist, the muscovite and the ganterite are seen to have two orientations. The first orientation, which is more abundant, is parallel to the dominant Alpine foliation. The second generation, much less common, is postkinematic, suggesting that there has been some recrystallization of ganterite. The two generations of mica are structurally and chemically identical. Such white-mica schists are found as thin bands in three different leucocratic rock-types, garnet-bearing two-mica augen gneiss, zoisite–biotite gneiss, and zoisite–celsian gneiss.

Ganterite also occurs as a rock-forming mineral in zoisite–celsian gneiss. At one outcrop of this gneiss, armenite, a rare barium silicate, is found. At this locality, the examples of ganterite richest in barium are observed in a metamorphic para-semblage of zoisite, celsian, margarite and quartz. The textural relationship

of the two barium silicate minerals celsian and ganterite indicate that they grew synkinematically during the main episode of Alpine deformation. Both minerals are elongate, lie parallel to the main foliation, and are chemically homogeneous, suggesting that barium enrichment of the rocks predates, or is coeval with, the peak of Alpine metamorphism, and that post-Alpine alteration was not an important process in their genesis.

PHYSICAL AND OPTICAL PROPERTIES

The properties of ganterite may be summarized as follows (Table 2). Ganterite is silver to light grey in color and has a vitreous luster. A Mohs hardness of 4–4½ was calculated using microhardness indentation measurements (VHN₁₀₀ = 260 kg/mm²). The streak is white. Ganterite is flexible, has no parting, displays a laminated fracture, and has a perfect cleavage on {001}. No fluorescence was observed, but the material does display very strong general fluorescence under a green argon laser (514.5 nm). The density of ganterite has been calculated from results of electron-microprobe analyses at 3.11 g cm⁻³.

Grains were immersed in index of refraction (Cargille) oils, and the values of β and γ are 1.619 and 1.622, respectively (λ = 589 nm). The value of α could not be measured directly, but was calculated to be 1.600 using the measured value of 2*V* and the Fresnel equation. Ganterite is biaxial negative and has a measured 2*V* in the range 42–45° (average 42.5°). In thin section, the mineral is colorless, has second-order birefringence colors, and shows no pleochroism. The average grain-size of a typical postkinematic crystal of ganterite from the Wasenhorn is 0.5 × 0.15 × 0.01 mm.

X-RAY DIFFRACTION

In the white-mica schist, of the two distinct orientations of ganterite, examples of the younger, less common, postkinematic generation have a better defined crystal habit. Therefore, examples of this generation were selected for single-crystal X-ray studies. Examples of both types were used in Gandolfi and Guinier–Hägg cameras for powder refinement, and nearly identical patterns were collected.

Single-crystal studies were carried out using Weissenberg and precession methods (Table 3). From the systematic absence of reflections of the type *hkl* with *h* + *k* ≠ 2*n* and for *h0l* with *h* ≠ 2*n* and *l* ≠ 2*n*, the space-group symmetry was identified as *C2/c*; however, given the mineral's extinction, *Cc* cannot be ruled out. The close relationship of ganterite to muscovite suggests *C2/c* to be the more probable and correct space-group; therefore ganterite is a 2*M*₁ mica polytype.

Powder diagrams were obtained from single crystals on a Gandolfi camera (diameter 114.6 mm, FeKα radiation), and from powdered material on Debye–Scherrer (diameter 90 mm, FeKα radiation) and

TABLE 2. PHYSICAL AND OPTICAL PROPERTIES OF GANTERITE

Morphology	Flexible laminae
Color	Light grey to silver
Luster	Vitreous
Cleavage	Perfect on {001}
Tenacity	Flexible
Streak	White
Hardness	Microhardness: VHN ₁₀₀ = 260 (± 60) kg/mm ² Mohs = 4–4½ (according to VHN)
Density	3.11 g/cm ³ (calculated)
Optical properties (wavelength 589 nm)	
Biaxial (negative)	2 <i>V</i> in the range 42–45°
Indices of refraction	α = 1.600 (calculated) β = 1.619 γ = 1.622
Dispersion of optical axes	Weak, visible
Pleochroism	None observed

Guinier-Hägg cameras (CuK α_1 radiation). Cell parameters were refined from the Guinier pattern (Table 3) and the X-ray powder-diffraction data are compiled in Table 4. Whereas all camera types yielded reproducible diagrams, resolving I_{meas} versus I_{calc} for basal reflections in particular was not always possible. The (002) and (004) reflections on the Guinier diagram were only detectable on strongly overexposed films. A powder-diffractometer study, using a Siemens D-5005 X-ray spectrometer, indicates that these discrepancies are mainly due to sample-orientation effects in the X-ray preparations; a diffractometer run on an oriented sample yields extremely high intensities for the basal reflections (Fig. 1).

