

**DESCRIPTION AND CRYSTAL STRUCTURE OF MANGANLOTHARMEYERITE,  
Ca(Mn<sup>3+</sup>,□,Mg)<sub>2</sub>{AsO<sub>4</sub>,[AsO<sub>2</sub>(OH)<sub>2</sub>]}<sub>2</sub>(OH,H<sub>2</sub>O)<sub>2</sub>, FROM THE STARLERA Mn DEPOSIT,  
SWISS ALPS, AND A REDEFINITION OF LOTHARMEYERITE**

JOËL BRUGGER<sup>§</sup>

*Department of Geology and Geophysics, Adelaide University, North Terrace, 5001 Adelaide,  
South Australia and South Australian Museum, North Terrace, 5000 Adelaide, South Australia*

SERGEY V. KRIVOVICHEV<sup>¶</sup>

*Department of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia*

UWE KOLITSCH

*Institut für Mineralogie und Kristallographie, Universität Wien, Geozentrum, A-1090 Wien, Austria*

NICOLAS MEISSER

*Musée Géologique et Laboratoire des Rayons-X, Institut de Minéralogie et de Géochimie,  
UNIL-BFSH2, CH-1015 Lausanne-Dorigny, Switzerland*

MICHAEL ANDRUT

*Institut für Mineralogie und Kristallographie, Universität Wien, Geozentrum, A-1090 Wien, Austria*

STEFAN ANSERMET

*Musée Géologique et Laboratoire des Rayons-X, Institut de Minéralogie et de Géochimie,  
UNIL-BFSH2, CH-1015 Lausanne-Dorigny, Switzerland*

PETER C. BURNS

*Department of Civil Engineering and Geological Sciences, University of Notre Dame,  
Notre Dame, Indiana 46556-5602, U.S.A.*

ABSTRACT

Manganlotharmeyerite, Ca(Mn<sup>3+</sup>,□,Mg)<sub>2</sub>{AsO<sub>4</sub>,[AsO<sub>2</sub>(OH)<sub>2</sub>]}<sub>2</sub>(OH,H<sub>2</sub>O)<sub>2</sub>, is a new member of the tsumcorite group of minerals, of general formula *Me*(1)*Me*(2)<sub>2</sub>(XO<sub>4</sub>)<sub>2</sub>(OH,H<sub>2</sub>O)<sub>2</sub>, in which *Me*(1) represents Pb<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup> and Bi<sup>3+</sup>, *Me*(2) represents Fe<sup>3+</sup>, Mn<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Al<sup>3+</sup> and Mg<sup>2+</sup>, and X can be P<sup>5+</sup>, As<sup>5+</sup>, V<sup>5+</sup> or S<sup>6+</sup>. Manganlotharmeyerite occurs with sailaufite, (Ca,Na,□)<sub>2</sub>Mn<sub>3</sub>O<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>(CO<sub>3</sub>)•3H<sub>2</sub>O, tilasite and calcite in discordant veinlets within massive braunite ores at the Starlera Mn deposit in the Eastern Alps of Switzerland. Manganlotharmeyerite and the associated arsenates are the product of the latest stage of As remobilization during retrograde Alpine metamorphism of Triassic carbonate-hosted, syngenetic exhalative Mn-ores. Manganlotharmeyerite forms elongate platy crystals and aggregates up to 1 mm in length, but optically homogeneous crystals do not exceed 100 μm in length. The mineral has a Mohs hardness of about 3, with a *D*<sub>calc</sub> of 3.75(2) and a *D*<sub>meas</sub> of 3.77(2) g/cm<sup>3</sup>; it is brittle, with an irregular fracture and a distinct cleavage parallel to {001}. Manganlotharmeyerite is transparent to translucent with an adamantine luster. It is brown-red to dark reddish orange in color, and has a light brown streak. The new mineral species is biaxial positive, with α 1.785(5), β 1.814(5) and γ 1.854(5), 2*V*(meas.) about 85°, 2*V*(calc.) 82°, dispersion *r* < *v* weak. The average composition of the mineral, measured with an electron microprobe, is [wt%]: V<sub>2</sub>O<sub>5</sub> 0.67, As<sub>2</sub>O<sub>5</sub> 53.41,

<sup>§</sup> E-mail address: brugger.joel@saugov.sa.gov.au

<sup>¶</sup> Present address: Mineralogisch-Petrographisches Institut, Universität Kiel, Olshausenstrasse 40, D-24098 Kiel, Germany.

MgO 3.95, Mn<sub>2</sub>O<sub>3</sub> 16.70, CaO 12.42, Fe<sub>2</sub>O<sub>3</sub> 0.91, NiO 1.07, minor quantities (< 1 wt%) of Al<sub>2</sub>O<sub>3</sub>, SrO, Na<sub>2</sub>O, CoO, and ZnO, H<sub>2</sub>O<sub>calc</sub> 8.84, sum 99.3, resulting in the empirical chemical formula (Ca<sub>0.94</sub>Sr<sub>0.01</sub>Na<sub>0.01</sub>)(Mn<sup>3+</sup><sub>0.45</sub>□<sub>0.26</sub>Mg<sub>0.20</sub>Ni<sub>0.03</sub>Fe<sub>0.02</sub>Zn<sub>0.02</sub>Al<sub>0.01</sub>Co<sub>0.01</sub>)<sub>2</sub>(As<sub>0.98</sub>V<sub>0.02</sub>)<sub>2</sub>O<sub>10</sub>H<sub>4.16</sub>. The structural chemical formula of the mineral derived on the basis of the crystal-structure refinement is Ca(Mn<sup>3+</sup><sub>0.59</sub>□<sub>0.24</sub>Mg<sup>2+</sup><sub>0.17</sub>)<sub>2</sub>{(AsO<sub>4</sub>)<sub>0.76</sub>[AsO<sub>2</sub>(OH)<sub>2</sub>]<sub>0.24</sub>]<sub>2</sub>[(OH)<sub>0.59</sub>(H<sub>2</sub>O)<sub>0.41</sub>]<sub>2</sub>. Manganlotharmeyerite is monoclinic, *C2/m*, *a* 9.043(1), *b* 6.2314(7), *c* 7.3889(9) Å, β 116.392(2)°, *V* 372.99(9) Å<sup>3</sup> and *Z* = 2. Single-crystal structure refinement (*R*<sub>1</sub> = 0.025) confirmed isotypy with the tsumcorite structure. The strongest ten lines in the X-ray powder-diffraction pattern [*d* in Å (*I*) (*hkl*)] are: 4.93(80)(110), 4.61(50)(111), 3.426(60)(202), 3.182(100)(112), 3.122(50)(020), 2.927(70)(201), 2.822(70)(021), 2.718(80)(311), 2.555(100)(221,312), 2.134(70)(202,221). Unit-cell parameters from the powder-diffraction data are: *a* 9.074(5), *b* 6.239(3), *c* 7.406(4), β 116.60(3)°. The nomenclature of members of the tsumcorite group with *Me*(1) = Ca and *X* = As (lotharmeyerite subgroup) is based on the occupant of the *Me*(2) site. Manganlotharmeyerite represents the Mn<sup>3+</sup>-dominant member of the group, and lotharmeyerite is redefined to represent the Zn-dominant member. The lotharmeyerite subgroup now contains six phases: cabalzarite with *Me*(2) = Mg, ferrilotharmeyerite (Fe<sup>3+</sup>), cobaltlotharmeyerite (Co), nickellotharmeyerite (Ni), lotharmeyerite (Zn) and manganlotharmeyerite (Mn<sup>3+</sup>).

**Keywords:** manganlotharmeyerite, new mineral species, lotharmeyerite, structure refinement, tsumcorite group, Starlera Mn deposit, Swiss Alps.

