Magnesiokoritnigite, $Mg(AsO_3OH) \cdot H_2O$, from the Torrecillas mine, Iquique Province, Chile: the Mg-analogue of koritnigite

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ABSTRACT

The new mineral magnesiokoritnigite (IMA 2013-049), ideally Mg(AsO₃OH)·H₂O, was found at the Torrecillas mine, Salar Grande, Iquique Province, Chile, where it occurs as a secondary alteration phase in association with anhydrite, chudobaite, halite, lavendulan, guartz and scorodite. Crystals of magnesiokoritnigite are colourless to pale-pink, thin to thick laths up to 2 mm long. Laths are elongated on [001], flattened on $\{010\}$ and exhibit the forms $\{010\}$, $\{110\}$, $\{1\overline{10}\}$, $\{101\}$, $\{031\}$ and $\{0\overline{3}1\}$. The crystals also occur in dense deep-pink intergrowths. Crystals are transparent with a vitreous lustre. The mineral has a white streak, Mohs hardness of \sim 3, brittle tenacity, conchoidal fracture and one perfect cleavage on $\{101\}$. The measured and calculated densities are 2.95(3) and 2.935 g cm⁻³, respectively. Optically, magnesiokoritnigite is biaxial (+) with $\alpha = 1.579(1)$, $\beta = 1.586(1)$ and $\gamma = 1.620(1)$ (measured in white light). The measured 2V is $50(2)^{\circ}$ and the calculated 2V is 50° . Dispersion is r < v, medium. The optical orientation is $Y \approx \mathbf{b}$; $Z^{\wedge} \mathbf{c} = 36^{\circ}$ in obtuse β (note pseudomonoclinic symmetry). The mineral is non-pleochroic. The empirical formula, determined from electron-microprobe analyses, is $(Mg_{0.94}Cu_{0.03}Mn_{0.02}Ca_{0.01})_{\Sigma_{1.00}}As_{0.96}O_5H_{3.19}$. Magnesiokoritnigite is triclinic, $P\bar{1}$, with a =821.06(19) Å³ and Z = 8. The eight strongest X-ray powder diffraction lines are $[d_{obs} \check{A}(I)(hkl)]$: $7.96(100)(020), 4.80(54)(101), 3.791(85)(\overline{2}10,210,\overline{1}\overline{3}1,\overline{1}31), 3.242(56)(0\overline{1}2,\overline{2}\overline{2}1,012),$ $3.157(92)(2\overline{1}1,\overline{2}30,230), 3.021(61)(1\overline{4}1,141,2\overline{2}1,221), 2.798(41)(0\overline{3}2,032)$ and 1.908(43)(multiple). The structure, refined to $R_1 = 5.74\%$ for 2360 $F_0 > 4\sigma F$ reflections, shows magnesiokoritnigite to be isostructural with koritnigite and cobaltkoritnigite.

Keywords: magnesiokoritnigite, new mineral, crystal structure, koritnigite, Torrecillas mine, Chile.

Introduction

THE Torrecillas mine, in the northern Atacama Desert of Chile, is a small, long-inactive arsenic mine consisting of several small pits and a shaft on Torrecillas Hill, overlooking the Pacific

* E-mail: akampf@nhm.org DOI: 10.1180/minmag.2013.077.8.03 Ocean. The deposit was probably discovered and first mined during the guano mining boom of the early 19^{th} century. During that period, the Peruvian Government owned and claimed several guano fields along the Chilean coast in Iquique and Tarapacá provinces, including the prolific Huanillos, Chanabaya and Pabellón de Pica deposits, which are not far from the Torrecillas area (Mortimer *et al.*, 1971). The guano mines under Peruvian administration, were exploited mainly by English companies; many Chinese coolies laboured in the mines and caves. Torrecillas mine was abandoned probably several years prior to 1950 (Pimentel, 1978).

Our mineralogical investigation of the Torrecillas deposit has shown it to host a remarkable secondary assemblage of rare chlorides, arsenates and arsenites. In addition to the new mineral magnesiokoritnigite, described here, the deposit has yielded the new atacamite-group mineral leverettite, $CoCu_3Cl_2(OH)_6$, (Kampf *et al.*, 2013; IMA2013-011), the recently approved new alluaudite-group mineral canutite, NaMn₃[AsO₄]₂[AsO₂(OH)₂] (IMA2013-070), a new mineral of formula Na(As,Sb)³⁺₄O₆Cl, currently awaiting approval (IMA2013-112), and several other potentially new secondary arsenates and arsenites, currently under study.