CHEMICAL COMPOSITION

Electron-microprobe analysis

Chemical analyses were carried out on the JEOL JXA-8600 electron microprobe at the University of Basel. The microprobe is equipped with four spectrometers and Voyager software provided by Noran Instruments. Analyses were made with a focussed electron beam in scanning mode over an area of 26 μm^2 . The accelerating voltage was 15 kV, the beam current was 10 nA, and the counting times were between 10 and 20 seconds.

The average composition of ganterite, with the standard deviation and range, and the relevant standards used for calibration of the electron microprobe, are shown in Table 5. The electron-microprobe data reported in Table 5 were calculated from results of 32 analyses on several crystals from three different samples. A ZAF-type correction procedure was used for all data reduction, and all iron was assumed to be ferrous. The H₂O content has been determined from the thermogravimetric analysis (TGA) data and is 3.9 wt.%. Where the H₂O content has been analytically determined, the chemical formula of ganterite was calculated on the basis of 12 atoms of oxygen per formula unit (Table 5). Results of some of the individual analyses are shown in Table 6; their H₂O content has not been

analytically determined. An idealized anion group is assumed, and the stoichiometry was calculated on the basis of 11 atoms of oxygen per formula unit. Cations

TABLE 4. POWDER-DIFFRACTION DATA FOR GANTERITE

<i>hkl</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{meas}	<i>I</i> _{calc}	<i>hkl</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{meas}	<i>I</i> _{calc}
0 0 2	9.98	9.94	<5		2 2 1	2.214	2.214	21	7
0 0 4	5.00	4.97	11	100	0 4 2	2.204	2.205	15	1
1 1 0	4.481	4.499	71	33	$\bar{2}$ 2 3	2.190	2.189	16	6
1 1 1	4.331	4.307	57	43	2 2 2		2.154		3
$\bar{1}$ 1 2	4.250	4.240	<5	29		2.151		14	
0 2 2	4.119	4.117	11	2	2 0 6		2.150		10
1 1 2	3.974	3.970	28	25	1 3 5	2.132	2.131	30	18
$\bar{1}$ 1 3	3.887	3.883	76	33	2 2 3	2.066	2.075	8	5
0 2 3	3.737	3.736	77	29	0 4 4	2.057	2.058	25	8
1 1 3	3.586	3.579	<5	14	0 2 9	1.9881	1.9845	8	5
$\bar{1}$ 1 4	3.495	3.491	71	18	1 3 7	1.9708	1.9707	12	14
0 2 4	3.347	3.345	49	12	2 0 6	1.9490	1.9484	10	7
0 0 6	3.315	3.313	<5	8	$\bar{2}$ 2 7	1.8417	1.8436	7	4
1 1 4	3.199	3.198	69	14	$\bar{1}$ 1 11	1.7288	1.7300	<5	3
$\bar{1}$ 1 5	3.119	3.118	14	1	0 2 11	1.6776	1.6779	<5	3
0 2 5	2.987	2.986	57	16	2 4 2		1.6614		4
1 1 5	2.858	2.857	51	14		1.6611		8	
$\bar{1}$ 1 6	2.785	2.787	34	10	$\bar{2}$ 0 10		1.6605		4
1 3 0		2.607		1	1 3 9	1.6458	1.6443	12	8
	2.602		95		$\bar{3}$ 1 5	1.6322	1.6322	10	3
$\bar{1}$ 3 1		2.602		1	3 1 3	1.6059	1.6067	8	2
$\bar{2}$ 0 2		2.573		17	1 5 4	1.5992	1.5991	7	3
	2.571		100		$\bar{2}$ 2 10	1.5593	1.5588	10	1
1 3 1		2.568		33	2 4 6		1.5581		3
$\bar{1}$ 3 3	2.469	2.469	10	28	0 6 0		1.5057		3
2 0 2	2.449	2.449	<5	14		1.5054		91	
0 2 7	2.405	2.405	19	8	2 0 10		1.5056		3
1 3 3	2.385	2.385	18	5	$\bar{1}$ 1 14	1.3896	1.3893	<5	1
$\bar{1}$ 1 8		2.260		5	1 5 8		1.3862		2
	2.258		41		$\bar{2}$ 2 11	1.3505	1.3520	6	1
$\bar{2}$ 2 1		2.257		5	1 1 15		1.3024		1
2 2 0		2.249		<1		1.3023		22	
	2.248		<5		$\bar{2}$ 0 14		1.3019		2
0 4 1		2.247		3	$\bar{2}$ 6 2		1.3008		4

