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MANGANOKUKISVUMITE, A NEW MINERAL SPECIES FROM MONT SAINT-HILAIRE, QUEBEC

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ABSTRACT

Manganokukisvumite, ideally $Na_6MnTi_4Si_8O_{28}•4H_2O$, is a new mineral species from the Poudrette Quarry, Mont Saint-Hilaire, Rouville County, Quebec (IMA 2002–029). It occurs in small cavities in an albite-rich syenite breccia associated with aegirine, microcline, albite, annite, chalcopyrite, pyrite, pyrrhotite, natrolite, labuntsovite-Mn, titanite, calcite, a chlorite-group mineral, magnetite, fluorapatite, elpidite and sodalite. Manganokukisvumite crystals are colorless and transparent with a vitreous luster and a white streak. It is non-fluorescent in short- and long-wave ultraviolet light. The crystals are extremely thin, flattened and sword-shaped to 0.5 mm in length, commonly forming rosette-like radiating groups. Forms observed are pinacoids {100} and {010} and a prism that we could not measure. No twinning was observed. The hardness is 5½ to 6. It is sectile, slightly flexible, with no apparent cleavage but with a splintery fracture. Manganokukisvumite is biaxial negative, α(calc.) 1.657, β 1.744 ± 0.003 and γ 1.792 ± 0.003 (for $\lambda = 589$ nm); $2V_{meas}$ 70° (Kamb's method). There is no dispersion or pleochroism; the optical orientation is $X = a$, $Y = b$ and $Z = c$. It is orthorhombic, space group *Pccn*, with unit-cell parameters refined from powder data: *a* 29.05(2), *b* 8.612(6), *c* 5.220(4) Å, *V* 1305.9(3) A^3 and $Z = 2$. The strongest X-ray powder-diffraction lines [*d* in Å(*I*)(*hkl*)] are: 14.47(100)(200), 6.43(20)(310), 4.83(10)(600), 3.743(10)(710), 3.025(40)(910), 2.881(20)(521), 2.591(10)(721), 2.458(10)(402) and 2.146(10)(930). An electron-microprobe analysis supported by infrared-absorption spectrometry gave Na_2O 15.61, K_2O 0.21, MgO 0.26, CaO 0.08, MnO 5.48, FeO 0.57, Al_2O_3 0.16, Ce_2O_3 0.18, SiO_2 41.74, TiO_2 26.90, Nb_2O_5 0.68, H_2O 6.25 (calculated by stoichiometry), total 98.12 wt.%. The empirical formula based on O = 32, is: $(Na_{5.81}K_{0.05}Ca_{0.02}Ce_{0.01})_{\Sigma 5.89}$ $(Mn_{0.89}Fe_{0.09}Mg_{0.07}Al_{0.04})_{\Sigma 1.09}(Ti_{3.88}Nb_{0.06})_{\Sigma 3.94}Si_{8.01}O_{28}•4H_2O$ or, ideally, $Na_6MnTi_4Si_8O_{28}•4H_2O$. The calculated density (from the empirical formula) is 2.88 g/cm^3, and the measured density is 2.86(1) g/cm^3. A Gladstone–Dale calculation gives a compatibility index of 0.038 (excellent). Manganokukisvumite is the manganese-dominant analogue of kukisvumite and is closely related to lintisite.

Keywords: manganokukisvumite, new mineral species, Mont Saint-Hilaire, Quebec.