Keller *et al.* (1979) described the mineral koritnigite, $Zn(AsO_3OH) \cdot H_2O$, from Tsumeb, Namibia, and just two years later Schmetzer *et al.* (1981) described its Co analogue cobaltkoritnigite, $Co(AsO_3OH) \cdot H_2O$, from the Schwarzenberg District, Erzgebirge, Saxony, Germany. Herein, we describe the third member of the koritnigite group, magnesiokoritnigite, Mg(AsO_3OH) \cdot H_2O, named as the Mg analogue,

from the Torrecillas mine, Iquique Province, Chile.

The new mineral and the name have been approved by the International Mineralogical Association (IMA2013-049). One holotype and two cotype specimens are deposited in the Natural History Museum of Los Angeles, Los Angeles, California, USA, under catalogue numbers 64057 (holotype), 64058 and 64059.

Occurrence

The Torrecillas mine is located on Torrecillas Hill near Salar Grande, Iquique Province, Tarapacá Region, Chile (approximately 20°58'13''S 70°8'17''W). The rare secondary chlorides, arsenates and arsenites have been found at three sites: an upper pit measuring ~8 m long and 3 m deep, a lower pit ~100 m from the upper pit and measuring ~5 m long and 3 m deep, and a mine shaft adjacent to the lower pit and lower on the hill (Fig. 1). Magnesiokorithigite was first found by one of the authors (AAMD) in early 2012 in the upper pit and this pit has produced the best crystals. Magnesiokorithigite has also been found in boulders on the hill slope just below the mine shaft.

Four different rock units are exposed on the hill. Rocks of the Coastal Range Batholith



FIG. 1. View looking southwest down Torrecillas Hill towards the Pacific coast. The three principle sites at which unusual secondary minerals have been recovered are labelled. The Pan-American Road can be seen at the base of the hill.

(mainly gabbros) extend from the seashore to the Pan-American Road along the base of the hill. At the foot of the hill is a small area of contact metamorphic rocks in which garnet crystals occur in metamorphosed shales. Higher on the hill, rocks are predominantly andesites and porphyritic lavas of the Jurassic La Negra Formation. The Torrecillas deposit, which the Torrecillas mine exploits, consists of two main veins rich in secondary arsenic and copper minerals that intersect metamorphosed marine shales and lavas. These veins are genetically related to the above-mentioned andesites and porphyritic lavas of the La Negra Formation. More information on the geology and mineralogy of the area is provided by Gutiérrez (1975).

The new mineral is associated with anhydrite, chudobaite, halite, lavendulan, guartz, scorodite, the recently approved new alluaudite-group mineral canutite, NaMn₃[AsO₄]₂[AsO₂(OH)₂] (IMA2013-070), a new mineral of formula Na(As,Sb)₄³⁺O₆Cl, currently awaiting approval (IMA2013-112), and at least two other potentially new arsenate minerals, currently under study. The recently approved new alluaudite-group mineral canutite, NaMn₃[AsO₄]₂[AsO₂(OH)₂], (IMA2013-070) has also been found in the upper pit on Torrecillas Hill, but not in direct association with magnesiokoritnigite. The assemblage is interpreted as having formed from the oxidation of native arsenic and other As-bearing primary phases, followed by later alteration by saline fluids derived from evaporating meteoric water under hyperarid conditions (cf. Cameron et al., 2007). The metallic elements thus far



Fig. 2. Pale-pink laths of magnesiokoritnigite. Field of view = 2 mm.



FIG. 3. Colourless laths of magnesiokoritnigite with blue lavendulan. Field of view 2 mm.

identified in the secondary minerals of this deposit include Na, Mg, Al, Ca, Mn, Fe, Co, Cu, Ni and Sb.



FIG. 4. Crystal drawing of magnesiokoritnigite (clinographic projection in standard orientation).