Guinier-Hägg camera (CuK α_1 radiation); cell parameters refined from Guinier diagram: *a* 5.212(1), *b* 9.046(2), *c* 19.978(4), β 95°48'. *I*_{meas}, intensities determined densitometrically, and *I*_{calc} calculated using LAZYPULVERIX. Bold figures highlight the strongest seven reflections.

TABLE 5. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF GANTERITE

	wt.%*	Range	Std. dev.	<i>apfu</i>	Site	Standard
BaO	15.54	14.05-17.15	0.750	Ba	0.44	<i>I</i> Sanbornite
K ₂ O	3.02	2.04-4.64	0.746	K	0.28	<i>I</i> Orthoclase
MgO	0.86	0.55-1.27	0.195	Mg	0.09	<i>M</i> Olivine
Al ₂ O ₃	36.5	34.93-38.49	0.946	Al	3.12	<i>M, T</i> Gehlenite
SiO ₂	37.47	36.08-38.47	0.586	Si	2.72	<i>T</i> Orthoclase
FeO	0.69	0.53-1.32	0.295	Fe	0.04	<i>M</i> Olivine
CaO	0.03	0.00-0.19	0.040	Ca	0.00	<i>I</i> Wollastonite
Na ₂ O	1.91	1.13-2.60	0.438	Na	0.27	<i>I</i> Albite
TiO ₂	0.73	0.03-0.92	0.215	Ti	0.04	<i>M</i> Titanite
MnO	0.03	0.0-0.2	0.057	Mn	0.00	<i>M</i> Graftonite
H ₂ O [†]	3.90			OH	1.89	<i>A</i>
Total	100.68					

* Average of 32 measurements; stoichiometry calculated on the basis of 12 atoms of oxygen; [†] Value for H₂O taken from results of the thermogravimetric analysis.

TABLE 3. SINGLE-CRYSTAL DIFFRACTION DATA FOR GANTERITE

Crystal system	Monoclinic
Space group	C2/c
Polytype	2M ₁
Cell parameters*	<i>a</i> 5.212 (1) Å <i>b</i> 9.046 (2) Å <i>c</i> 19.978 (4) Å β 95°48'
Cell volume	<i>V</i> 937.6(2) Å ³
Cell content	4 × [(Ba,Na,K)(Al,Mg) ₂ (Si,Al) ₄ O ₁₀ (OH) ₂]

* Refined from Guinier-Hägg diagram.

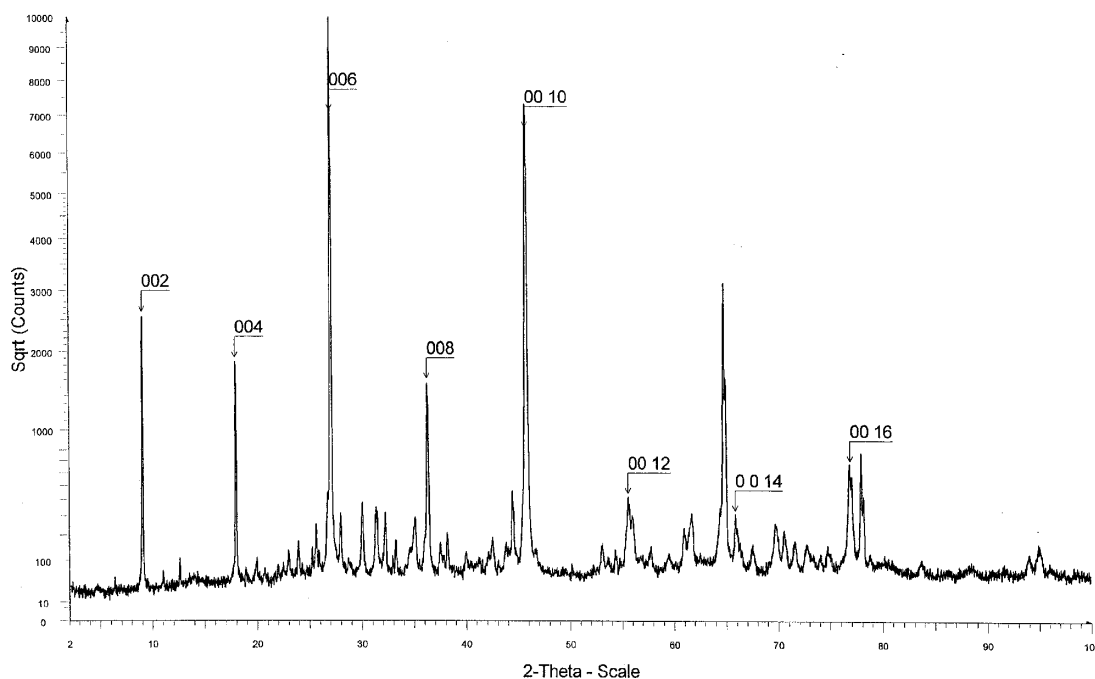
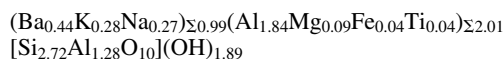