SOMMAIRE

La manganokukisvumite, de formule idéale $Na_6MnTi_4Si_8O_{28}•4H_2O$, est une nouvelle espèce minérale découverte à la carrière Poudrette, au mont Saint-Hilaire, comté de Rouville, Québec (IMA 2002–029). On la trouve dans de petites vacuoles d'une brèche syénitique riche en albite; lui sont associés aegyrine, microcline, albite, annite, chalcopyrite, pyrite, pyrrhotite, natrolite, labuntsovite-Mn, titanite, calcite, un membre du groupe de la chlorite, magnétite, fluorapatite, elpidite et sodalite. Les cristaux de manganokukisvumite sont incolores à transparents avec un éclat vitreux et une rayure blanche. Elle est non-fluorescente en lumière ultra-violette (ondes courtes ou longues). Les cristaux sont extrêmement minces, aplatis et en forme d'épée, jusqu'à 0.5 mm en longueur, et généralement en regroupés en rosette. Les formes observées sont les pinacoïdes {100} et {010} et un prisme que nous étions incapables de mesurer. Il ne semble pas y avoir de macle. La dureté est entre 5½ et 6. Le minéral est sectile, légèrement flexible, sans clivage apparent, mais avec une fracture en échapes. La manganokukisvumite est biaxe négative, avec α(calc.) 1.657, β 1.744 ± 0.003 et γ 1.792 ± 0.003 (pour $\lambda = 589$ nm); $2V_{mes}$ 70° (méthode de Kamb). Il n'y a aucune dispersion et aucun pléochroïsme; l'orientation optique est $X = a$, $Y = b$ et $Z = c$. Il s'agit d'un minéral orthorhombique, groupe spatial *Pccn*, ayant les paramètres réticulaires suivants, affinés à partir des données sur poudre: *a* 29.05(2), *b* 8.612(6), *c* 5.220(4) Å, *V* 1305.9(3) A^3 et $Z = 2$. Les raies les plus intenses du spectre de diffraction, méthode des poudres [*d* en Å(*I*)(*hkl*)] sont: 14.47(100)(200), 6.43(20)(310), 4.83(10)(600), 3.743(10)(710), 3.025(40)(910), 2.881(20)(521), 2.591(10)(721), 2.458(10)(402) et 2.146(10)(930). Une analyse obtenue avec une microsonde électronique, complémentée avec un spectre d'absorption infra-rouge, a donné Na_2O 15.61, K_2O 0.21, MgO 0.26, CaO 0.08, MnO 5.48, FeO 0.57, Al_2O_3 0.16, Ce_2O_3 0.18, SiO_2 41.74, TiO_2 26.90, Nb_2O_5 0.68, H_2O 6.25 (quantité calculée par stoéchiométrie), pour un total de 98.12% (poids). La formule empirique, calculée sur une base de 32 atomes d'oxygène, est: $(Na_{5.81}K_{0.05}Ca_{0.02}Ce_{0.01})_{\Sigma 5.89}$ $(Mn_{0.89}Fe_{0.09}Mg_{0.07}Al_{0.04})_{\Sigma 1.09}$ $(Ti_{3.88}Nb_{0.06})_{\Sigma 3.94}Si_{8.01}O_{28}•4H_2O$ ou, en termes

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plus simples, $Na_6MnTi_4Si_8O_{28}•4H_2O$. La densité calculée (à partir de la formule empirique) est 2.88 g/cm^3, et la densité mesurée est 2.86(1) g/cm^3. L'indice de compatibilité selon la loi de Gladstone et Dale est 0.038 (excellent). La manganokukisvumite est l'analogue à dominance de manganèse de la kukisvumite; elle montre un lien étroit avec la lintisite.

(Traduit par la Rédaction)

Mots-clés: manganokukisvumite, nouvelle espèce minérale, mont Saint-Hilaire, Québec.

INTRODUCTION

Manganokukisvumite (formerly UK 112) was first discovered at Mont Saint-Hilaire, Quebec in 1987 by one of the authors (JVV), and the similarity of its X-ray powder-iffraction pattern and that of UK 74 (Chao *et al.* 1990) from Mont Saint-Hilaire was noted. Because of the small size and extremely thin nature of the crystals, nothing more was done with this material until recently. The species UK 74 from Mont Saint-Hilaire was later found to be lintisite, first described from Mount Alluaiv, Lovozero complex, Russia by Khomyakov *et al.* (1990), and whose structure was determined by Merlino *et al.* (1990). Kukisvumite was described the following year from the Khibina massif, Russia (Yakovenchuk *et al.* 1991), and the close structural and chemical relationship between it and lintisite was established by Merlino *et al.* (2000). In this paper, we describe the manganese-dominant analogue of kukisvumite as a new species and compare its relationship with kukisvumite and lintisite. The new species and its name have been unanimously approved by the Commission on New Minerals and Mineral Names, IMA (2002–029). Cotype material is housed in the collection of the Canadian Museum of Nature, Ottawa under catalogue numbers CMNMC 83392 and CMNMC 83393.