Constituent	Wt.%	Range	SD	Norm. wt.%	Standard
MgO	19.88	19.27-20.54	0.42	20.86	Diopside
CaO	0.36	0.12 - 0.72	0.18	0.38	Diopside
MnO	0.90	0.40 - 1.46	0.37	0.94	Rhodonite
CuO	1.03	0.74 - 1.24	0.21	1.08	Cu metal
As ₂ O ₅	58.02	57.40-58.74	0.48	60.88	Syn. GaAs
H ₂ O	15.11			15.86	2
Total	95.30			100.00	

TABLE 1. Electron microprobe analyses of magnesiokoritnigite.

TABLE 2. Powder X-ray data for magnesiokoritnigite.

I _{obs}	$d_{\rm obs}$	d _{calc}	I _{calc.}	hkl	I _{obs}	$d_{\rm obs}$	$d_{\text{calc.}}$	I _{calc.}	hkl
100	7.96	7.903	2 100	020			(2.3404	2	330
17	7.05	(7.021	1 6	110	15	2.332	2.3344	2	330
1/	/.05	(7.003	3 6	110			2.3212	3	161
5	5 57	j 5.569	2 2	120			2.2969	3	161
3	5.57	5.551	4 2	120	12	2 1 7 2	∫ 2.1799	3	140
17	5.07	£ 5.070	7 8	111	15	2.1/3	2.1735	3	340
1 /	5.07	5.041	59	111			2.0867	2	171
54	4.80	4.796	0 28	101			(2.0725	2	171
12	3.972	3.951	6 15	040	10	2.050	2.0615	2	242
		(3.800	4 13	210	19	2.030	2.0471	2	113
05	2 701) 3.794	7 13	210			2.0395	4	113
85	3./91	3.767	3 13	131			1.9561	2	400
		3.731	6 13	<u>1</u> 31			1.9285	2	133
		(3.531	8 4	140			1.9197	3	143
14	2 505) 3.522	8 4	140	12	1 009	1.9186	2	411
14	5.505	3.455	1 2	211	43	1.908	1.9027	3	342
		3.447	9 2	211			1.8980	3	143
		(3.239	5 17	012			1.8918	3	342
56	3.242	{ 3.234	2 3	221			(1.7907	2	352
		(3.220	8 24	012	26	1 772	1.7845	2	262
		(3.157	8 2	211	20	1.//5	1.7794	2	352
92	3.157	3.145	8 21	2 30			1.7624	2	262
		(3.136	2 19	230	27	1 659	∫ 1.6907	2	163
		3.096	1 2	112	37	1.038	1.6499	8	004
		(3.068	6 10	141	16	1 5722	(1.5725	2	380
61	2 0 2 1	3.031	3 10	141	10	1.5752	1.5567	2	510
01	5.021	2.989	3 2	221			1.5341	2	520
		2.969	2 2	221			1.5331	2	173
		2.934	3 4	150	26	1 5 2 8	1.5160	2	423
		2.927	8 4	150	50	1.526	1.5113	2	1 <u>7</u> 3
41	2 708	£ 2.814	9 15	032			1.5068	2	1.10.1
41	2.798	2.778	5 12	032			1.4957	2	1.10.1
17	2.672	2.668	2 10	202	15	1.460	1.4565	2	214
		2.634	4 3	060			(1.4163	2	234
12	2.527	2.520	3 5	301	20	1 402	1.4061	2	234
14	2 165	f 2.462	7 5	250	50	1.403	1.4038	2	373
14	2.403) 2.455	0 5	250			1.3851	2	542
10	2.402	2.398	0 5	202					

Only calculated lines with intensities of 2 or greater are shown. Numerous lower-intensity lines also contribute to the observed peaks.

Physical and optical properties

Crystals of magnesiokoritnigite (Figs 2 and 3) are colourless to pale pink, thin to thick laths up to 2 mm long. The laths are elongated on [001], flattened on {010} and exhibit the forms {010}, {110}, {110}, {101}, {031} and {031} (Fig. 4). The crystals also occur in dense intergrowths that are deep pink in colour. Crystals are transparent with a vitreous lustre. The mineral has white streak, Mohs hardness of ~3, brittle tenacity, conchoidal fracture and one perfect cleavage on {101}. The density measured by flotation in Clerici solution is 2.95(3) g cm⁻³. The calculated densities are 2.935 g cm⁻³ based on the empirical formula and 2.948 g cm⁻³ based on the ideal formula.