FIG. 1. Powder-diffraction pattern of ganterite.

have been assigned to the structural formula assuming that the *T* site is completely filled by Si^{4+} and Al^{3+} . The remaining Al^{3+} , as well as all Ti^{4+} , Fe^{2+} , Mg^{2+} and Mn^{2+} were assigned to the octahedrally coordinated site (*M* site). The *M* site is, in the majority of cases, close to being optimally filled for a dioctahedral mica (Σ cations at the *M* site = $2.005^{+0.035}_{-0.025}$). The cations Ba^{2+} , K^+ , Na^+ and any Ca^{2+} present were all assigned to the interlayer site (*I* site), which is nearly always completely filled (Σ cations at the *I* site = $0.99^{+0.045}_{-0.025}$). The existence of only one sharp peak at 3622 cm^{-1} in the infrared spectra (see below) suggests that there are only hydroxyl groups present, and no H_2O . The hydroxyl groups were all assigned to the *A* site (nomenclature of Rieder *et al.* 1998).

The empirical formula of ganterite, as obtained from the chemical data presented in this study, is:



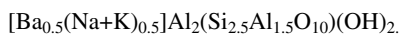
The high concentrations of Ba atoms are compensated for by higher concentrations of Al and lower concentrations of Si than is normally expected in muscovite (Tables 5, 6). Thus, the increase in partial charge in the interlayer site by the substitution of K^+ by Ba^{2+} in the white mica is being totally compensated for by an exchange of Al^{3+} for Si^{4+} at the tetrahedral site (Fig. 2) (Hetherington *et al.* 2003).

TABLE 6. REPRESENTATIVE CHEMICAL COMPOSITIONS OF GANTERITE

	White-mica schist		Leucocratic zoisite-celsian gneiss				
BaO wt.%	16.03	17.04	16.12	16.21	16.25	16.68	17.15
K ₂ O	3.88	2.57	2.97	3.36	2.64	2.67	2.84
MgO	1.17	0.76	0.66	0.9	0.91	0.92	0.96
Al ₂ O ₃	36.19	37.55	38.48	37.31	37.17	37.91	36.91
SiO ₂	36.87	35.01	36.74	36.46	36.52	37.85	36.87
FeO	1.31	1.26	0.61	0.76	0.72	0.61	0.82
CaO	0.03	0.01	0.03	0.02	0.02	0.06	0.07
Na ₂ O	1.43	1.61	2.06	1.58	2.08	2.17	1.97
TiO ₂	0.43	0.34	0.58	0.4	0.25	0.55	0.45
MnO	0.03	0.04	<0.01	0.14	<0.01	0.09	0.01
Total ^a	97.37	96.2	98.24	97.14	96.56	99.51	98.05
Ba apfu	0.46	0.50	0.45	0.46	0.47	0.46	0.48
K	0.36	0.24	0.27	0.31	0.24	0.24	0.26
Na	0.20	0.23	0.28	0.22	0.30	0.30	0.27
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Sum	1.02	0.97	1.01	0.99	1.01	1.00	1.02
Mn	0.00	0.00	0.00	0.01	0.00	0.01	0.00
Ti	0.02	0.08	0.07	0.02	0.01	0.03	0.04
Mg	0.13	0.08	0.03	0.19	0.10	0.10	0.10
Fe ²⁺	0.08	0.02	0.03	0.04	0.04	0.03	0.06
^{VI} Al	1.88	1.85	1.86	1.85	1.85	1.83	1.78
Sum	2.01	2.03	1.99	2.01	2.00	2.00	1.98
Si	2.68	2.58	2.62	2.64	2.65	2.67	2.62
^{IV} Al	1.32	1.42	1.38	1.36	1.35	1.33	1.38
Sum	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Σ Cations	7.03	7.00	7.00	7.00	7.01	7.00	7.00