OCCURRENCE

Manganokukisvumite occurs in the Poudrette (formerly Demix) Quarry, Mont Saint-Hilaire, Rouville County, Quebec. Mont Saint-Hilaire is an alkaline complex located 40 km east of Montreal. The pluton, a 350 m high, circular monadnock protruding above the surrounding, flat-lying Ordovician limestones of the St. Lawrence Lowlands, is one of a string of related intrusions known collectively as the Monteregian Hills. The quarry is located on the northeastern flank of the mountain. The mineral formed late in the paragenesis but before the final zeolite phase, in small cavities in an albite-rich syenite breccia. It is associated with aegirine, microcline, albite, annite, pyrite, pyrrhotite, chalcopyrite, natrolite, calcite, a chlorite-group mineral, magnetite, fluorapatite, elpidite, sodalite, labuntsovite-Mn and titanite. Manganokukisvumite likely formed through the hydrothermal dissolution of other titanium-bearing min-

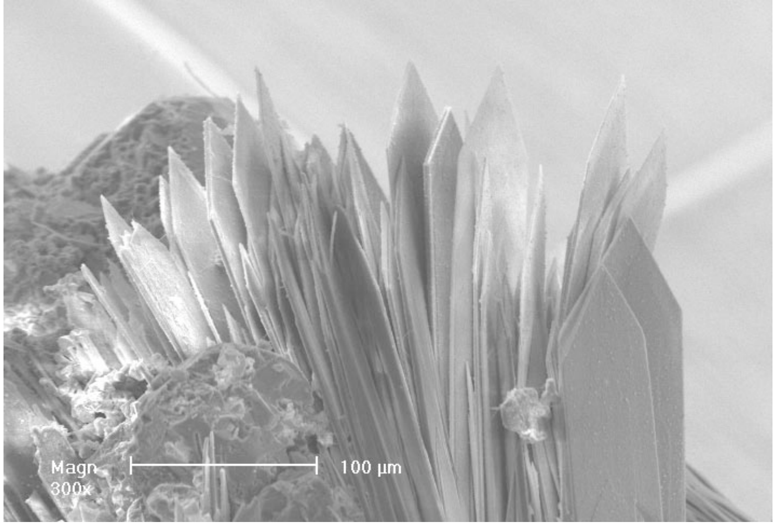

FIG. 1. Scanning electron photomicrograph of manganokukisvumite from Mont Saint-Hilaire, Quebec.

erals, especially aegirine, which is strongly enriched in titanium in this association, with a maximum recorded 3.10 wt.% TiO_2 (Piilonen *et al.* 1998). It is very rare, occurring sparsely in the breccia cavities; however, owing to its thin, somewhat flexible crystals and small size, it could be easily mistaken for mica or overlooked entirely. Collectors are advised to more closely re-examine specimens of igneous breccia collected during the late 1980s.

Physical and Optical Properties

Manganokukisvumite occurs as extremely thin, flattened, sword-shaped crystals to 0.5 mm in length. It typically forms radiating, fan-shaped groups of crystals (Fig. 1). The crystals are flattened on {100} and elongate parallel to [001]. The only observed forms are {100} and {010} pinacoids and a prism that could not be measured. No twinning was observed. It is colorless and transparent, with a white streak and vitreous luster. It is non-fluorescent in short- and long-wave ultraviolet light. It is sectile, slightly flexible and has a splintery fracture with no cleavage. The density, measured by suspension in a solution of bromoform and butyl alcohol is 2.86(1) g/cm^3, which compares well with 2.88 g/cm^3, calculated for the empirical formula.

Manganokukisvumite is biaxial negative, α (calc.) 1.657, β 1.744 ± .003, γ 1.792 ± .003 (for $\lambda = 589$ nm); $2V_{\text{meas}} = 70°$ (Kamb's method). The optical orientation is $X = a$, $Y = b$, $Z = c$. There is no dispersion or pleochroism. A Gladstone–Dale calculation gives a compatibility index of 0.038, which is regarded as excellent (Mandarino 1981).