Optically, magnesiokoritnigite is biaxial (+) with $\alpha = 1.579(1)$, $\beta = 1.586(1)$ and $\gamma = 1.620(1)$

(measured in white light). The 2V measured directly using a spindle stage is $50(2)^{\circ}$ and the calculated 2V is 50°. Dispersion is r < v, moderate. The optical orientation is $Y \approx \mathbf{b}$; $Z \wedge \mathbf{c} = 36^{\circ}$ in obtuse β (note that the mineral exhibits pseudomonoclinic symmetry). The mineral is non-pleochroic.

The mineral is slowly soluble in concentrated HCl or HNO_3 and very slowly soluble in concentrated H_2SO_4 .

Composition

Quantitative analyses (9) were performed at the University of Utah using a Cameca SX-50 electron microprobe (EMPA) with four wavelength-dispersive spectrometers. Analytical conditions were 15 kV accelerating voltage, 20

TABLE 3.	Data	collection	and	structure-ref	inement o	details	for	magnesio	koritnigi	te.

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation/power	MoK α ($\lambda = 0.71075$ Å)/50 kV, 40 mA
Temperature	293(2) K
Structural formula	Mg(AsO ₃ OH)·H ₂ O
Space group	PĪ
Unit-cell dimensions	a = 7.8702(7) Å
	b = 15.8081(6) Å
	c = 6.6389(14) Å
	$\alpha = 90.814(6)^{\circ}$
	$\beta = 96.193(6)^{\circ}$
	$\gamma = 90.094(7)^{\circ}$
V	821.06(19) Å ³
Z	8
Density (for formula above)	2.948 g cm^{-3}
Absorption coefficient	8.330 mm^{-1}
F(000)	704
Crystal size (µm)	$150 \times 80 \times 10$
θ range	3.09 to 25.03°
Index ranges	$-9 \leq h \leq 8, -18 \leq k \leq 18, -7 \leq l \leq 7$
Reflections collected/unique	$10865/2877; R_{int} = 0.106$
Reflections with $F_{0} > 4\sigma(F)$	2360
Completeness to $\theta = 25.03^{\circ}$	99.4%
Max. and min. transmission	0.921 and 0.368
Refinement method	Full-matrix least-squares on F^2
Parameters refined	253
GoF	1.059
Final R indices $[F_{\alpha} > 4\sigma(F)]$	$R_1 = 0.0574, wR_2 = 0.1218$
R indices (all data)	$R_1 = 0.0695, wR_2 = 0.1294$
Largest diff. peak/hole	+1.127/-1.237 e A ⁻³

* $R_{\text{int}} = \Sigma |F_o^2 - F_o^2(\text{mean})| \Sigma [F_o^2]$. GoF = $S = \{\Sigma [w(F_o^2 - F_o^2)^2]/(n-p)\}^{1/2}$. $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. $wR_2 = \{\Sigma [w(F_o^2 - F_o^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where *a* is 0.0279, *b* is 8.5788 and *P* is $[2F_o^2 + \text{Max}(F_o^2, 0)]/3$.