^a Electron-microprobe data, with no determination of H_2O . An idealized anion group is assumed, and stoichiometry is calculated on the basis of 11 atoms of oxygen.

The empirical formula of ganterite shows that Ba, although dominant at the *I* site, does not occupy more than 50% of the available sites. Therefore, chemically, ganterite is defined as a true mica. As a result, ganterite does not fulfill the “50% rule” that applies in a ganterite–muscovite binary system, by which a new mineral species is defined (Nickel & Grice 1998). However, we have shown that the increasing concentrations of Ba and Al in the mica are also correlated with increases in Na (Fig. 3a; Hetherington *et al.* 2003). Ganterite thus does not participate in a simple binary solid-solution with muscovite, but a more complicated ternary solid-solution that includes paragonite. In examples where three or more species may occupy a site, a new mineral species is defined by the predominance of one atom, in this case Ba. In light of these observations (Fig. 3b; Hetherington *et al.* 2003), the proposed simplified formula of ganterite is:



Combustion studies

Combustion analyses in both oxygen and nitrogen atmospheres were made with a LECO–RC 412 device (Table 7). Samples of 50 mg were placed in ceramic crucibles and heated on a temperature ramp of 70°C min⁻¹. The DOMTAR international gypsum standard (GYP–C) was used for calibration. A thermogravimetric analysis (TGA) was made using a TA–Instruments SDT–2960 with a temperature ramp of 20°C/min, and a gas flow of 100 mL O₂/min over a temperature range between 25 and 1300°C. The weighing mechanism was calibrated using calcium oxalate.

During combustion in both atmospheres, and during TGA, small and comparable losses in weight occur below 600°C (Table 7) (by TGA, 0.36%). From the combustion analysis, we can attribute this loss to the expulsion of formational H₂O and the combustion of graphite (Table 7).

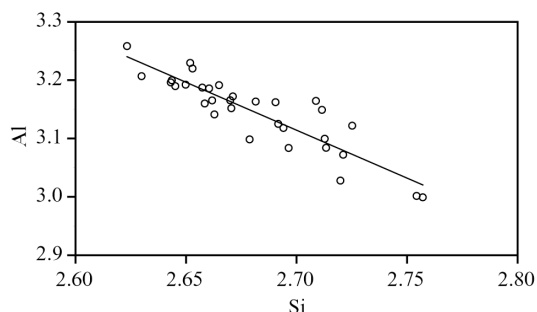


FIG. 2. Variation of Al(total) versus Si in ganterite, in atoms per formula unit, *apfu* ($y = -1.64x + 7.55$; $r^2 = 0.80$) ($n = 32$; Table 5).

During combustion between 600 and 1100°C, there is a weight loss of 3.96% in the oxidizing atmosphere and 3.64% in the nitrogen atmosphere, as a result of the dehydration of the mica (Table 7). We believe that the discrepancy between the two LECO analyses is caused by a small difference between the final end-point temperature of each run, and physical variations in the operating conditions of the apparatus. Between 600 and 1300°C in the TGA scan, there is a total decrease in weight of 3.9%. This decrease is quite consistent with the weight loss obtained by LECO analysis in O₂.

Using the evidence from each of the three combustion analyses, we conclude that the quantity of H₂O present in ganterite is close to that expelled from the structure between 600 and 1300°C during TGA (3.9 wt.%). This figure has subsequently been re-introduced, as H₂O, into the chemical analysis (Table 5), and is deemed to be representative of the H₂O content of ganterite. The LECO analysis suggests that weight loss in this temperature range due to expulsion of carbon phases is negligible, and a similar argument can be made for the weight-gain effect due to Fe²⁺ oxidation. Furthermore, the TGA was completed at higher temperatures and thus, it must be assumed to have gone further toward completion.

