FERRILOTHARMEYERITE, A NEW Ca–Zn–Fe³⁺ HYDROXYL ARSENATE FROM TSUMEB, NAMIBIA¹

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ABSTRACT

Ferrilotharmeyerite occurs at the Tsumeb mine. Tsumeb, Namibia, as multiple subhedral crystallites and as tabular to wedge- or lozenge-shaped crystals associated with tennantite, scorodite, conichalcite, schneiderhöhnite and beudantite. The mineral is monoclinic, space group C2. Cm or C2/m (diffraction aspect $C^*/*$), with refined unit-cell parameters a 8.997(7), b 6.236(2), c 7.390(3) Å, β 115.74(4)°, V 373.5(5) Å³, a:b:c 1.443:1:1.185, Z = 2. The strongest seven lines of the X-ray powder-diffraction pattern ſd in $\dot{A}(I)(hkI)$ are: 4.95(70)(110). 3.175(100)(112). 3.398(100)(202). 2.938(100)(201). 2.823(70)(021), 2.702(70)(311), 2.544(100)(221). The crystallites are transparent to translucent, medium to brownish yellow with an adamantine to greasy lustre and a pale yellow streak. The mineral is brittle, with an uneven fracture and a good [001] cleavage. D(meas.) 4.25(5), D(calc.) 4.25 and 4.38 g/cm³ for two empirical formulas. Optically, the mineral is biaxial positive, with α 1.811(5), β 1.844(5), γ 1.88(1), 2V(meas.) 85(5)°, 2V(calc.) 89°, X approximately || a, Y || b. Pleochroism is strong: X olive green, Y pale green, Z colorless. Absorption is X> $Y \gg Z$. Inclined dispersion of the optic axes is distinct, $r > \nu$. The ideal chemical formula is Ca(Zn,Cu)(Fe³⁺,Zn)(AsO₃OH)₂(OH)₃, derived from electron-microprobe analyses, water determination and microchemical tests. Ferrilotharmeyerite is the ferric iron analogue of lotharmeyerite, and is named to reflect this relationship.

Keywords: ferrilotharmeyerite, calcium zinc ferric iron hydroxyl arsenate, new mineral species, X-ray data, chemical composition, Tsumeb mine, Namibia.

SOMMAIRE

La ferrilotharmeyerite, nouvelle espèce minérale provenant de la mine Tsumeb, en Namibie, est présente sous forme de petits cristaux sub-idiomorphes ou en tablettes ou en losanges, associés à tennantite, scorodite, conichalcite, schneiderhöhnite et beudantite. Elle est monoclinique, groupe spatial C2, Cm ou C2/m (aspect de diffraction $C^*/*$; les paramètres réticulaires ont été affinés: a 8.997(7), b 6.236(2), c 7.390(3) Å, β 115.74(4)°, V 373.5(5) Å³, *a:b:c* 1.443:1:1.185, Z = 2. Les sept raies les plus intenses du cliché de diffraction (méthode des Å(I)(hkl)] sont: 4.95(70)(110), poudres) [d en $3.398(100)(20\overline{2}),$ 3.175(100)(112), 2.938(100)(201), 2.823(70)(021), 2.702(70)(31T), 2.544(100)(22T). Les petits cristaux sont transparents à translucides, jaune moyen à jaune brunâtre, avec un éclat adamantin ou gras et une rayure jaune pâle. C'est un minéral cassant dont la fracture est irrégulière; le clivage [001] est bon. Densité 4.25(5) (mesurée), 4.25 et 4.38 (valeurs calculées pour les deux formules empiriques). Biaxe positif, avec α 1.811(5), β 1.844(5), γ 1.88(1), 2V(mes.) 85(5)°, 2V(calc.) 89°, X à peu près || a, Y || b. Le pléochroïsme est intense: X vert olive, Y vert pâle, Z incolore. L'absorption est X > $Y \gg Z$. La dispersion inclinée des axes optiques est distincte, r > v. La formule chimique idéale, $Ca(Zn,Cu)(Fe^{3+},Zn)(AsO_3OH)_2(OH)_3$, est dérivée de données obtenues à la microsonde électronique, des déterminations de la teneur en H₂O, et de tests microchimiques. Le ferrilotharmeyerite est l'analogue

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ferrifère de la lotharmeyerite, et son nom témoigne de cette relation.

(Traduit par la Rédaction)

Mots-clés: ferrilotharmeyerite, arsenate de calcium, zinc, fer ferrique hydroxylé, nouvelle espèce minérale, données aux rayons X, composition chimique, mine de Tsumeb, Namibie.

INTRODUCTION

A new mineral, ferrilotharmeyerite, has been identified on a specimen (NMC 64573) in the National Mineral Collection of the Geological Survey of Canada. The sample was collected in 1983 by John Innes, from the Tsumeb mine (32 level, W40 stope), Tsumeb, Namibia. The mineral occurs as multiple subhedral crystallites, averaging 0.2 mm in length, with crudely formed faces slightly elongate in the *b* direction. The matrix appears to be feldspathic quartzite showing pervasive staining by hematite. Ferrilotharmeyerite rims conichalcite and is in contact with tennantite. Large crystals of scorodite and schneiderhöhnite also occur on the specimen.