## SOMMAIRE

La manganlotharmeyerite, Ca(Mn<sup>3+</sup>,□,Mg)<sub>2</sub>{AsO<sub>4</sub>,[AsO<sub>2</sub>(OH)<sub>2</sub>]}<sub>2</sub>(OH,H<sub>2</sub>O)<sub>2</sub>, est un nouveau membre du groupe de la tsumcorite, dont la formule générale est *Me*(1)*Me*(2)<sub>2</sub>(XO<sub>4</sub>)<sub>2</sub>(OH,H<sub>2</sub>O)<sub>2</sub>, dans laquelle *Me*(1) représente Pb<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup> et Bi<sup>3+</sup>, *Me*(2) représente Fe<sup>3+</sup>, Mn<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Al<sup>3+</sup> et Mg<sup>2+</sup>, et *X* pourrait être P<sup>5+</sup>, As<sup>5+</sup>, V<sup>5+</sup> ou S<sup>6+</sup>. On trouve la manganlotharmeyerite avec la sailaufite, (Ca,Na,□)<sub>2</sub>Mn<sub>3</sub>O<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>(CO<sub>3</sub>)•3H<sub>2</sub>O, la tilasite et la calcite dans des veinules discordantes d'un minerai de braunite massive du gisement de manganèse de Starlera, dans les Alpes orientales en Suisse. La manganlotharmeyerite et les arsenates qui lui sont associés sont le produit du stade ultime de remobilisation de l'arsenic au cours de la rétrogression du minerai carbonaté syngénétique exhalatif, d'âge triassique, et métamorphisé lors de l'événement alpin. La manganlotharmeyerite se présente en cristaux allongés en plaquettes et en agrégats jusqu'à 1 mm de taille, mais les cristaux, optiquement homogènes, ne dépassent pas 100 μm. Sa dureté de Mohs est environ 3, la densité calculée, 3.75(2), et la densité mesurée, 3.77(2) g/cm<sup>3</sup>; elle est cassante, avec une fracture irrégulière et un clivage distinct parallèle à {001}. La manganlotharmeyerite est transparente à translucide, avec un éclat adamantin. Les cristaux sont brun-rouge à orange rougeâtre foncé, et la rayure est brun pâle. Il s'agit d'un minéral biaxe positif, avec α 1.785(5), β 1.814(5) et γ 1.854(5), 2*V*(mes.) d'environ 85°, 2*V*(calc.) 82°, dispersion *r* < *v*, faible. La composition moyenne du minéral, mesurée avec une microsonde électronique, en % (poids), est: V<sub>2</sub>O<sub>5</sub> 0.67, As<sub>2</sub>O<sub>5</sub> 53.41, MgO 3.95, Mn<sub>2</sub>O<sub>3</sub> 16.70, CaO 12.42, Fe<sub>2</sub>O<sub>3</sub> 0.91, NiO 1.07, avec des quantités mineures (< 1%) de Al<sub>2</sub>O<sub>3</sub>, SrO, Na<sub>2</sub>O, CoO, et ZnO, H<sub>2</sub>O<sub>calc</sub> 8.84, somme 99.3, ce qui mène à la formule empirique (Ca<sub>0.94</sub>Sr<sub>0.01</sub>Na<sub>0.01</sub>)(Mn<sup>3+</sup><sub>0.45</sub>□<sub>0.26</sub>Mg<sub>0.20</sub>Ni<sub>0.03</sub>Fe<sub>0.02</sub>Zn<sub>0.02</sub>Al<sub>0.01</sub>Co<sub>0.01</sub>)<sub>2</sub>(As<sub>0.98</sub>V<sub>0.02</sub>)<sub>2</sub>O<sub>10</sub>H<sub>4.16</sub>. La formule structurale, dérivée d'après les données obtenues par affinement de la structure, est Ca(Mn<sup>3+</sup><sub>0.59</sub>□<sub>0.24</sub>Mg<sup>2+</sup><sub>0.17</sub>)<sub>2</sub>{(AsO<sub>4</sub>)<sub>0.76</sub>[AsO<sub>2</sub>(OH)<sub>2</sub>]<sub>0.24</sub>]<sub>2</sub>[(OH)<sub>0.59</sub>(H<sub>2</sub>O)<sub>0.41</sub>]<sub>2</sub>. La manganlotharmeyerite est monoclinique, *C2/m*, *a* 9.043(1), *b* 6.2314(7), *c* 7.3889(9) Å, β 116.392(2)°, *V* 372.99(9) Å<sup>3</sup> et *Z* = 2. L'affinement de la structure, effectué sur cristal unique (*R*<sub>1</sub> = 0.025) confirme l'isotypisme avec la tsumcorite. Les dix raies les plus intenses du spectre de diffraction (méthode des poudres) [*d* en Å (*I*) (*hkl*)] sont: 4.93(80)(110), 4.61(50)(111), 3.426(60)(202), 3.182(100)(112), 3.122(50)(020), 2.927(70)(201), 2.822(70)(021), 2.718(80)(311), 2.555(100)(221,312), et 2.134(70)(202,221). Les paramètres réticulaires calculés à partir du spectre de diffraction *X* sur poudre sont: *a* 9.074(5), *b* 6.239(3), *c* 7.406(4), β 116.60(3)°. La nomenclature des membres du groupe de la tsumcorite ayant *Me*(1) = Ca et *X* = As (sous-groupe de la lotharmeyerite) est fondée sur l'occupant du site *Me*(2). La manganlotharmeyerite représente le membre du groupe à dominance de Mn<sup>3+</sup>, et la lotharmeyerite, ici redéfinie, en serait le membre à dominance de Zn. Le sous-groupe de la lotharmeyerite contient maintenant six phases: cabalzarite avec *Me*(2) = Mg, ferrilotharmeyerite (Fe<sup>3+</sup>), cobaltlotharmeyerite (Co), nickellotharmeyerite (Ni), lotharmeyerite (Zn) et manganlotharmeyerite (Mn<sup>3+</sup>).

(Traduit par la Rédaction)

**Mots-clés:** manganlotharmeyerite, nouvelle espèce minérale, lotharmeyerite, affinement de la structure, groupe de la tsumcorite, Starlera, gisement de manganèse, Alpes, Suisse.

## INTRODUCTION

The tsumcorite group of minerals is characterized by the general formula *Me*(1)*Me*(2)<sub>2</sub>(XO<sub>4</sub>)<sub>2</sub>(OH,H<sub>2</sub>O)<sub>2</sub>, where the site *Me*(1) can contain Pb, Ca, Na and Bi, *Me*(2) can contain Fe<sup>3+</sup>, Mn<sup>3+</sup>, Cu<sup>2+</sup>, Zn, Co, Ni, Al, and Mg, and *X* can contain P<sup>5+</sup>, As<sup>5+</sup>, V<sup>5+</sup> and S<sup>6+</sup> (Krause *et al.* 1998, 2002, Brugger *et al.* 2000). In this paper, we

describe the occurrence, the physical and chemical properties, and results of a crystal-structure refinement of a Zn-free, Mn-rich tsumcorite-group mineral with *Me*(1) = Ca, *Me*(2) = Mn<sup>3+</sup> (mainly), and *X* = As. This mineral has been named manganlotharmeyerite, with the simplified chemical formula Ca(Mn<sup>3+</sup>,□,Mg)<sub>2</sub>{AsO<sub>4</sub>,[AsO<sub>2</sub>(OH)<sub>2</sub>]}<sub>2</sub>(OH,H<sub>2</sub>O)<sub>2</sub>. The holotype specimen is deposited at the Musée géologique cantonal, Lausanne,

Switzerland (MGL #54000; cotype specimen MGL #54014). The name acknowledges the relation with lotharmeyerite, whose ideal chemical formula is redefined as  $\text{Ca}(\text{Zn}, \text{Mn}^{3+})_2(\text{AsO}_4)_2(\text{H}_2\text{O}, \text{OH})_2$ . The new mineral and the revision of lotharmeyerite have been approved by the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA 2001–026).

#### OCCURRENCE

##### *The Val Ferrera Fe–Mn province*

The Starlera Fe–Mn deposit belongs to a group of small Fe–Mn–(Ba, V, As, Sb, Be, W, REE) deposits hosted in Triassic platform carbonates belonging to the Middle Penninic domain (Briançonnais) of the Eastern Swiss Alps (Trümpy 1980). At Val Ferrera, these sedimentary rocks have been segmented into four distinct tectonic units during the Alpine orogeny (the Tambo, Suretta, Starlera and Schams nappes; Baudin *et al.* 1995, Schmid *et al.* 1997). Décollement and stacking of the nappes predated the Tertiary Alpine metamorphism and thus, all of these units and the related ore deposits underwent a similar Tertiary metamorphic evolution, characterized by an early, cryptic blueschist-facies metamorphism followed by a pervasive event under greenschist-facies conditions (D<sub>1</sub>; Schreurs 1995, Marquer *et al.* 1996, Schmid *et al.* 1997). The age bracket 35–40 Ma is the most realistic estimate for the timing of the thermal peak during D<sub>1</sub> (Hurford *et al.* 1989). A later greenschist-facies metamorphism took place before the intrusion of the Bergell granodiorite at  $30.13 \pm 0.17$  Ma (von Blanckenburg 1992), and is linked to a phase of rapid decompression (Baudin & Marquer 1993). D<sub>3</sub> produced a fine crenulation in the most incompetent rocks, and the last event (D<sub>4</sub>), occurring under brittle conditions, was responsible for the formation of subvertical N–S striking faults.

The carbonate-hosted ores at Val Ferrera have a complex Fe–Mn–(Ba, V, As, Sb, Be, W, REE) geochemical association that arose mainly from their syngenetic exhalative origin and their location above a granite-rich continental basement (Brugger & Gieré 2000). The complex ore mineralogy observed nowadays is a consequence of small-scale ( $\mu\text{m}$  to dm) redistribution of elements and recrystallization during the Alpine metamorphism (Brugger & Gieré 2000).

##### *The Starlera deposit*

The Starlera mine is located at an altitude of 2400 m in Val Ferrera, Eastern Swiss Alps. The mine first produced Fe-ore from 1825 to 1845, and small-scale mining for asbestos took place around 1880. Following the discovery of manganese at Starlera in 1917, the mine became the only deposit of Val Ferrera to be exploited

for Mn, producing 145 tonnes of Mn ore between 1918 and 1920.