SPECTROSCOPIC STUDIES

Infrared spectroscopy

Several small samples of ganterite have been studied on a Perkin–Elmer 983 infrared spectrophotometer. The material was crushed in a corundum mortar, mixed with KBr, and then pressed to pellets 13 mm in diameter. The spectra were recorded over a range from 4000 to 250 cm⁻¹.

The close relationship among the three muscovite-type micas ganterite, muscovite and paragonite, and the clear difference with margarite, are easily derivable (Fig. 4). The single peak around 1000 cm⁻¹ underlines the similarities among ganterite, muscovite and paragonite. In contrast, margarite exhibits a doublet (988 and 924 cm⁻¹) in the same region. In addition, the spec-

TABLE 7. RESULTS OF LECO COMBUSTION ANALYSIS FOR CARBON AND H₂O IN GANTERITE UNDER OXYGEN AND NITROGEN ATMOSPHERES

Species and Temperature range	O ₂ Atmosphere Weight loss (%)	N ₂ Atmosphere Weight loss (%)
C < 600°C (organic)	0.0679	0.0051
C > 600°C (inorganic)	0.0038	0.0266
C _{total}	0.0717	0.0317
CO ₂ equiv. (inorganic)	0.0139	0.0975
H ₂ O < 600°C	0.3008	0.2234
H ₂ O > 600°C	3.9574	3.6394
Total (organic C + CO ₂ + H ₂ O)	4.3401	3.9654

trum of margarite at lower wavenumbers is more complicated than those of the muscovite-type micas.

In the 3600 cm^{-1} region of the spectra, there is only one peak in the ganterite spectrum compared with two in both the margarite and the muscovite spectra, and two, less obvious peaks, in paragonite. Vibrational stretching in this region is typical of O–H bonds, especially those associated with H_2O . In the case of ganterite, the existence of only one peak suggests that there are only hydroxyl (OH) groups present, and no H_2O .

Another observation of interest is that the ganterite peak at 3622 cm^{-1} is very sharp. Such sharp peaks, with small peak-widths, are rarely seen in dioctahedral micas owing to the interactions of the hydroxyl groups with the two octahedrally coordinated Al atoms, and the high sensitivity of the stretching frequency of OH groups (Farmer 1974). Such sharp peaks have only ever been recorded in well-ordered structures of sheet silicates such as pyrophyllite or in regularly substituted celadonite, where the hydroxyl group is coordinated to

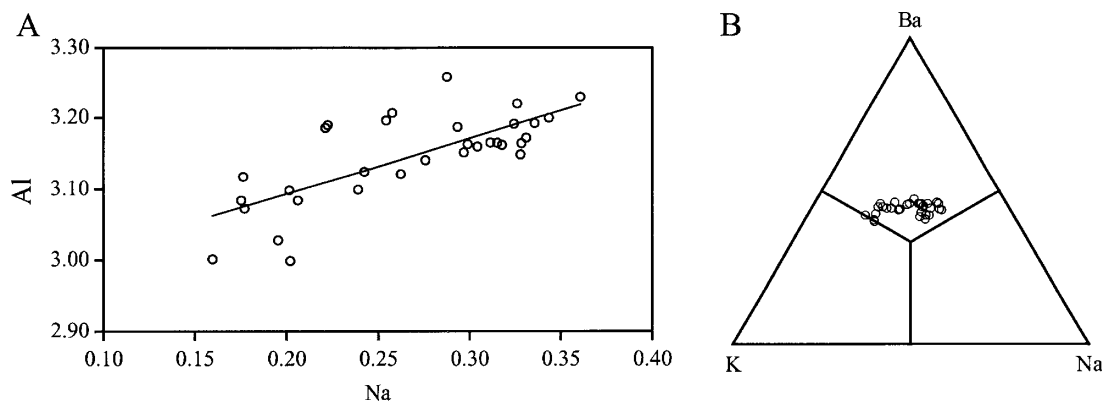


FIG. 3. A) Variation of Al(total) versus Na in ganterite, in *apfu* ($y = 0.78x + 2.94$; $r^2 = 0.54$) ($n = 32$; Table 5). B) Proportion of I-site cations in ganterite ($n = 32$; Table 5).