After most of the data needed to define the species had been obtained on the NMC specimen, additional ferrilotharmeyerite from the same locality was found on a specimen of massive tennantite and calcite from the Museum of Victoria, Melbourne, Australia (M38092). This specimen has a 7×7 cm crust of dark brown tabular beudantite crystals up to 1 mm across, and yellowish brown ferrilotharmeyerite crystals up to about 0.6 mm in size. The water analysis for ferrilotharmeyerite was obtained from this specimen because of the dearth of material on the NMC specimen.

The mineral is the ferric iron analogue of lotharmeyerite (Dunn 1983, Kampf *et al.* 1984) and is named to reflect this relationship. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, I.M.A. The two specimens described above have been designated cotype, and are the only known specimens of ferrilotharmeyerite.

X-RAY CRYSTALLOGRAPHY

Precession studies were undertaken on several fragments of ferrilotharmeyerite 0.1 to 0.2 mm in size from NMC 64573, but in all cases orientation photographs indicate that single-crystal multiple crystallites are present. Even the smallest fragment is composed of at least four individuals. Nevertheless, h0l and $b^* \Lambda 201^*$ photographs of one fragment clearly show monoclinic symmetry and gave measured unit-cell parameters: a 8.98, b 6.23, c

7.38 Å, β 115.57°. These data are consistent with those reported for lotharmeyerite by Kampf *et al.* (1984). Because upper-level precession photography was impossible and the X-ray powder patterns of the two minerals are very similar, it was decided to index the powder pattern of ferrilotharmeyerite by analogy with the powder data provided for lotharmeyerite by Kampf *et al.* (1984). Ferrilotharmeyerite crystals from specimen M38092 are also unsuitable for single-crystal precession study.

The X-ray powder-diffraction data for specimen NMC 64573 (Table 1) were refined using twelve reflections between 3.544 and 1.559 Å for which unambiguous indexing was possible. The refined unit-cell parameters are: a 8.997(7), b 6.236(2), c 7.390(3) Å, β 115.74(4)°, V 373.5(5) Å³, a:b:c 1.443:1:1.185, with Z = 2. The possible space-groups, also by analogy, are C2, Cm or C2/m (diffraction aspect C*/*). The cell parameters and cell volume are slightly lower than those reported by Kampf *et al.* (1984) for lotharmeyerite. Contributing factors for the smaller unit cell are the small but significant differences in ionic radii between Fe³⁺ (0.64 Å) and Mn³⁺ (0.66 Å), and between Cu²⁺ (0.72 Å) and Zn²⁺ (0.74 Å).

PHYSICAL AND OPTICAL PROPERTIES

Ferrilotharmeyerite on specimen NMC 64573 occurs as subhedral crystals, averaging 0.2 mm in

TABLE 1. X-I	RAY POWDER	DATA	FOR	FERRILOTHARMEYERITE
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lest.	d(meas.)	d(calc.)	hkl	lest.	d(meas.)	d(calc.)	hkl
30	6.66	6.66	001	5	2.070	2.069	311
70	4.95	4.94	110	5	2.026	2.026	400
30	4.60	4.59	111	5	1.983	(1.988	131
10	4,44	4.42	201	3	1.985	¹ 1.986	403
20	3.544	3.544	111	5	1.925	1,924	223
100	3.398	3.395	202		1.047	(1.850	113
100	3.175	3.178	112	30	1.847	¹ 1.847	204
20	3.121	3.118	020		1 011	(1.812	132
100	2.938	2.940	201	20	1.811	1.808	023
70	2.823	2.824	021	10	1.773	1.772	222
70	2.702	2.702	311	50	1.701	1.721 f	114
100	2.544	2.547	221	50	1.701	۱.708 ^۱	331
	A 197	2.474	112	60	1.674	(1.691	312
50	2.475	۱ 2.471	220	50	1.074	^{ا 1.675}	423
10	2.297	2.296	222	20	1.589	1.589	224
		2.276	022	30	1.559	1.559	040
10	2.268	{ 2.260	113		1 510	(^{1,519}	421
		2.219	003	20	1.518	1,509	331
10	2.210	1 2.208	402		1 460	(1.469	223
		, 2.154	202	30	1.468	^ا 1.468	205
20	2.147	{ _{2.139}	221				