The Starlera deposit is characterized by a complicated paleogeographic and structural position. The present thickness of the ore (up to 12 m) is due to deposition in a trough and to doubling of the series through isoclinal folding (Brugger & Gieré 2000). Breccias with a matrix rich in asbestiform magnesioriebeckite are abundant and characteristic of the Starlera deposit. Compared to other deposits of the province, the Mn-ores are characterized by relatively low Si-contents and high As-contents. Braunite is the main ore-mineral, whereas the Mn-silicates rhodonite and spessartite are absent. Numerous discordant veins of roméite  $[(\text{Ca}, \text{Fe}, \text{Mn}, \text{Na})_2(\text{Sb}, \text{Ti})_2\text{O}_6(\text{O}, \text{OH}, \text{F})]$ , tilasite  $[\text{CaMgAsO}_4\text{F}]$ , calcite  $\pm$  aegirine, phlogopite, fluorite and triphuyite up to 30 cm in thickness cut the ore (Brugger & Gieré 1999). Greenish tilasite is also the main constituent of some concordant bands and lenses (up to  $3 \times 0.5$  cm in size) in some hematite – carbonate – quartz ores. Furthermore, a complex association of Ti, As, Sb, Be, Ba ( $\pm$ REE, W, Sr) minerals has been described by Brugger & Gieré (1999) from quartz-rich, pink, muscovite – aegirine – albite schists interbedded with the Fe–Mn ores. Aligned in the main S<sub>1</sub> schistosity are strontian barite, As-poor fluorapatite, Sb-free rutile, and possibly Ce-rich roméite and Sb-bearing pyrophanite  $[\text{MnTiO}_3]$ . A later paragenesis, overgrowing S<sub>1</sub>, contains As-rich fluorapatite, REE-rich roméite, bergslagite  $[\text{CaBeAsO}_4(\text{OH})]$ , Sb-rich rutile, Sb-bearing pyrophanite, and Sb–As-bearing titanite, as well as aegirine porphyroblasts. Arsenic-rich fluorapatite, bergslagite, stibian rutile, and stibian pyrophanite occur in fractures within titanite crystals.

##### *Appearance and association of manganlotharmeyerite*

Manganlotharmeyerite has been discovered in small (cm to dm), late (D<sub>4</sub>?), open fissures inside massive braunite ore. Manganlotharmeyerite forms elongate platy crystals and aggregates up to 1 mm in length. These aggregates and crystals are mostly translucent. Clear, optically homogeneous grains usually do not show crystal faces, and their size does not exceed 100  $\mu\text{m}$ . Subparallel intergrowths are common (Fig. 1). Manganlotharmeyerite is associated with calcite, tilasite, and sailaufite,  $(\text{Ca}, \text{Na}, \square)_2\text{Mn}_3\text{O}_2(\text{AsO}_4)_2(\text{CO}_3) \cdot 3\text{H}_2\text{O}$ , a new species discovered in the Sailauf rhyolite quarry, Spessart, Germany (Wildner *et al.*, in press); the nature of the latter mineral was confirmed by a single-crystal structure refinement. The sailaufite from Starlera forms thin platy brown crystals grouped in rosettes up to 1 mm in diameter.

Manganlotharmeyerite and sailaufite represent the latest stage of the retrograde remobilization of As in the Starlera ores. In this way, the formation of these minerals may be compared to that of fianelite  $[\text{Mn}_2\text{V}(\text{V}, \text{As})\text{O}_7 \cdot 2\text{H}_2\text{O}]$  found in a nearby lens of V-rich ore (Brugger & Berlepsch 1996).

## PHYSICAL AND OPTICAL PROPERTIES

Manganlotharmeyerite is brown-red to dark reddish orange, with an adamantine luster. The streak is light brown, and the Mohs hardness is about 3. The mineral is brittle, with an irregular fracture and a distinct cleavage parallel to {001}. The density of the mineral was measured using a test tube in which a density gradient is created using the Tl formate – Tl malonate – water system (Clerici solution). The solution at the level of the crystal has been sampled using a fine chromatography syringe, and its density deduced from its index of refraction. The measured density is 3.77(2) g/cm<sup>3</sup>. This compares well to a calculated density of 3.75(2) g/cm<sup>3</sup> obtained using the average formula in Table 1, a cell volume of 372.99 Å<sup>3</sup> and Z = 2. The uncertainty for the calculated density arises from the compositional range listed in Table 1.

Manganlotharmeyerite is biaxial positive, with  $\alpha$  1.785(5),  $\beta$  1.814(5) and  $\gamma$  1.854(5) (white light);  $2V_{\text{calc}}$  82.4°,  $2V_{\text{meas}}$  about 85°, dispersion  $r < v$ , weak. Using the average chemical analytical data, the calculated density and the mean index of refraction, the compatibility index according to the Gladstone–Dale relationship is

–0.037 (excellent; Mandarino 1981). The orientation of the optical indicatrix is unknown.

## CHEMICAL COMPOSITION

The chemical composition of manganlotharmeyerite and of a crystal of lotharmeyerite from the type locality in Mexico (South Australian Museum specimen G26280) have been established using a Cameca SX–50 electron microprobe (Table 1). High sums for lotharmeyerite are due to the small size of the analyzed grains, and the necessity to work with a highly focused beam. Empirical formulae were derived from the electron-microprobe analyses on the basis of full occupancy of the tetrahedral sites, *i.e.*, As + V = 2. The number of hydrogen atoms per formula unit (*apfu*) was calculated to obtain a total of 10 atoms of oxygen. For manganlotharmeyerite, it was further assumed that one [AsO<sub>2</sub>(OH)<sub>2</sub>]<sup>–</sup> group replaces an [AsO<sub>4</sub>]<sup>3–</sup> group for each Me(2) vacancy (see below). The resulting empirical formula for manganlotharmeyerite is: (Ca<sub>0.94</sub>Sr<sub>0.01</sub>Na<sub>0.01</sub>)(Mn<sup>3+</sup><sub>0.45</sub>□<sub>0.26</sub>Mg<sub>0.20</sub>Ni<sub>0.03</sub>Fe<sub>0.02</sub>Zn<sub>0.02</sub>Al<sub>0.01</sub>Co<sub>0.01</sub>)<sub>2</sub>(As<sub>0.98</sub>V<sub>0.02</sub>)<sub>2</sub>O<sub>10</sub>H<sub>4.16</sub>. A detailed discussion of the crystal-chemical formula of manganlotharmeyerite is given in the Crystal Structure section.

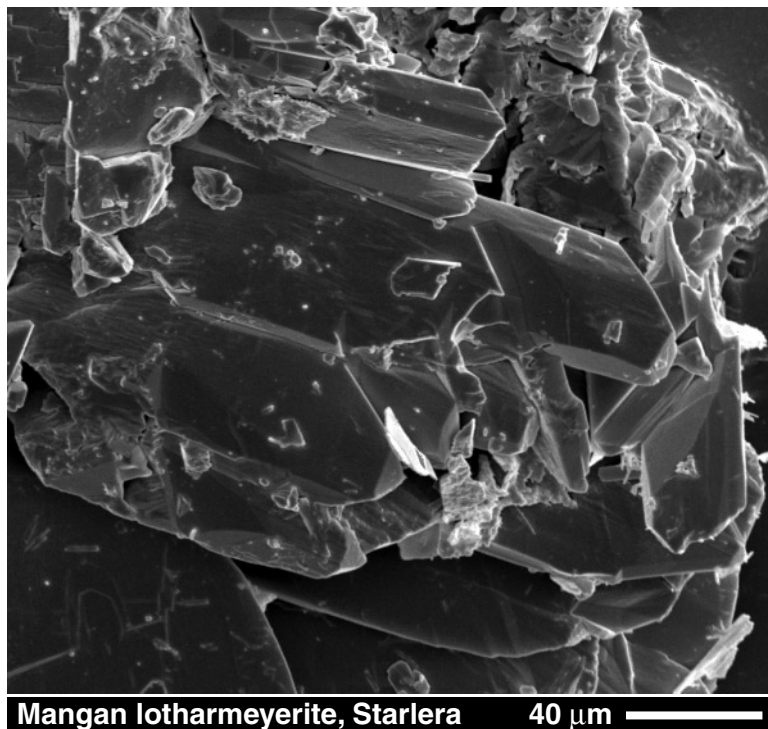


FIG. 1. Scanning electron micrograph of subparallel crystals of manganlotharmeyerite.

## RAMAN AND IR SPECTROSCOPY

Raman spectra of single crystals of manganlotharmeyerite were recorded in the spectral range from 100 to 4000  $\text{cm}^{-1}$ , using excitation with an argon laser (488 nm line) and a Renishaw M1000 Raman system (spectral resolution 2  $\text{cm}^{-1}$ ). A typical spectrum (Fig. 2) clearly shows the presence of strong hydrogen bonding (broad bump of medium intensity centered around 3000  $\text{cm}^{-1}$  in the O–H stretching vibrational region). This band agrees with the results from the structure determination, indicative of strong hydrogen bonds, with O...O distances of 2.59(2) and 2.62(2) Å (see below). In some spectra, a very small broad bump at roughly 1630–1570  $\text{cm}^{-1}$  was recognizable; we assigned it to H–O–H bending, indicating the presence of molecular  $\text{H}_2\text{O}$ .