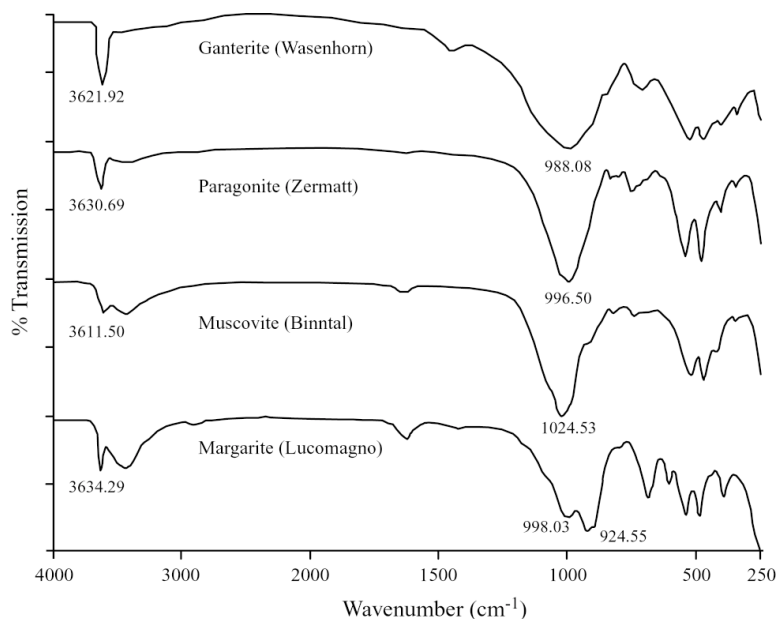


FIG. 4. Infrared spectra of ganterite, paragonite, muscovite and margarite.

a divalent and a trivalent cation (Farmer 1974). That the peak in ganterite is sharp, and has a half-peak width of less than 20 cm^{-1} , may be the result of either a very high degree of hydroxyl-group order in the structure or some complex electronic interaction brought about by the increase in charge at the *I* site.

Raman spectroscopy

Raman spectra of ganterite were obtained with a RENISHAW 1000 Raman System equipped with a CCD Peltier detector and a confocal argon laser (514 nm) with a power of 25 mW at the Swiss Gemmological Institute, Basel. The Raman system is connected to an Olympus BH microscope to adjust the laser beam on the sample surface. An optical magnification of $20\times$ was used, and for each analysis, 50 scans were taken in the extended scan mode from 100 to 1200 cm^{-1} Raman shift. The data were recorded with GRAMS™ software. The accuracy of the detector is $\pm 2\text{ cm}^{-1}$ for peaks. Raman spectra were made *in situ* on single crystals of ganterite in polished thin section chips. Several spectra of each crystal studied were made, and the sample was

rotated between each run to ensure that any anisotropic effects are minimized. The Raman spectra of ganterite are compared with examples of muscovite, paragonite and margarite (Fig. 5).

The Raman shift of the Si–O and Al–O vibrations in different species of mica does not differ very greatly, as it is generally not affected by the incorporation of different atoms in other structural positions (McKeown *et al.* 1999), and the structural similarities of each mineral should result in spectra that are quite similar owing to the directional nature of the bonds. Differences should be due to either the occupancy of the interlayer site, the ratio between Al^{3+} and Si^{4+} at the tetrahedral site, or a shift related to the OH site relative to the *I*-site constituent (McKeown *et al.* 1999).

Comparison of the muscovite, paragonite and ganterite spectra with that of margarite shows that the brittle mica has two distinct peaks at 300 and 325 cm^{-1} and a single peak at 810 cm^{-1} that are not observed in the other micas. Furthermore, there is a very different distribution of peaks at lower Raman shift. Thus the brittle mica is distinct from the other micas in terms of response to Raman spectroscopic methods.