	x/a	y/b	z/c	$U_{\rm eq}$	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mg1	0.0964(4)	0.06260(19)	0.3760(4)	0.0195(6)	0.0194(15)	0.0231(17)	0.0160(15)	0.0025(11)	0.0021(12)	-0.0005(12)
Mg2	0.1403(3)	0.45809(19)	0.3656(4)	0.0189(6)	0.0144(15)	0.0273(18)	0.0157(15)	0.0023(12)	0.0049(11)	-0.0012(12)
Mg3	0.4050(4)	0.5627(2)	0.1291(4)	0.0222(7)	0.0190(16)	0.0302(18)	0.0178(16)	0.0027(12)	0.0033(12)	-0.0002(12)
Mg4	0.3591(4)	0.95876(19)	0.1303(4)	0.0209(7)	0.0177(15)	0.0304(18)	0.0148(15)	0.0020(12)	0.0027(12)	0.0009(12)
Asl	0.08007(11)	0.10410(6)	0.88440(13)	0.0213(3)	0.0192(5)	0.0265(6)	0.0182(5)	0.0022(4)	0.0014(4)	-0.0007(4)
As2	0.17790(11)	0.41844(6)	0.86145(13)	0.0216(3)	0.0188(5)	0.0262(6)	0.0198(5)	0.0015(4)	0.0022(4)	-0.0005(4)
A_{S3}	0.42138(11)	0.60426(6)	0.62370(13)	0.0217(3)	0.0197(5)	0.0265(6)	0.0189(5)	0.0024(4)	0.0019(4)	-0.0008(4)
A_{S4}	0.32086(11)	0.91790(6)	0.63236(13)	0.0213(3)	0.0185(5)	0.0271(6)	0.0183(5)	0.0031(4)	0.0024(4)	-0.0005(4)
01	0.0573(8)	0.0446(4)	0.6732(8)	0.0229(14)	0.030(4)	0.026(4)	0.013(3)	0.000(2)	0.005(3)	-0.002(3)
02	0.1700(7)	0.0535(4)	0.0880(9)	0.0230(14)	0.021(3)	0.025(4)	0.022(3)	0.006(3)	0.000(3)	0.007(3)
OW3	0.2159(8)	0.1774(4)	0.4400(9)	0.0283(15)	0.022(3)	0.031(4)	0.032(4)	0.004(3)	0.002(3)	-0.008(3)
04	0.3313(7)	0.5531(4)	0.4153(9)	0.0224(14)	0.023(3)	0.026(4)	0.018(3)	-0.001(2)	0.000(3)	-0.003(3)
05	0.0851(7)	0.4748(4)	0.6680(9)	0.0237(14)	0.021(3)	0.029(4)	0.020(3)	0.005(3)	-0.001(3)	0.005(3)
0H6	0.3737(8)	0.3695(4)	0.4260(9)	0.0259(15)	0.021(3)	0.036(4)	0.020(3)	0.004(3)	0.000(3)	-0.007(3)
OW7	0.0326(8)	0.3390(4)	0.3590(10)	0.0328(16)	0.027(4)	0.034(4)	0.038(4)	0.001(3)	0.005(3)	-0.007(3)
08	0.1962(7)	0.4773(4)	0.0757(9)	0.0219(14)	0.024(3)	0.021(3)	0.021(3)	0.000(2)	0.004(3)	-0.004(3)
0W9	0.2870(8)	0.6774(4)	0.0746(9)	0.0267(15)	0.020(3)	0.027(4)	0.034(4)	-0.002(3)	0.003(3)	0.003(3)
010	0.3041(8)	0.9769(4)	0.4227(9)	0.0248(14)	0.025(3)	0.030(4)	0.020(3)	0.007(3)	0.002(3)	0.000(3)
0W11	0.4673(8)	0.8402(4)	0.1327(10)	0.0333(16)	0.023(4)	0.036(4)	0.039(4)	0.002(3)	-0.003(3)	0.007(3)
OH12	0.1241(7)	0.8696(4)	0.0633(9)	0.0239(14)	0.017(3)	0.032(4)	0.023(3)	0.003(3)	0.001(3)	0.004(3)
013	0.1895(8)	0.1915(4)	0.8410(9)	0.0269(15)	0.024(3)	0.027(4)	0.032(4)	0.004(3)	0.011(3)	0.001(3)
OH14	0.0481(8)	0.3337(4)	0.8955(10)	0.0284(15)	0.020(3)	0.030(4)	0.036(4)	0.005(3)	0.011(3)	-0.007(3)
015	0.3623(7)	0.3750(4)	0.8053(9)	0.0237(14)	0.021(3)	0.030(4)	0.021(3)	0.005(3)	0.003(3)	-0.002(3)
016	0.4426(8)	0.5444(4)	0.8300(9)	0.0238(14)	0.029(4)	0.023(4)	0.019(3)	0.004(2)	0.000(3)	-0.001(3)
017	0.3145(8)	0.6921(4)	0.6734(10)	0.0299(15)	0.031(4)	0.025(4)	0.034(4)	0.002(3)	0.006(3)	0.004(3)
018	0.1364(8)	0.8750(4)	0.6871(9)	0.0257(14)	0.024(3)	0.029(4)	0.025(4)	-0.003(3)	0.006(3)	-0.002(3)
019	0.4137(7)	0.9737(4)	0.8315(8)	0.0229(14)	0.020(3)	0.034(4)	0.014(3)	0.000(3)	-0.002(2)	-0.009(3)
OH20	0.4481(8)	0.8328(4)	0.5923(10)	0.0293(15)	0.021(3)	0.025(4)	0.043(4)	0.004(3)	0.009(3)	0.006(3)

 T^{ABLE} 4. Atom coordinates and displacement parameters (Å $^2)$ for magnesiokoritnigite.