TABLE 1. SELECTED CHEMICAL DATA ON MANGANLOTHARMEYERITE FROM STARLERA, SWITZERLAND, AND ON LOTHARMEYERITE FROM OJUELA MINE, DURANGO, MEXICO

	Manganlotharmeyerite			Lotharmeyerite
	Average (6 pts)	Min	Max	Average (3 pts)
$\text{V}_2\text{O}_5$ wt%	0.67	0.20	1.25	<0.04
$\text{As}_2\text{O}_5$	53.41	52.54	54.26	51.00
$\text{Al}_2\text{O}_3$	0.27	<0.04	0.65	0.04
MgO	3.95	3.66	4.37	<0.04
$\text{Fe}_2\text{O}_3$	0.91	<0.03	1.99	0.93
$\text{Mn}_2\text{O}_3$	16.70	15.28	18.46	12.54
SrO	0.20	<0.05	0.54	<0.05
CaO	12.42	12.18	12.66	11.26
$\text{Na}_2\text{O}$	0.08	0.04	0.11	0.75
NiO	1.07	0.51	1.36	<0.04
CoO	0.19	0.15	0.29	<0.04
ZnO	0.58	0.35	0.73	19.04
$\text{H}_2\text{O}_{\text{calc}}$	8.84	8.57	9.50	7.32
Sum	99.3	98.4	100.2	102.9
V <i>apfu</i>	0.03	0.01	0.06	<0.01
As	1.97	1.94	1.99	2.00
Sum	2.00	2.00	2.00	2.00
$\text{Mn}^{3+}$	0.90	0.82	0.99	0.72
Al	0.02	<0.01	0.05	0.004
$\text{Fe}^{3+}$	0.05	0.00	0.11	0.05
Mg	0.41	0.38	0.46	<0.01
Zn	0.03	0.02	0.04	1.05
Ni	0.06	0.03	0.08	<0.01
Co	0.01	0.01	0.02	<0.01
$\Sigma\text{Me}2$	1.48	1.39	1.53	1.82
Sr	0.01	<0.01	0.02	<0.01
Ca	0.94	0.91	0.95	0.90
Na	0.01	0.01	0.02	0.11
$\Sigma\text{Me}1$	0.96	0.95	0.97	1.01
H	4.16	4.02	4.40	3.66
OH on O(1)	0.87	0.82	0.95	0.34
$\text{H}_2\text{O}$ on O(1)	1.13	1.05	1.18	1.66
O	10.0	10.0	10.0	10.0

The sample of manganlotharmeyerite also contains 0.07 wt% BaO, 0.07% CuO, <0.03%  $\text{P}_2\text{O}_5$ , 0.14% PbO and <0.16%  $\text{SiO}_2$ . No additional element with atomic number > 9 was detected. Probe standards: V, Mn, Ni, Co, Cu, Zn: pure metals; Pb: galena; As: arsenopyrite; Ca, Si: wollastonite; Al: corundum; Sr: barite; Ba: benitoite; Fe: hematite; Mg: periclase. Conditions of analysis: 15 kV, 25 nA, counting times 10 s/peak, 5 s/background, beam diameter 1–10  $\mu\text{m}$ . Lotharmeyerite sample: G26280

The bands at 880, 830 (broad), 475 + 426 and 344 + 365  $\text{cm}^{-1}$  are assigned to the normal vibrations  $\nu_3$ ,  $\nu_1$ ,  $\nu_4$  and  $\nu_2$ , respectively, of the  $\text{AsO}_4$  group. In the free arsenate ion with  $T_d$  symmetry, these Raman-active vibrations occur at 878, 837, 463 and 349  $\text{cm}^{-1}$  (e.g., Griffith 1970). The observed splitting and broadening of the majority of bands are the result of two effects: firstly, the reduction of the local site-symmetry of the  $\text{AsO}_4$  group, and secondly, the substitution of Mn, Mg and vacancies at the  $Me(2)$  site resulting in considerably different local crystal-fields. The band at 765  $\text{cm}^{-1}$  consequently may be attributed to locally different  $\nu_1$  vibrations. The remaining bands below 600  $\text{cm}^{-1}$  are attributed to vibrations involving the Mn and Mg cations, and lattice vibrations.

Single-crystal infrared spectra of small irregular crystal fragments were recorded in the range between 4000 and 650  $\text{cm}^{-1}$  using a Bruker IFS 66v/S FTIR spectrometer with attached microscope. These spectra also showed the broad, strong bump in the spectral region from 2500 to 3500  $\text{cm}^{-1}$ , with a maximum at around 2980  $\text{cm}^{-1}$  (O–H stretch). A distinct, slightly broadened peak at about 1630  $\text{cm}^{-1}$  confirms the presence of molecular  $\text{H}_2\text{O}$  inferred from the results of the crystal-structure analysis. Owing to very strong absorption below 1200  $\text{cm}^{-1}$ , the crystals become opaque at these wavenumbers. Choosing very thin grains did not result in sufficient lowering of the absorption or any other improvement of the generally poor spectra.

Monoclinic tsumcorite-group minerals can contain up to 3 H *apfu* located around the O(1) atom, in which case the hydrogen-bonding scheme results in an  $[\text{H}_3\text{O}_2]^-$  group (see Effenberger *et al.* 2000 for a review):



In the case of tsumcorite-group minerals that contain 4 H *apfu*, the hydrogen bonds rearrange, with the development of hydrogen bonds involving the O(3) atoms of oxygen. The ordering of the hydrogen bonds is indicated by weak superstructure reflections in X-ray patterns, and results in a triclinic superstructure in the members of the “helmutwinklerite group” (Effenberger *et al.* 2000). Broad to very broad IR and Raman absorption bands in the spectral region from 2500 to 3500  $\text{cm}^{-1}$  are typical for tsumcorite-group minerals containing either a mixture of  $\text{H}_2\text{O}$  and OH, or only OH (Brugger *et al.* 2000, Krause *et al.* 1998, 2001a). Among existing tsumcorite-group minerals, only those containing two  $\text{H}_2\text{O}$  molecules per formula unit and no OH groups (*i.e.*, of helmutwinklerite type) do not show such a broad band, but instead sharp bands between 3500 and 3800  $\text{cm}^{-1}$ , which provide evidence for relatively weak hydrogen bonds (Krause *et al.* 1998, Effenberger *et al.* 2000). IR and Raman spectroscopy, therefore, indicates that long-range ordering of H-bonds, such as that found in

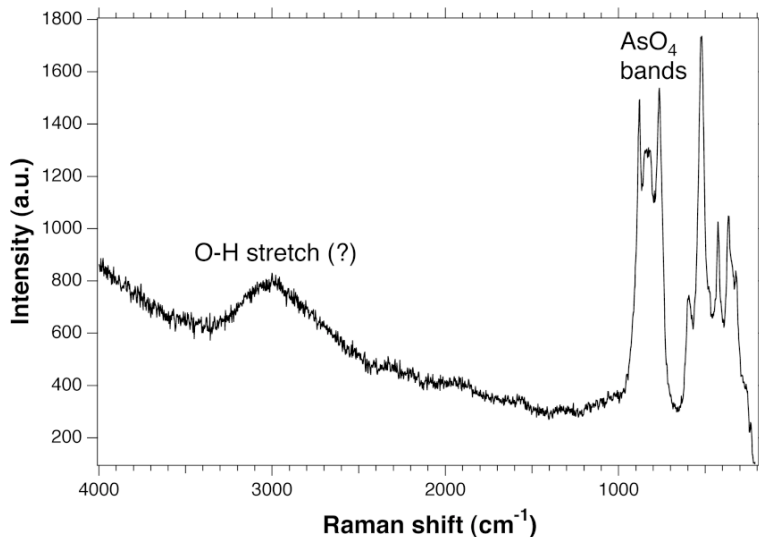


Fig. 2. Unpolarized Raman spectrum of manganlotharmeyerite crystal with random orientation.

helmutwinklerite-group minerals, does not occur in manganlotharmeyerite. This result also agrees with the occupancy of the O(1) site by nearly equal amounts of OH and H<sub>2</sub>O derived from the results of the chemical analysis (Table 1) and the crystal-structure refinement (see below).

### CRYSTAL STRUCTURE

#### Data collection

A crystal of manganlotharmeyerite with approximate dimensions  $0.08 \times 0.06 \times 0.03$  mm was selected and mounted on a Bruker PLATFORM goniometer equipped with a 1K SMART CCD detector with a crystal-to-detector distance of 5 cm. The data were collected using MoK $\alpha$  X-radiation and frame widths of  $0.3^\circ$  in  $\omega$ , with 45 s used to acquire each frame. More than a hemisphere of three-dimensional data was collected. The unit-cell dimensions were refined on the basis of 628 reflections using least-squares techniques (Table 2). The data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical absorption-correction based upon the intensities of equivalent reflections was done by modeling the crystal as an ellipsoid, and reduced  $R_{\text{int}}$  of 457 intense reflections [ $>10\sigma(I)$ ] from 4.7 to 2.7%.

#### Structure refinement

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *In-*

TABLE 2. CRYSTAL-STRUCTURE DATA AND REFINEMENT PARAMETERS FOR MANGANLOTHARMEYERITE.

Unit cell		$C2/m, Z = 2$	
$a$	9.043(1) Å	$b$	5.2314(7) Å
$\beta$	116.392(2) $^\circ$	$V$	372.99(8) Å <sup>3</sup>
		$c$	7.3889(9) Å
Diffractometer	Bruker SMART CCD	X-radiation	MoK $\alpha$ (0.71073 Å)
X-ray power	50 kV, 40 mA	Temperature	293 K
Crystal size	$0.08 \times 0.06 \times 0.03$ mm <sup>3</sup>		
Detector-to-sample distance:	5.0 cm	Detector $2\theta$ angle:	$27^\circ$
Resolution	0.77 Å	Rotation axis:	$\omega$
Rotation width	$0.3^\circ$	Total number of frames:	1271
Frame size	512 * 512 pixels	Collection time per frame:	45 s
Collection mode:	automated hemisphere	Reflections collected:	1187
Maximum $2\theta$	56.44		
Index range	$-11 \leq h \leq 11, -8 \leq k \leq 8, -9 \leq l \leq 6$		
Unique reflections:	489	Unique reflections $> 4\sigma(I)$ :	387
$R_{\text{int}}$	3.4%	$R_{\sigma}$	4.6%
	(after empirical absorption correction)		
Least-squares parameters:	48	GoodF	0.890
$R_{\text{int}} > 4\sigma(I)$	2.5%	$R_{\text{int}}$ , all data	3.9%
$wR_2$ (on $F^2$ )	5.8%		