 ^{114.6} mm Debye-Scherrer powder camera, Cu radiation Ni-filter (λCuKα 1.54178 Å)
intermities estimated visually, values of d quoted in Å

intensities estimated visually, values of d quoted in Å
indexed with a 8.997, b 6.236, c 7.390 Å, B 115.74°

size, in randomly oriented to subparallel aggregates up to 3 mm in maximum dimension. The crystals are transparent, medium yellow to brownish yellow, with an adamantine lustre and a very pale yellow streak. For M38092, the ferrilotharmeyerite crystals are tabular to wedge- or lozenge-shaped, average about 0.6 mm in size, and are commonly intergrown with beudantite. These crystals are translucent, with a greasy lustre and a pale yellow streak. The mineral is brittle, with an uneven fracture and a good {001} cleavage. The Mohs hardness is approximately 3. Ferrilotharmeyerite is not fluorescent under either long- or short-wave ultraviolet light. The density for ferrilotharmeyerite from NMC 64573, as determined by the heavy-liquid flotation technique using Clerici solution, is 4.25(5) g/cm^3 . The calculated value is 4.25 g/cm^3 on the basis of the empirical formula for M38092, and 4.38 g/cm³ on the basis of the empirical formula for NMC 64573.

Optically, the mineral from NMC 64573 is biaxial positive, with α 1.811(5), β 1.844(5), γ 1.88(1), 2V(meas.) 85(5)°, as determined in sodium light (λ 589 nm), and 2V(calc.) 89°, X approximately parallel to a, and Y parallel to b. Pleochroism is strong: X olive green, Y pale green, Z colorless. Absorption is X > Y > Z. Inclined dispersion of the optic axes is distinct, r > v.

CHEMICAL COMPOSITION

Ferrilotharmeyerite was analyzed by electron microprobe in two laboratories, at the Department of Geology, University of Melbourne, Australia, and the Smithsonian Institution, Washington. Operating conditions, standards and analytical results are given in Table 2. A wavelength-dispersion scan revealed no elements heavier than oxygen other than those reported. The Australian Mineral Development Laboratories (AMDEL) in Mel-

TABLE 2. CHEMICAL COMPOSITION OF FERRILOTHARMEYERITE	TABLE 2. CHEMICAL	COMPOSITION O	F FERRILOTHARMEYERITE
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NMC 64573		M38092	
CuO wt.%	2.9	5.75	(3.82-7.91)
ZnO	15.8	13.94	(12.35-15.25)
Fe ₂ O ₃	14.1	13.96	(13.20-15.20)
CaO	12.1	10.86	(10.50-11.23)
PbO	n.d.	2.13	(0.67-3.47)
Al ₂ O ₃	n.d.	0.13	(0.02-0.30)
MnO	tr.	n.d.	
MgO	tr.	n.d.	
As ₂ O ₅ H ₂ O	46.7	48.66	(48.38-48.90)
H ₂ O	n.g.	5.85*	•
Total	91.6	101.28	

tr. = trace; n.d. = not detected; n.g. = not given; * = determined by C-H-N analyser.

- NMC 64573: SEMQ electron microprobe operated at 15 kV, 0.025 µA sample current, with standards: manganite (Mn), cuprite (Cu), fluorapatite (Ca), zinc oxide (Zn), olivenite (As), and hornblende (Fe,Mg).
- M38092: JEOL electron microprobe operated at 15 kV, 0.02 µA sample current, with standards: copper (Cu), wollastonite (Ca), zinc (Zn), arsenopyrite (As), hematite (Fe), corundum (Al), and galena (Pb). Values in brackets are the ranges.

bourne, Australia, provided the water analysis by CHN Analyzer. Microchemical tests were negative for Fe^{2+} and positive for Fe^{3+} .

The empirical formula for NMC 64573, on the basis of As = 2, is $Ca_{1.06}(Zn_{0.82}Cu_{0.18})_{\Sigma 1.00}$ $(Fe_{0.87}Zn_{0.14})_{\Sigma 1.01}[AsO_{3.10}(OH)_{0.90}]_2(OH)_{2.80}$ The empirical formula for M38092, on the basis of As $(Ca_{0.92}Pb_{0.05})_{\Sigma 0.97}(Zn_{0.66}Cu_{0.34})_{\Sigma 1.00}$ 2, is $(Fe_{0.83}Zn_{0.15}Al_{0.01})_{\Sigma 0.99}[AsO_{3.41}(OH)_{0.58}]_2(OH)_{1.90}$ By analogy with lotharmeyerite, the idealized formula is $Ca(Zn,Cu)(Fe^{3+},Zn)(AsO_3OH)_2(OH)_3$. Because proven cases of solid solution involving Cu²⁺ and Fe³⁺ are unknown, but Cu-Zn solid solution has been reported in secondary arsenates and phosphates, such as philipsburgite (Peacor et al. 1985) and kipushite (Piret et al. 1985), all Cu is assumed to substitute for Zn.

The compatibility indices of NMC 64573 ferrilotharmeyerite, on the basis of the Gladstone-Dale relationship (Mandarino 1979) are 0.025 (for the measured density) and 0.054 (for the calculated density), indicating a good to excellent agreement between the physical and chemical data.

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