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nA beam current and a beam diameter of 20 µm. Counting times were 20 s on peak and background. Wavelength scans were performed across the As $L\alpha_1$ and Mg $K\alpha_{1,2}$ peaks in order to establish that there was no peak shift for As $L\alpha_1$ between the GaAs standard and magnesiokoritnigite, and to aid in the selection of appropriate background positions due to the proximity of the two analytical peaks. No other elements were detected by energy dispersive spectroscopy. Other likely elements were sought by EMPA. Co, Ga and Sb were detected, but were below the limits of analytical significance. Raw X-ray intensities were corrected for matrix effects with a $\phi(\rho z)$ algorithm (Pouchou and Pichoir, 1991).

Because insufficient material was available for a direct determination of H_2O , the amount of water was calculated on the basis of (Mg + Ca + Mn + Cu) = 1, charge balance and 5 O atoms p.f.u., as determined by the crystal structure analysis. Analytical data and standards are given in Table 1. Note that magnesiokoritnigite crystals did not take a good polish, to which is attributed the low analytical total; consequently, we also provide the analytical values normalized to 100%.

The empirical formula is $(Mg_{0.94}Cu_{0.03})$ $Mn_{0.02}Ca_{0.01})_{\Sigma1.00}As_{0.96}O_5H_{3.19}$. The simplified structural formula is $Mg(AsO_3OH)$ ·H₂O, which requires MgO 22.12, As₂O₅ 63.06, H₂O 14.83, total 100 wt.%. The Gladstone-Dale compatibility index 1 – (K_P/K_C) is –0.020 for the empirical formula and –0.026 for the ideal formula, in both cases in the range of excellent compatibility (Mandarino, 2007).

X-ray crystallography and structure refinement

Both powder and single-crystal X-ray studies were carried out using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer, with monochromatized Mo $K\alpha$ radiation. For the powder-diffraction study, a Gandolfi-like motion on the ϕ and ω axes was used to randomize the sample and observed d spacings and intensities were derived by profile fitting using JADE 2010 software (Materials Data, Inc.). The powder data presented in Table 2 show good agreement with the pattern calculated from the structure determination. Unit-cell parameters refined from the powder data using JADE 2010 with wholepattern fitting are a = 7.868(7), b = 15.838(7),c = 6.626(7) Å, $\alpha = 91.064(18)$, $\beta = 96.394(17)$, $\gamma = 90.02(3)^{\circ}$ and $V = 820.4(12) \text{ Å}^3$.

0·0M·0	105.3(2)		108.7(2)		105.3(2)		107.8(2)				
	2.682(9) 2.698(9)	2.760(9)	2.962(9)	2.672(9)	2.709(9)	2.736(9)	2.937(9)	2.530(8)	2.513(9)	2.549(9)	2.547(9)
Hdonor Hacceptor	0W3…0H20 0W3…013	OW7017	OW7OW3	OW90H14	OW9017	OW11013	0W110W9	0H6015	OH12018	OH14…013	OH20017
2.050(7)	2.060(7) 2.071(6)	2.091(6)	2.114(7)	2.324(7)	2.118		1.678(6)	1.679(6)	1.680(6)	1.714(6)	1.688
Mg4-010	Mg4-0W11 Mg4-019	Mg4-019	Mg4-02	Mg4-OH12	<mg4-0></mg4-0>		As4-019	As4-O18	As4-O10	As4-OH20	<as1-0></as1-0>
2.053(6)	2.055(7) 2.057(7)	2.079(7)	2.081(7)	2.122(6)	2.075		1.669(6)	1.672(6)	1.681(6)	1.732(6)	1.689
Mg3-04	Mg3-016 Mg3-0W9	Mg3-015	Mg3-016	Mg3-08	<mg3-0></mg3-0>		As3-016	As3-017	As3-04	As3-OH6	<as1-0></as1-0>
2.047(6)	2.061(7) 2.061(7)	2.112(7)	2.121(6)	2.315(7)	2.120		1.676(6)	1.682(6)	1.682(6)	1.715(6)	1.689
Mg2-08	Mg2-05 Mg2-0W7	Mg2-05	Mg2-04	Mg2-OH6	<mg2-0></mg2-0>		As2-O5	As2-O8	As2-015	As2-OH14	<as1-0></as1-0>
2.053(6)	2.060(7) 2.061(7)	2.082(7)	2.087(7)	2.124(7)	2.078		1.670(6)	1.671(6)	1.672(6)	1.730(6)	1.686
-01	-02 -0W3	-01	-018	-010	1 - 0 >		-01	-02	-013	-OH12	^ -