*ternational Tables for X-Ray Crystallography, Vol. IV* (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5.1 set of programs was used for refinement of the crystal structure on the basis of  $F^2$ . The starting model used the atom coordinates given for the monoclinic members of the tsumcorite-group minerals by Krause *et al.* (1998). Refinement of all atom-position parameters, allowing for anisotropic displacement of all atoms, and the inclusion of a weighting scheme of the structure factors, resulted in a final agreement index ( $R_1$ ) of 2.5%, calculated for the 387 unique observed reflections ( $|F_o| > 4\sigma_F$ ), and a goodness-of-fit ( $S$ ) of

TABLE 3. ATOMIC POSITIONAL AND DISPLACEMENT PARAMETERS FOR MANGANLOTHARMEYERITE

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>99</sub>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
<i>Me</i> (1)*	0	0	0	0.0144(5)	0.0166(9)	0.0150(9)	0.0105(8)	0	0.0051(7)	0
<i>Me</i> (2)**	0.25	0.25	0.5	0.0099(3)	0.0096(6)	0.0101(6)	0.0080(6)	0.0002(4)	0.0021(4)	0.0000(4)
As	0.91498(7)	0.5	0.20524(8)	0.0102(2)	0.0089(3)	0.0112(3)	0.0089(3)	0	0.0026(2)	0
O(1)***	0.3385(5)	0.5	0.4098(6)	0.0195(10)	0.015(2)	0.022(2)	0.019(2)	0	0.006(2)	0
O(2)	0.3170(5)	0	0.3573(6)	0.0190(10)	0.019(2)	0.019(2)	0.022(2)	0	0.012(2)	0
O(3)	0.0351(3)	0.2793(4)	0.2468(4)	0.0186(8)	0.0168(14)	0.0164(14)	0.020(2)	-0.0010(12)	0.0061(12)	0.0008(11)
O(4)	0.2420(5)	0.5000	0.0237(6)	0.0222(10)	0.017(2)	0.031(2)	0.013(2)	0	0.002(2)	0

\* *Me*(1) = Ca<sub>1.00</sub>, \*\* *Me*(2) = Mn<sup>3+</sup><sub>0.59</sub>□<sub>0.24</sub>Mg<sup>2+</sup><sub>0.17</sub>, \*\*\* O(1) = (OH)<sub>0.59</sub>(H<sub>2</sub>O)<sub>0.41</sub>

TABLE 4. SELECTED BOND-LENGTHS (Å) FOR MANGANLOTHARMEYERITE

<i>Me</i> (1)-O(4)	2.416(4) 2×	As-O(4)	1.656(4)
<i>Me</i> (1)-O(3)	2.437(3) 4×	As-O(3)	1.694(3) 2×
<i>Me</i> (1)-O(2)	2.909(4) 2×	As-O(2)	1.712(4)
< <i>Me</i> (1)-O>	2.55	<As-O>	1.69
<i>Me</i> (2)-O(1)	1.997(2) 2×		
<i>Me</i> (2)-O(3)	2.019(3) 2×		
<i>Me</i> (2)-O(2)	2.115(3) 2×		
< <i>Me</i> (2)-O>	2.04		

TABLE 5. BOND-VALENCE ANALYSIS (vu) FOR MANGANLOTHARMEYERITE\*

	O(1)	O(2)	O(3)	O(4)	Σ
<i>Me</i> (1)		0.08 <sup>4+</sup>	0.28 <sup>4+</sup>	0.30 <sup>2+</sup>	1.88
As		1.16	1.22 <sup>2+</sup>	1.35	4.95
Σ <sup>+</sup> **	0.00	1.32	1.50	1.65	
<i>Me</i> (2)	0.53 <sup>2+</sup>	0.38 <sup>2+</sup>	0.50 <sup>2+</sup>		2.82
Σ <sup>+</sup> **	1.06	2.08	2.00	1.65	

\* Calculated using bond-valence parameters. Ca<sup>2+</sup>-O for *Me*(1)-O bonds, Mn<sup>3+</sup>-O for *Me*(2)-O bonds. Bond-valence parameters from Brown & Altermatt (1985).

\*\* Σ<sup>+</sup>: bond-valence sum without contribution of the *Me*(2)-O bonds.

Σ<sup>+</sup>: bond-valence sum with contribution of the *Me*(2)-O bonds.

0.890. The final atom parameters are listed in Table 3, selected interatomic distances are in Table 4, and the bond-valence analysis is given in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

#### Notes on symmetry

The CCD camera detected weak streaking in areas of the diffraction pattern, consistent with presence of local domains in the structure. It is possible that vacan-

cies at the *Me*(2) site lower the local symmetry of manganlotharmeyerite to triclinic. We were unable to index the diffraction pattern using a large triclinic cell (as suggested by Effenberger *et al.* 2000), and were unable to account for the streaking in the refinement.

#### Description of the structure

The structure of manganlotharmeyerite is identical to that of other tsumcorite-group minerals (Fig. 3a). The *Me*(2)<sub>φ</sub> octahedra (φ: O<sup>2-</sup>, OH<sup>-</sup>, H<sub>2</sub>O) share *trans* edges, resulting in chains that extend along the *b* axis. These chains are linked by sharing corners with AsO<sub>4</sub> tetrahedra, resulting in sheets of composition *Me*(2) (AsO<sub>4</sub>)(OH,H<sub>2</sub>O) that are parallel to (001) (Fig. 3b). The topology of the sheet is identical to that in natrochalcite, NaCu<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(H<sub>3</sub>O<sub>2</sub>) (Hawthorne *et al.* 2000). Its graphical representation (octahedra shown by black vertices, tetrahedra, by white vertices; links indicate the number of O atoms shared between adjacent polyhedra) is shown in Figure 3c. Ca<sup>2+</sup> cations are located between the sheets; they provide linkage between the sheets along the *a* axis.

#### The *Me*(1) site

The *Me*(1) site is coordinated by eight anions with an average *Me*(1)-O bond length of 2.55 Å. Refinement of the site-scattering factor indicated that this position is fully occupied by Ca, in good agreement with the chemical data and the bond-valence sum of 1.88 *vu* (valence units; Brown & Altermatt 1985).

#### The *Me*(2) site

The *Me*(2) site is octahedrally coordinated by six ligands. Bond-valence sums, calculated with the parameters for Mn<sup>3+</sup> and Mn<sup>2+</sup> (Brown & Altermatt 1985) are 2.82 and 3.11 *vu*, respectively, consistent with occupancy by Mn<sup>3+</sup>. The Jahn-Teller distortion of the *Me*(2) octahedral coordination (Burns *et al.* 1994, Foley *et al.*

1997) (Table 4) is also consistent with occupancy by  $Mn^{3+}$ . Occupancy refinement for the *Me*(2) site using scattering factors for Mn and Mg, and allowing for vacancy, lead to  $Mn^{3+}_{0.59}Mg^{2+}_{0.17}\square_{0.24}$ , which corresponds to an average scattering power of  $\sim 19.2 e$ . The *Me*(2) occupancy derived from the structure determination is very close to that obtained from the electron-microprobe data (Table 1).

#### The O(1) site

In minerals of the tsumcorite group, the O(1) site is occupied by OH or  $H_2O$  groups (or both). The O(1) atom is bonded to two *Me*(2) cations. According to Krause *et al.* (1998), exclusive occupancy of the *Me*(2) site with trivalent cations causes the O(1) sites to be fully occupied by hydroxyl groups, whereas exclusive occupancy of the *Me*(2) site with divalent cations causes a complete occupation of the O(1) sites by  $H_2O$  molecules. The latter is also valid in the case where the *Me*(2) site is vacant. In the case of manganlotharmeyerite, the refined occupancy of the *Me*(2) site is  $Me^{3+}_{0.59}Me^{2+}_{0.17}\square_{0.24}$ . Taking into account the points of Krause *et al.* (1998), the occupancy of the O(1) site in manganlotharmeyerite is  $(OH)_{0.59}(H_2O)_{0.41}$ .

#### The $AsO_4$ group

The  $AsO_4$  group in monoclinic members of the tsumcorite group (space group  $C2/m$ ) contains three crystallographic types of O atoms. The O(4) atom is strongly bonded to As [ $As-O(4) = 1.655(4) \text{ \AA}$ ] and to Ca [ $Ca-O(4) = 2.417(4) \text{ \AA}$ ]. Its bond-valence sum is

$1.65 vu$ , which corresponds to the full occupancy of the O(4) site by O atoms, and its additional bond-valence requirements are met by hydrogen bonding [ $O(4)\dots O(1) = 2.59(2) \text{ \AA}$ ]. The O(2) atom forms a slightly lengthened bond to As [ $As-O(2) = 1.712(4) \text{ \AA}$ ], two short bonds to *Me*(2) [ $Me(2)-O(2) = 2.116(3) \text{ \AA}$ ] and one weak bond to Ca [ $Ca-O(2) = 2.909(4) \text{ \AA}$ ]. Where the *Me*(2) site is occupied by  $Mn^{3+}$ , the bond-valence sum incident upon the O(2) site is  $2.08 vu$  (Table 5). However, where the *Me*(2) site is vacant, the O(2) bond-valence sum is  $1.32 vu$ , which is consistent with a hydroxyl group. Thus, the occupancy of the O(2) site in manganlotharmeyerite is  $O_{0.76}(OH)_{0.24}$ . The O(3) atom is bonded to As [ $2 \times As-O(3) = 1.694(3) \text{ \AA}$ ], Ca [ $Ca-O(3) = 2.437(3) \text{ \AA}$ ] and *Me*(2) [ $Me(2)-O(3) = 2.020(3) \text{ \AA}$ ]. If the *Me*(2) site is occupied by  $Mn^{3+}$ , the bond-valence sum for the O(3) site is  $2.00 vu$  (Table 5). If the *Me*(2) site is vacant, the bond-valence sum for the O(3) site is  $1.50 vu$ , which suggests a hydroxyl group. The As is bonded to two O(3) atoms, and it is unlikely that both of these positions are occupied by OH. Rather, we suggest that the local symmetry of the  $AsO_4$  group is lowered where the *Me*(2) site is vacant, and the O(3) site is split into two sites, O(3a) and O(3b), one of which is occupied by O and another one by OH. In summary, a vacancy at the *Me*(2) site results in lowering of the local symmetry and replacement of an  $AsO_4^{3-}$  group by an  $[AsO_2(OH)_2]^-$  group. For manganlotharmeyerite, this results in the replacement of the  $AsO_4^{3-}$  group by  $\{(AsO_4)_{0.76}[AsO_2(OH)_2]_{0.24}\}^{2.52-}$ .