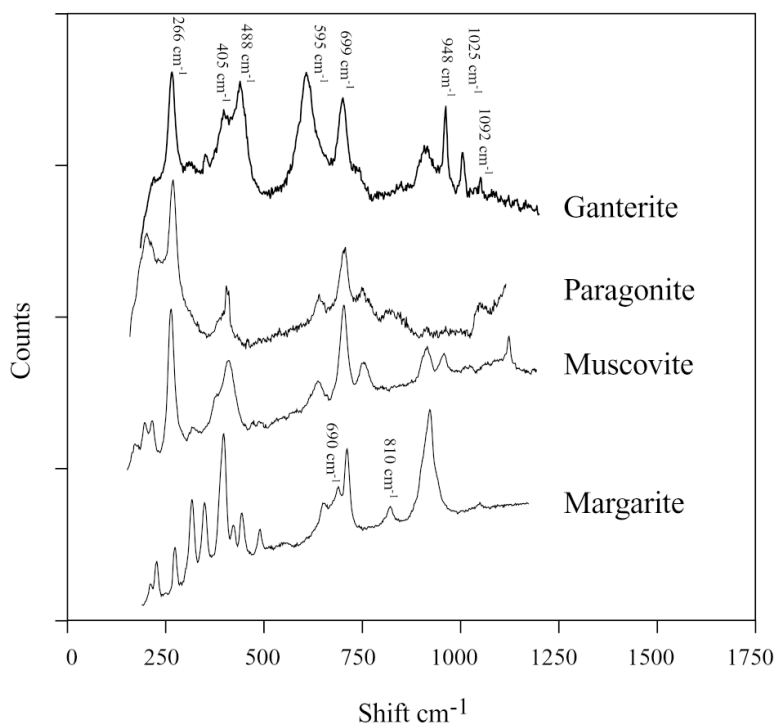


Fig. 5. Raman spectra of ganterite, paragonite, muscovite and margarite. Ganterite and paragonite crystals are from the Berisal Complex, and muscovite and margarite spectra from the SSEF Raman Spectroscopy reference library (material source unknown).

TABLE 8. COMPARISON OF IMPORTANT FEATURES OF SEVERAL SPECIES OF MICA

	Muscovite	Paragonite	Margarite	Kinoshitalite	Anandite	Ganterite
Formula	KAl ₂ (AlSi ₃)O ₁₀ (OH) ₂	NaAl ₂ (AlSi ₃)O ₁₀ (OH) ₂	CaAl ₂ (Al ₂ Si ₂)O ₁₀ (OH) ₂	BaMg ₃ (Al ₂ Si ₂)O ₁₀ (OH) ₂	Ba(Fe,Mg) ₃ (Si,Al,Fe) ₂ O ₁₀ (OH) ₂	[Ba _{0.5} (Na+K) _{0.5}]Al ₂ (Si _{2.5} Al _{1.5} O ₁₀) (OH) ₂
Space Group	C2/c	C2/c	Cc	C2/m	C2/c	C2/c
Polytype	2M ₁	2M ₁	2M ₁	1M	2M ₁	2M ₁
a (Å)	5.2	5.15	5.11	5.32	5.4	5.21
b (Å)	9.0	8.0	8.8	9.23	9.4	9.05
c (Å)	20	19.3	19.2	10.19	19.95	19.98
β (°)	93	94	95	100.06	94.5	95.48
M-site ions	2	2	2	3	3	2
I (dominant)	K	Na	Ca	Ba	Ba	Ba
M (dominant)	Al	Al	Al	Mg	Fe ³⁺	Al
Hardness	2½–3	2½	3½–4½	2½–3.	3–4	4–4½
β	1.587–1.618	1.600–1.609	1.644–1.650	1.635	1.88	1.619
γ	1.552–1.576	1.564–1.580	1.630–1.638	1.619	1.85	1.622
Density	2.77–2.88	2.85	3.0–3.1	3.30–3.33	3.94	3.11
Source	(1)	(1)	(1)	(2)	(3)	(4)

Data compiled from: Deer *et al.* (1992)⁽¹⁾, Gnos & Armbruster (2000)⁽²⁾, Kato (1975)⁽²⁾, and Pattiaratchi *et al.* (1967)⁽³⁾. (4) This work.

CONCLUSIONS

The chemical composition of ganterite, with a divalent cation at the *I* site and Al³⁺ dominance at the *M* site, is closely related to that of margarite (Table 8). However, the data derived by X-ray diffraction and spectroscopic studies (infrared and Raman spectra) suggest a close relationship to the white micas muscovite and paragonite (Figs. 4, 5, Table 8).

Studies of barium-rich samples of white mica from the Wasenhorn in the Berisal Complex indicate that Ba is the dominant interlayer cation in a normal dioctahedral white-mica type structure. With the inclusion of the larger divalent cation in the interlayer site, the structural properties of normal white micas were retained, and no deviation toward a trioctahedral form was observed.

As a result, we have classified ganterite as a dioctahedral true white mica. This makes ganterite the first known example of a Ba-dominant dioctahedral white mica.

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