As1 As1 As1 As1 As1 SAs

TABLE 5. Selected bond distances (\check{A}) and angles $(^{\circ})$ for magnesiokoritnigite

H20			. 1	. –		.15	.21							.73
0				94		7 1	0							7 2
0				0.3 0.3		1.2								1.9
018	0.34					1.27						0.31		1.92
017					-	1.29			0.19	0.20				$0.27 \\ 1.95$
016			$0.38 \\ 0.35$		-	1.30								2.03
015			0.35		1.26			0.29						1.90
OH14					1.15					0.21			0.73	2.09
013					1.29		0.20				0.19		0.27	1.95
OH12				0.18	1.11							0.69		1.98
0W11				0.37							0.81	0.87		2.05
010	0.31			0.38		1.27								1.96
0W9			0.37							0.80		0.13		2.09
08		0.38	0.31		1.26									1.96
OW7		0.37						10.0	0.88					2.06
0H6		0.19			-	1.10		0.71						2.00
05		$0.37 \\ 0.32$			1.28									1.97
04		0.31	0.38			1.20								1.95
OW3	0.37						0.80 0.79		0.12					2.08
02	0.37			0.32	1.30									1.99
01	$0.38 \\ 0.35$				1.30									2.03

TABLE 6. Bond-valence analysis for magnesiokoritnigite. Values are expressed in valence units.

å 5 Π ā nogon. , () ñ 5 ĉ allu) NIN 1 The Rigaku *CrystalClear* software package was used for processing structure data, including the application of an empirical multi-scan absorption correction using *ABSCOR* (Higashi, 2001). The structure was solved by direct methods using *SIR2004* (Burla *et al.*, 2005), after which atom positions were transformed to correspond to those reported for the structure of koritnigite (Keller *et al.*, 1980). *SHELXL-2013* (Sheldrick, 2008) was used for the refinement of the structure. A high degree of mosaicity, particularly in the [010] direction, made necessary the use of a rather small crystal, which provided a limited data set with a relatively large R_{int} . The resulting data did not permit the determination of H atom positions.

Data collection and refinement details are given in Table 3, atom coordinates and displacement parameters in Table 4, selected bond distances in Table 5 and a bond-valence analysis in Table 6.

Description of the structure

The structure is considered isostructural with those of koritnigite (Keller *et al.*, 1980) and cobaltkoritnigite (Zettler *et al.*, 1979). It contains 4 Mg sites, 4 As sites and 20 O sites. The structure consists of zig-zag edge-sharing chains of MgO₅(H₂O) octahedra running parallel to $[10\bar{1}]$ that are joined by corner-sharing with AsO₃(OH) tetrahedra to form sheets parallel to {010}. Two



FIG. 5. The crystal structure of magnesiokoritnigite viewed down [101] with [010] vertical. Unit cell shown by dashed line. Hydrogen bonds shown as solid lines.

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FIG. 6. One polyhedral sheet in the structure of magnesiokoritnigite viewed down [010] with [101] horizontal. Unit cell shown by dashed line.

of the four vertices of each of the AsO₃(OH) tetrahedra are O atoms of Mg octahedra, while the other two are unlinked, except by hydrogen bonding. The sheets are linked in the [010] direction only by hydrogen bonds (Figs 5 and 6). The Mg1 and Mg4 octahedra form one set of chains linked into a sheet centred at 0 along *b* and the Mg2 and Mg3 octahedra form another set of chains linked into a sheet centred at $\frac{1}{2}$ along *b*.