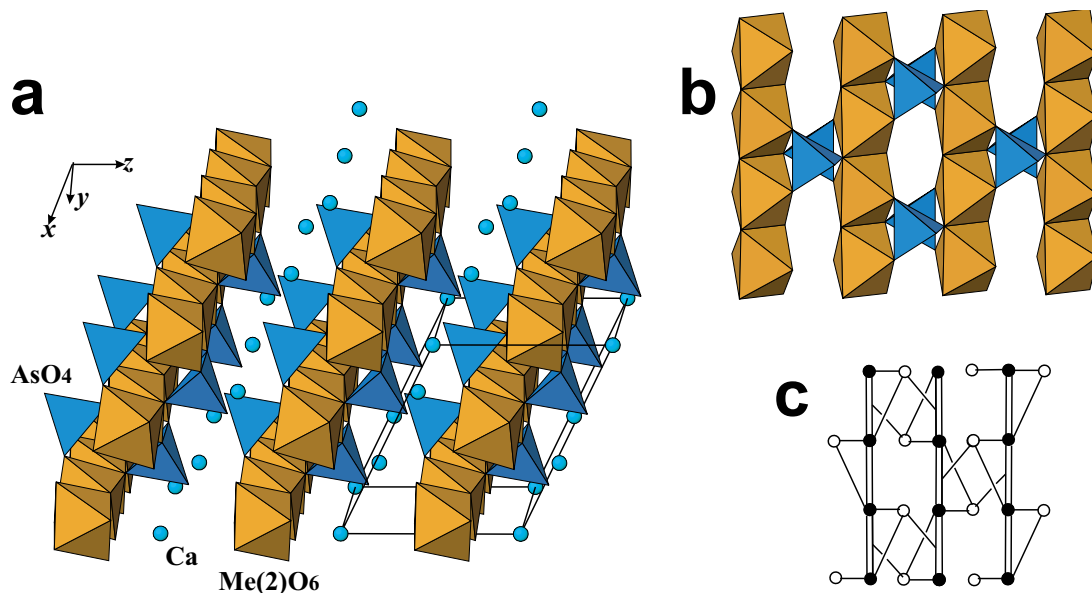


FIG. 3. Crystal structure of manganlotharmeyerite (a); *Me*(2)( $AsO_4$ )(OH, $H_2O$ ) sheet (b) and its graphical representation (c).

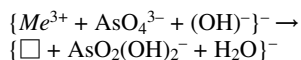


The protonation of the  $XO_4$  group ( $X = As, P, V, S$ ) in tsumcorite-group minerals was discussed in detail by Krause *et al.* (1998). These authors focused their attention on the O(2) site and pointed out that it cannot be occupied by OH in all the structures they studied because: (1) the O(2) atom is in fourfold coordination, and therefore its bond-valence requirements are satisfied; (2) protonated anion groups show a decrease of the OH–X–O angles (Baur 1974), whereas in the tsumcorite-group minerals studied by Krause *et al.* (1998), the only decreased angles are O(2)–X–O(4) ( $102.4\text{--}107.4^\circ$ ), whereas the other O(2)–X–O angles are larger than  $108.9^\circ$ . However, these observations are not applicable to manganlotharmeyerite owing to the presence of vacancies at the *Me*(2) site. Where *Me*(2) is vacant, both the O(2) and O(3) atoms become 2-coordinated with the As–O(2) bond lengthened, and the geometry of the  $AsO_2(OH)_2$  group is different from that of the  $AsO_3(OH)$  group. The latter was demonstrated for the  $As(2)O_2(OH)_2$  group in the structure of  $Ca(H_2AsO_4)_2$ , which was determined by Ferraris *et al.* (1972) using neutron diffraction. The As(2)–OH bond lengths are 1.695 and 1.732 Å, whereas the As(2)–O bond lengths are 1.652 and 1.677 Å. The OH–As–O angles vary from  $100.4$  to  $114.1^\circ$ . In manganlotharmeyerite, the OH–As–O angles vary from  $102.2$  to  $112.0^\circ$ . However, taking into account our hypothesis about the lowering of symmetry and the splitting of the O(3) position, the observed bond-lengths and angles are average values of those in the real structure.

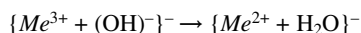
The existence of vacancies in the *Me*(2) position is a key feature that distinguishes lotharmeyerite from other members of the tsumcorite group. We suggest that the presence of vacancies results in the protonation of some  $AsO_4$  groups, and in the rearrangement of the system of hydrogen bonds.

#### Structural formula and charge-balance mechanism

On the basis of our crystal-structure analysis, the structural formula for manganlotharmeyerite is  $Ca(Me^{3+}_{0.59}\square_{0.24}Me^{2+}_{0.17})_2\{(AsO_4)_{0.76}[AsO_2(OH)_2]_{0.24}\}_2((OH)_{0.59}(H_2O)_{0.41})_2$ . The charge-balance mechanism responsible for the incorporation of vacancies at the *Me*(2) site is described by:



The divalent *Me*(2) cations are accommodated *via* the coupled substitution:



Consequently, the composition of the manganlotharmeyerite specimen from Starlera can be expressed in terms of three theoretical end-members:

1.  $CaMn^{3+}_2[AsO_4]_2(OH)_2$  59%
2.  $Ca\square_2[(AsO_2(OH)_2)_2(H_2O)_2]$  24%
3.  $CaMg^{2+}_2[AsO_4]_2(H_2O)_2$  17%

The simplified formula is  $Ca(Mn^{3+}, \square, Mg)_2\{AsO_4, [AsO_2(OH)_2]\}_2(OH, H_2O)_2$ .

#### X-RAY POWDER-DIFFRACTION STUDY

The X-ray powder-diffraction pattern of manganlotharmeyerite, obtained using a 114.6 mm Gandolfi camera and Mn-filtered  $FeK\alpha$  radiation, is given in Table 6. The powder pattern is similar to that of other monoclinic members of the tsumcorite group. The intensities were estimated visually. Weak reflections at  $5.46$  Å ( $I_{obs}=10$ ),  $3.361(30)$ ,  $2.999(5)$ , and  $2.354(5)$  could not be indexed, and were omitted. The strongest ten lines in the X-ray powder-diffraction pattern [ $d$  in Å ( $I(hkl)$ )] are:  $4.93(80)(110)$ ,  $4.61(50)(\bar{1}11)$ ,  $3.426(60)(\bar{2}02)$ ,  $3.182(100)(\bar{1}12)$ ,  $3.122(50)(020)$ ,  $2.927(70)(201)$ ,  $2.822(70)(021)$ ,  $2.718(80)(\bar{3}11)$ ,  $2.555(100)(\bar{2}21, \bar{3}12)$ ,  $2.134(70)(202, 221)$ . The unit-cell parameters of manganlotharmeyerite were obtained by least-squares refinement of the powder-diffraction data (program UnitCell: Holland & Redfern 1997):  $a$   $9.074(5)$  Å,  $b$   $6.239(3)$  Å,  $c$   $7.406(4)$  Å,  $\beta$   $116.60(3)^\circ$ . The theoretical  $d$ -values and intensities listed in Table 6 were calculated for the formula  $Ca(Mn_{0.45}Mg_{0.20}Ni_{0.06}\square_{0.29})_2As_2O_{10}$  with the program CrystalDiffra of D.C. Palmer ([www.crystallmaker.com](http://www.crystallmaker.com)).