Chemical Composition

Electron-microprobe analyses

Chemical analyses were performed on a JEOL 733 electron microprobe in wavelength-dispersion mode using Tracor Northern 5500 and 5600 automation. Data reduction was done with the $\phi(\rho Z)$ routine in XMAQNT (pers. commun., C. Davidson, CSIRO). The operating voltage was 15 kV, and the beam current was 20 nA. The beam was defocused to 30 μm to reduce the effects of Na volatilization and general burn-up of the sample. We used the following standards in the probe analyses: tugtupite (Na$K\alpha$), diopside (Ca$K\alpha$, Mg$K\alpha$), almandine (Fe$K\alpha$, Si$K\alpha$), synthetic $CePO_4$ (Ce$L\alpha$), chrysoberyl (Al$K\alpha$), synthetic $MnNb_2O_6$ (Nb$L\alpha$), rutile (Ti$K\alpha$), sanidine (K$K\alpha$), zincite (Zn$L\alpha$) and tephroite (Mn$K\alpha$). Several 100-s energy-dispersion scans indicated no elements with Z > 8 other than those reported here. Zinc and F were specifically sought but not detected. Data for all elements in the samples were collected for 25 s or 0.50% precision, whichever was attained first. The average result of two analyses is reported in Table 1. Back-scattered electron (BSE) imaging indicated that the crystals of manganokukisvumite from Mont Saint-Hilaire are homogeneous in composition. The presence of H_2O was confirmed by infrared absorption spectrometry (IR).

For comparison, we analyzed two crystals of kukisvumite from the type locality at Mount

TABLE 1. CHEMICAL COMPOSITION OF MANGANOKUKISVUMITE AND KUKISVUMITE

	1	2a	2b		1	2a	2b
Na_2O wt.%	15.61	16.73	16.71	Na *apfu*	5.81	6.20	6.29
K_2O	0.21	0.00	0.00	K	0.05	0.00	0.00
CaO	0.08	0.00	0.00	Ca	0.02	0.00	0.00
MgO	0.26	0.00	0.00	Mg	0.07	0.00	0.00
MnO	5.48	5.74	0.91	Mn	0.89	0.93	0.15
FeO	0.57	0.16	0.15	Fe^{2+}	0.09	0.03	0.02
ZnO	0.00	0.00	5.67	Zn	0.00	0.00	0.81
Al_2O_3	0.16	0.00	0.00	Al	0.04	0.00	0.00
Ce_2O_3	0.18	0.26	0.23	Ce^{3+}	0.01	0.02	0.02
TiO_2	26.90	26.78	26.54	Ti	3.88	3.85	3.88
SiO_2	41.74	42.16	41.05	Si	8.01	8.06	7.98
Nb_2O_5	0.68	0.39	0.62	Nb	0.06	0.03	0.05
H_2O*	6.25	6.27	6.17				
Total	98.12	98.49	98.05		18.93	19.12	19.20

The proportion of cations, expressed in atoms per formula unit (*apfu*) is recalculated on the basis of 32 anions. 1: Manganokukisvumite from Mont Saint-Hilaire, Quebec (average of 2 analyses); contains trace Sr, Ba and Y. 2a: Core of manganokukisvumite from a zoned crystal from Mount Kukisvumchorr, Russia; contains trace Sr. 2b: Kukisvumite part of the zoned crystal from Mount Kukisvumchorr, Russia; contains trace Sr. * The amount of H_2O is calculated to give 4 H_2O.

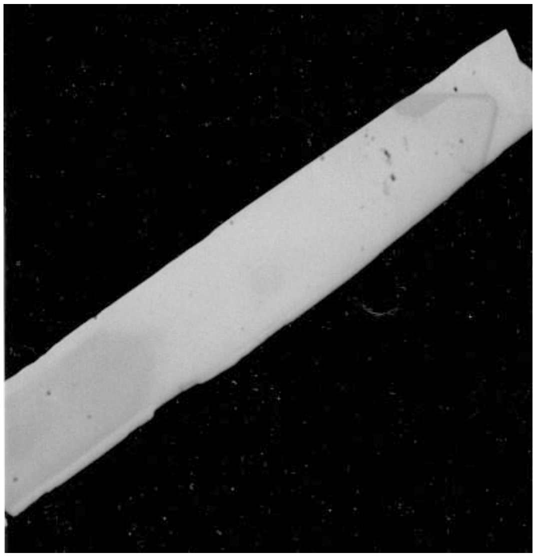

FIG. 2. Back-scattered electron image of a crystal of manganokukisvumite (dark area) – kukisvumite (light area) from Mount Kukisvumchorr, Russia, showing Mn–Zn zoning. Length of the crystal: 715 μm.

Kukisvumchorr, Khibina Massif, Kola Peninsula, Russia. In both crystals, BSE imaging showed distinct Mn–Zn zonation (Fig. 2), with manganokukisvumite forming the core of the crystals and the zinc-dominant kukisvumite forming the later and more extensive stage of growth. The image also shows a brief enrichment of Mn near the final stage of growth of the crystals. Results of chemical analyses of these two zones are included in Table 1. No attempt was made to secure holotype material for analysis. No mention of Mn–Zn zoning was made in either the original description of kukisvumite by Yakovenchuk *et al.* (1991) or in the structure paper by Merlino *et al.* (2000).