The assignment of O sites as O, OH or H₂O (OW) was straightforward based upon bondvalence considerations. Each of the four arsenate groups has one significantly longer As-O bond, which corresponds to an unshared tetrahedral vertex; the corresponding O atoms must correspond to OH groups because they cannot otherwise achieve bond-valence balance. The hydrogen bond scheme proposed also takes into consideration the O·OW·O angles for potential hydrogen bonds. In the proposed scheme, O-O bond lengths corresponding to proposed hydrogen bonds fall in the range 2.51-2.96 Å, O·OW·O angles are in the range 105-109°, and all O atoms have resulting bond-valence sums in the range 1.92-2.09 vu. This is the same hydrogen bonding scheme proposed for koritnigite by Keller et al. (1980).

The Mg coordinations all include 5 O atoms shared with $AsO_3(OH)$ tetrahedra and one

unshared H₂O vertex. The Mg1 and Mg3 coordinations are MgO₅(H₂O), while the Mg2 and Mg4 octahedra include one arsenate OH ligand and, therefore, are MgO₄(OH)(H₂O). The Mg2–OH6 (2.315 Å) and Mg4–OH12 (2.324 Å) bonds are significantly longer than the other Mg-O bonds. These bonds are even longer in the koritnigite structure, with a Zn2-OH6 bond length of 2.487 Å and a Zn4–OH12 bond length of 2.495 Å. The cobaltkoritnigite is somewhat different in this respect. Although the atom positions and labels for the cobaltkoritnigite structure are generally analogous to the other structures, it is the Co1 and Co3 coordinations in the cobaltkoritnigite structure that include one arsenate OH ligand; however, the bond lengths Co1–OH18 (2.186 Å) and Co3–OH15 (2.188 Å) are not appreciably longer than those for the other Co-O bonds. Nevertheless, the bond topologies of all three structures are essentially identical, except that the directions of the O6...O15 and O12...O18 hydrogen bonds are reversed in the cobaltkoritnigite structure; that is, instead of the OH6...O15 and OH12...O18 hydrogen bonds in the structures of koritnigite and magnesiokoritnigite, there are OH15...O6 and OH18...O12 hydrogen bonds in the structure of cobaltkoritnigite.

MAGNESIOKORITNIGITE: THE MG-ANALOGUE OF KORITNIGITE

	Koritnigite*	Magnesiokoritnigite	Cobaltkoritnigite [§]
Ideal formula	Zn(AsO ₃ OH)·H ₂ O	Mg(AsO ₃ OH)·H ₂ O	Co(AsO ₃ OH)·H ₂ O
Space group	PĪ	PĪ	$P\bar{1}$
a (Å)	7.948(2)	7.8702(7)	7.95
$b(\mathbf{A})$	15.829(5)	15.8081(6)	15.83
$c(\dot{A})$	6.668(2)	6.6389(14)	6.67
α (°)	90.86(2)	90.814(6)	90.9
β(°)	96.56(2)	96.193(6)	96.6
γ (°)	90.05(2)	90.094(7)	90.0
$V(Å^3)$	833.3(4)	821.06(19)	834
Z	8	8	8
Density calc. (g cm^{-3})	3.54	2.935	3.46
Optical character	biaxial (+)	biaxial (+)	biaxial (+)
α	1.632(5)	1.579(1)	1.646(2)
β	1.652(3)	1.586(1)	1.668(2)
γ	1.693(3)	1.620(1)	1.705(5)
2V (°)	70(5)	50(2)	78(2)

TABLE 7. Comparative data for koritnigite, magnesiokoritnigite and cobaltkoritnigite.

* Keller et al. (1979). § Schmetzer et al. (1981).

Comparative crystallographic, density and optical data for koritnigite, magnesiokoritnigite and cobaltkoritnigite are given in Table 7. It is worth noting that, in spite of the generally comparable cell parameters, the density and indices of refraction for magnesiokoritnigite are dramatically smaller than those of for koritnigite and cobaltkoritnigite. Obviously, this is due to the much lower atomic number of Mg.

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