#### DISCUSSION

##### Nomenclature of the lotharmeyerite subgroup

The cation composition of the *Me*(2) site is the main guide for the naming of the minerals of the lotharmeyerite subgroup. The lotharmeyerite subgroup

TABLE 6. X-RAY POWDER-DIFFRACTION DATA FOR MANGANLOTHARMEYERITE

$hkl$	$d_{calc}$ [Å]	$I_{calc}$	$d_{obs}$ [Å]	$I_{obs}$	$hkl$	$d_{calc}$ [Å]	$I_{calc}$	$d_{obs}$ [Å]	$I_{obs}$
001	6.62	1	not observed		$\bar{2}22$	2.306	7	not observed	
110	4.95	57	4.93	80	003	2.207	2	2.206	5
111	4.61	39	4.61	50	202	2.139	13		
$\bar{2}01$	4.46	1	4.52	10	221	2.134	21	2.134	70
111	3.528	14	3.530	30	311	2.062	3	2.063	5
$\bar{2}02$	3.424	63	3.426	60	113	1.838	19	1.838	10
$\bar{1}12$	3.182	100	3.182	100	$\bar{1}32$	1.813	10	1.815	20
020	3.120	29	3.122	50	$\bar{3}11$	1.713	17	1.715	30
201	2.925	71	2.927	70	$\bar{4}04$	1.712	14		
021	2.822	39	2.822	70	$\bar{4}23$	1.688	49	1.688	40
$\bar{3}11$	2.720	56	2.718	80	$\bar{2}24$	1.591	16	1.591	10
$\bar{2}21$	2.557	59			040	1.560	23	1.561	10
$\bar{3}12$	2.551	25	2.555	100	421	1.516	19	1.517	10
112	2.459	28	2.459	30					

contains monoclinic tsumcorite-group minerals with  $Me(1) = Ca$  and  $X = As$ . Lotharmeyerite was originally described from the oxidation zone of the Ojuela mine, Mapimi, Mexico as red crystals with the formula  $CaZnMn^{3+}(AsO_4)_2(OH) \cdot 2H_2O$  (Dunn 1983). Its chemical formula was revised to  $CaZnMn(AsO_3OH)_2(OH)_3$  by Kampf *et al.* (1984). On the basis of a crystal-structure refinement of the  $Fe^{3+}$  analogue of lotharmeyerite (ferrilotharmeyerite), Krause *et al.* (1998) revised the chemical formula for lotharmeyerite to  $Ca(Mn^{3+}, Zn)_2(AsO_4)_2(OH, H_2O)_2$ . Because the available chemical composition of lotharmeyerite and ferrilotharmeyerite showed a small range, with  $(Fe+Mn) : Zn$  values close to 1, Krause *et al.* (1998) followed the IMA guidelines for the nomenclature of solid solutions (Nickel 1992), and did not define different names for the  $Mn^{3+}$  and  $Zn^{2+}$  end-members.

Manganlotharmeyerite clearly has a  $Me(2)$ -site occupancy very different from the lotharmeyerite from the

type locality (Fig. 4, Table 1). Thus, according to Krause *et al.* (1998), and in accordance with the IMA rules, a new name is warranted for manganlotharmeyerite. In cabalzarite, another recently described mineral of the lotharmeyerite subgroup, the  $Me(2)$  site is occupied mainly by  $Mg^{2+}$  and  $Al^{3+}$ , with the  $Mg:Al$  ratio scattered about 1 (Fig. 4; Brugger *et al.* 2000). In the absence of clearly Mg- or Al-dominant crystals, only one name was given, and by convention it was decided to define cabalzarite as the Mg end-member. There is no evidence for ordering of cations at the  $Me(2)$  site in lotharmeyerite, manganlotharmeyerite, and cabalzarite. Such  $Me^{2+}-Me^{3+}$  ordering results in a symmetry reduction in "gartrellite-type" tsumcorite-group minerals, hence justifying a new name for intermediate compositions (Effenberger *et al.* 2000). As the new mineral from Starlera is relatively Mn-rich (Fig. 4), we define manganlotharmeyerite to represent the  $Mn^{3+}$ -dominant end-member of the lotharmeyerite subgroup.

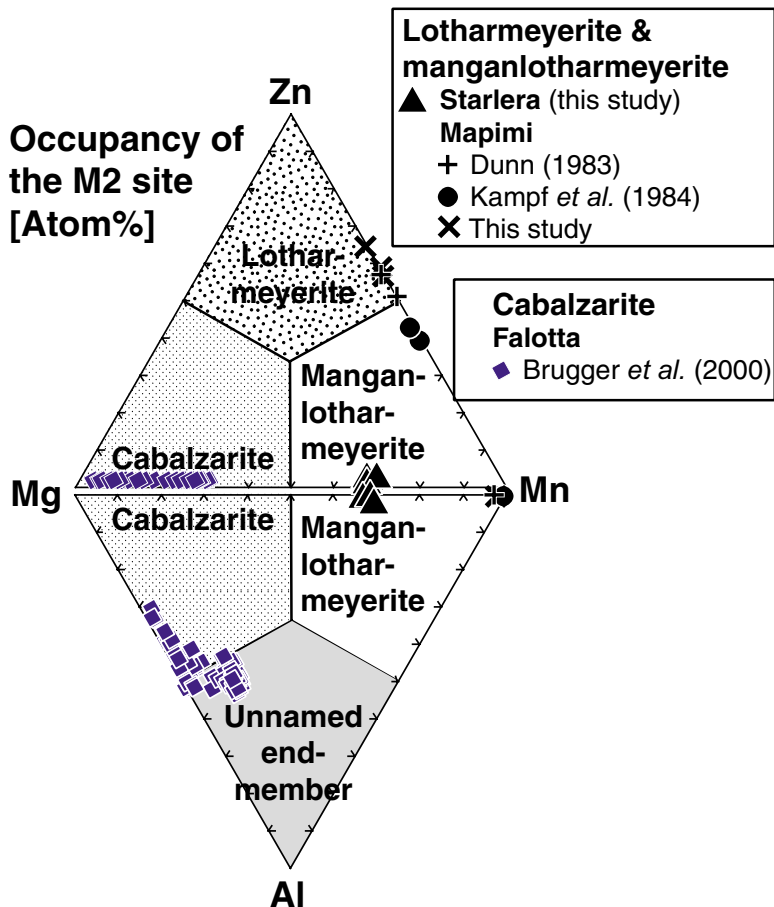


FIG. 4. New proposed nomenclature for Ca-dominant tsumcorite-group minerals (lotharmeyerite subgroup) with  $Mn^{3+}$ ,  $Mg^{2+}$ ,  $Zn^{2+}$  and  $Al^{3+}$  at the  $Me(2)$  site.

TABLE 7. NOMENCLATURE OF LOTHARMEYERITE, FERRILOTHARMEYERITE AND MANGANLOTHARMEYERITE

Published as	Sample No.	Ref	Valid name	Proportion of ions at the <i>Me(2)</i> site*						
				Zn	Co	Ni	Cu	Al	Fe <sup>3+</sup>	Mn <sup>3+</sup>
lotharmeyerite	#1	1	lotharmeyerite	0.99					0.06	0.95
lotharmeyerite	#2	1	lotharmeyerite	1.05					0.16	0.79
lotharmeyerite	#1	2	manganlotharmeyerite	0.85						1.15
lotharmeyerite	#2	2	manganlotharmeyerite	0.80						1.20
ferrilotharmeyerite	NMC64573	3	lotharmeyerite	0.95			0.18		0.87	
ferrilotharmeyerite	M38092	3,4	ferrilotharmeyerite	0.82			0.34	0.01	0.83	
ferrilotharmeyerite	#241	5	lotharmeyerite	1.06						0.94
ferrilotharmeyerite	#242	6	ferrilotharmeyerite	0.11	0.27	0.71		0.01	0.90	

References: (1) Dunn (1983), (2) Kampf *et al.* (1984), (3) Ansell *et al.* (1992), (4) Krause *et al.* (2001b), (5) Krause *et al.* (1998), and (6) Krause *et al.* (2001a).

The type specimen of lotharmeyerite was reported to contain more Zn than Mn (Dunn 1983). Our analyses on a sample from the same locality also show Zn > Mn (Table 1). Consequently, we redefine lotharmeyerite to represent the Zn-dominant member, Ca(Zn,Mn<sup>3+</sup>)<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O,OH)<sub>2</sub>. Note that the “lotharmeyerite” sample studied by Kampf *et al.* (1984) contains more Mn than Zn, and should be named manganlotharmeyerite according to the new nomenclature. The consequences of the updated nomenclature for the naming of published occurrences of lotharmeyerite and ferrilotharmeyerite are summarized in Table 7.

There are now six phases in the lotharmeyerite subgroup: *Me(2)* = Mg (cabalzarite, Brugger *et al.* 2000), Zn (lotharmeyerite, Dunn 1983, and this paper), Mn<sup>3+</sup> (manganlotharmeyerite, this paper), Fe<sup>3+</sup> (ferrilotharmeyerite, Ansell *et al.* 1992, Krause *et al.* 1998), Co (cobaltlotharmeyerite, Krause *et al.* 1999), and Ni (nickellotharmeyerite, Krause *et al.* 2001a). Manganlotharmeyerite is the first tsumcorite-group mineral with a significant amount of *Me(2)* vacancies. The crystal-structure refinement indicates that the investigated crystal from Starlera contains 24% of the Ca□<sub>2</sub>[(AsO<sub>4</sub>(OH)<sub>2</sub>)]<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> end-member.

#### Occurrence of tsumcorite-group minerals

The great majority of the tsumcorite-group minerals are found in the oxidation zone of polymetallic ore deposits; however, two recently described species, cabalzarite Ca(Mg,Al,Fe)<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O,OH)<sub>2</sub> (Brugger *et al.* 2000) and krettnichite, PbMn<sup>3+</sup><sub>2</sub>(VO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub> (Brugger *et al.* 2001), occur in association with Fe–Mn ores. Cabalzarite is a product of the remobilization of arsenic during retrograde metamorphism (in the zeolite facies) in syngenetic exhalative ores. In contrast, krettnichite is a primary *hydrothermal* mineral crystallizing late in the paragenetic sequence in a vein of manganite. Hence, cabalzarite and manganlotharmeyerite share a very similar geological origin. This similarity is reflected in the crystal chemistry of both minerals. The *Me(1)* and X

sites have almost identical occupancy, and the *Me(2)* sites both contain significant amounts of Mn, Mg and Al (Fig. 4).

#### ACKNOWLEDGEMENTS

We thank J.A. Mandarino, E. Sokolova, I.V. Pekov and W. Krause for helpful reviews, and R.F. Martin for helping us to integrate this large amount of information and for his own review.

#### REFERENCES

- ANSELL, H.G., ROBERTS, A.C., DUNN, P.J., BIRCH, W.D., ANSELL, V.E. & GRICE, J.D. (1992): Ferrilotharmeyerite, a new Ca–Zn–Fe<sup>3+</sup> hydroxyl arsenate from Tsumeb, Namibia. *Can. Mineral.* **30**, 225–227.
- BAUDIN, T. & MARQUER, D. (1993): Métamorphisme et déformation dans la nappe de Tambo (Alpes Centrales Suisses): évolution de la substitution phengitique au cours de la déformation alpine. *Schweiz. Mineral. Petrogr. Mitt.* **73**, 285–299.
- \_\_\_\_\_, \_\_\_\_\_, BARFETY, J.-C., KERCHKOVE, C. & PERSOZ, F. (1995): A new stratigraphical interpretation of the Mesozoic cover of the Tambo and Suretta nappes: evidence for early thin-skinned tectonics (Swiss Central Alps). *C.R. Acad. Sci. Paris* **321**, sér. **IIa**, 401–408.
- BAUR, W.H. (1974): The geometry of polyhedral distortions. Predictive relationships for the phosphate groups. *Acta Crystallogr.* **B30**, 1195–1215.
- BROWN, I.D. & ALTERMATT, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.* **B41**, 244–247.
- BRUGGER, J., ARMBRUSTER, T., CRIDDLE, A., BERLEPSCH, P., GRAESER, S. & REEVES, S. (2001): Description, crystal structure, and paragenesis of krettnichite, PbMn<sup>3+</sup><sub>2</sub>(VO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>, the Mn<sup>3+</sup> analogue of mounanaite. *Eur. J. Mineral.* **13**, 145–158.

- \_\_\_\_\_ & BERLEPSCH, P. (1996): Description and crystal structure of fianelite  $Mn_2V(V,As)O_7 \cdot 2H_2O$ , a new mineral from Fianel, Val Ferrera, Graubünden, Switzerland. *Am. Mineral.* **81**, 1270-1276.
- \_\_\_\_\_ & GIERÉ, R. (1999): As, Sb, and Ce enrichment in minerals from a metamorphosed Fe–Mn deposit Val Ferrera, Eastern Swiss Alps. *Can. Mineral.* **37**, 37-52.
- \_\_\_\_\_ & \_\_\_\_\_ (2000): Origin and distribution of some trace elements in metamorphosed Fe–Mn deposits, Val Ferrera, Eastern Swiss Alps. *Can. Mineral.* **38**, 1075-1101.
- \_\_\_\_\_, MEISSER, N., SCHENK, K., BERLEPSCH, P., BONIN, M., ARMBRUSTER, T., NYFELER, D. & SCHMIDT, S. (2000): Description and crystal structure of cabalzarite  $Ca(Mg,Al,Fe)_2(AsO_4)_2(H_2O,OH)_2$ , a new mineral of the tsumcorite group. *Am. Mineral.* **85**, 1307-1314.
- BURNS, P.C., COOPER, M.A. & HAWTHORNE, F.C. (1994): Jahn–Teller-distorted  $Mn^{3+}O_6$  octahedra in fredrikssonite, the fourth polymorph of  $Mg_2Mn^{3+}(BO_3)O_2$ . *Can. Mineral.* **32**, 397-403.
- DUNN, P.J. (1983): Lotharmeyerite, a new mineral from Mapimi, Durango, Mexico. *Mineral. Rec.* **14**, 35-36.
- EFFENBERGER, H., KRAUSE, W., BERNHARDT, H.-J. & MARTIN, M. (2000): On the symmetry of tsumcorite group minerals based on the new species rappoldite and zincgartrellite. *Mineral. Mag.* **64**, 1109-1126.
- FERRARIS, G., JONES, D.W. & YERKES, J. (1972): A neutron diffraction study of the crystal structure of calcium bis(dihydrogen arsenate),  $Ca(H_2AsO_4)_2$ . *Acta Crystallogr.* **B28**, 2430-2437.
- FOLEY, J.A., HUGHES, J.M. & LANGE, D. (1997): The atomic arrangement of brackebuschite, redefined as  $Pb_2(Mn^{3+}, Fe^{3+})(VO_4)_2(OH)$ , and comments on  $Mn^{3+}$  octahedra. *Can. Mineral.* **35**, 1027-1033.
- GRIFFITH, W.P. (1970): Raman studies on rock-forming minerals. II. Minerals containing  $MO_3$ ,  $MO_4$  and  $MO_6$  groups. *J. Chem. Soc.* **A1970**, 286-291.
- HAWTHORNE, F.C., KRIVOVICHEV, S.V. & BURNS, P.C. (2000): The crystal chemistry of sulfate minerals. In *Sulfate Minerals: Crystallography, Geochemistry and Environmental Significance* (C.N. Alpers & J.L. Jambor, eds.). *Rev. Mineral. Geochem.* **40**, 1-112.
- HOLLAND, T.J.B. & REDFERN, S.A.T. (1997): Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Mineral. Mag.* **61**, 65-77.
- HURFORD, A.J., FLYSCH, M. & JÄGER, E. (1989): Unraveling the thermo-tectonic evolution of the Alps: a contribution from fission track analysis and mica dating. In *Alpine Tectonics* (M. P. Coward, D. Dietrich & R.G. Park, eds). *Geol. Soc., Spec. Publ.* **45**, 369-398.
- IBERS, J.A. & HAMILTON, W.C., eds. (1974): *International Tables for X-ray Crystallography* IV. The Kynoch Press, Birmingham, U.K.
- KAMPF, A.R., SHIGLEY, J.E. & ROSSMAN, G.R. (1984): New data on lotharmeyerite. *Mineral. Rec.* **15**, 223-226.
- KRAUSE, W., BELENDORFF, K., BERNHARDT, H.-J., MCCAMMON, C., EFFENBERGER, H. & MIKENDA, W. (1998): Crystal chemistry of the tsumcorite-group minerals. New data on ferilotharmeyerite, tsumcorite, thometzekite, mounanaite, helmetwinklerite, and a redefinition of gartrellite. *Eur. J. Mineral.* **10**, 179-206.
- \_\_\_\_\_, BERNHARDT, H.-J., EFFENBERGER, H. & MARTIN, M. (2001a): Cobalttsumcorite and nickellotharmeyerite, two new minerals from Schneeberg, Germany: description and crystal structure. *Neues Jahrb. Mineral., Monatsh.*, 558-576.
- \_\_\_\_\_, \_\_\_\_\_ & WITZKE, T. (2002): Schneebergite and nickelschneebergite from Schneeberg, Saxony, Germany: the first Bi-bearing members of the tsumcorite group. *Eur. J. Mineral.* **14**, 115-126.
- \_\_\_\_\_, BLASS, G., BERNHARDT, H.-J. & EFFENBERGER, H. (2001b): Lukrahnite,  $CaCuFe^{3+}(AsO_4)_2(H_2O)(OH)$ , the calcium analogue of gartrellite. *Neues Jahrb. Mineral., Monatsh.*, 481-492.
- \_\_\_\_\_, EFFENBERGER, H., BERNHARDT, H.-J. & MARTIN, M. (1999): Cobaltlotharmeyerite,  $Ca(Co,Fe,Ni)_2(AsO_4)_2(OH,H_2O)_2$ , a new mineral from Schneeberg, Germany. *Neues Jahrb. Mineral., Monatsh.*, 505-517.
- MANDARINO, J.A. (1981): The Gladstone–Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.* **19**, 441-450.
- MARQUER, D., CHALLANDES, N. & BAUDIN, T. (1996): Shear zone patterns and strain distribution at the scale of a Penninic nappe: the Suretta nappe (Eastern Swiss Alps). *J. Struct. Geol.* **18**, 753-764.
- NICKEL, E.H. (1992): Solid solutions in mineral nomenclature. *Can. Mineral.* **30**, 231-234.
- SCHMID, S.M., PFIFFNER, O.A. & SCHREURS, G. (1997): Rifting and collision in the Penninic zone of eastern Switzerland. In *Deep structure of the Swiss Alps - Results from NFP/ PNR 20* (A. Pfiffner, ed). Birkhäuser AG, Basel, Switzerland (160-185).
- SCHREURS, G. (1995): Geometry and kinematics of the Schams nappes and adjacent tectonic units in the Penninic zone. *Beiträge zur Geologischen Karte der Schweiz* **167**, 111 p.
- TRÜMPY, R. (1980): An outline of the geology of Switzerland, a Guide Book. A. Schweizerische geologische Kommission, Wepf & Co., Basel, Switzerland.
- VON BLANCKENBURG, F. (1992): Combined high-precision chronometry and geochemical tracing using accessory minerals applied to the central-Alpine Bergell intrusion (central Europe). *Chem. Geol.* **100**, 19-40.
- WILDNER, M., TILLMANN, E., ANDRUT, M. & LORENZ, J. (2003): Sailaufite,  $(Ca,Na,□)_2Mn_3O_2(AsO_4)_2(CO_3) \cdot 3H_2O$ , a new mineral from Hartkoppe hill, Ober-Sailauf (Spessart Mountains, Germany), and its relationship to mitridatite-group minerals. *Eur. J. Mineral.* **15** (in press).

Received March 11, 2002, revised manuscript accepted November 11, 2002.