Infrared analysis

The infrared spectrum of manganokukisvumite was obtained using a Bomem Michelson MB–120 Fourier-transform infrared spectrometer with a diamond-anvil-cell microsampling device. Two hundred scans were collected in the range 4000–660 cm^{-1} (Fig. 3). The broad absorption band centered in the 3400 cm^{-1} region, at the O–H stretching frequency, indicates the presence of OH^- anions or H_2O groups. The absorption band at 1640 cm^{-1} is attributable to H–O–H bending, which confirms the presence of H_2O. The bands in the 1000 cm^{-1} region are assigned to the symmetric stretching of $[SiO_4]$ and indicate considerable splitting of the $[SiO_4]$ vibration modes, attributable to a structure with more than one crystallographically distinct $[SiO_4]$ group. The band at approximately 700 cm^{-1} is assigned to bending of $[SiO_4]$.

X-RAY CRYSTALLOGRAPHY

Unit-cell parameters were refined from powder data collected with a Debye–Scherrer camera, 114.6 mm in diameter, with Cu$K\alpha$ (Ni filtered) radiation. X-ray powder-diffraction data are given in Table 2. A calculated powder-diffraction pattern was used to resolve some potential line-overlaps [calculated from the kukisvumite structure of Merlino *et al.* (2000) using the LAZY PULVERIX routine associated with the ICSD database]. The intensity data for the calculated pattern show that the kukisvumite pattern of Yakovenchuk *et al.* (1991) suffers from the effects of preferred orientation. Manganokukisvumite is orthorhombic *Pccn*, with unit-cell parameters *a* 29.05(2), *b* 8.612(6), *c* 5.220(4) Å, *V* 1305.9(3) $Å^3$, $Z = 2$. The unit-cell parameters of manganokukisvumite, kukisvumite and lintisite are closely related, and the X-ray powder-diffraction patterns are almost identical in all the strongest lines. The acquisition of single-crystal data for manganokukisvumite was not possible owing to the extremely thin, flexible and divergent nature of the crystals.

Merlino *et al.* (2000) obtained single-crystal diffraction data on a specimen of kukisvumite from the type locality, Mount Kukisvumchorr, Russia. They related kukisvumite to lintisite by the coupled substitution: $Zn^{2+} + \square = 2\,Li^+$. Compositional data presented in Table 1 indicate that kukisvumite is related to manganokukisvumite by the simple homovalent substitution, $Zn^{2+} = Mn^{2+}$. This takes place at the tetrahedrally coordinated Zn site. Refined unit-cell parameters support these contentions: manganokukisvumite has a larger

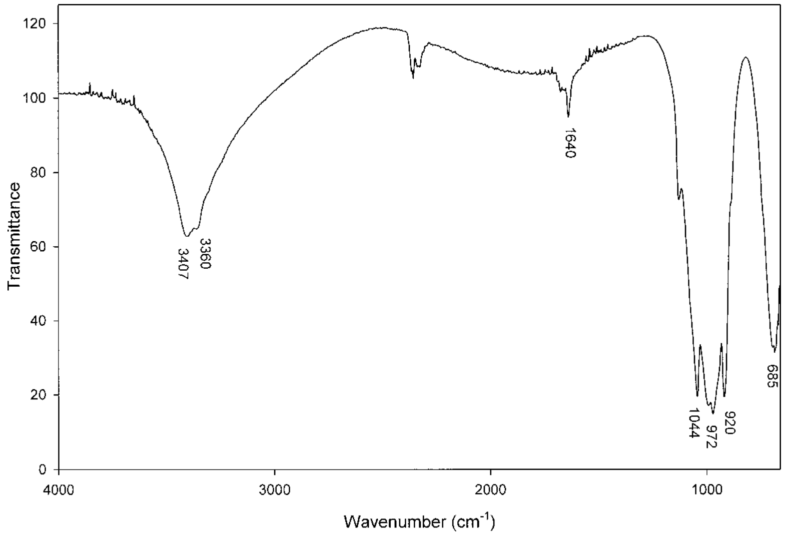

FIG. 3. Infrared spectrum of manganokukisvumite.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR TYPE KUKISVUMITE AND MANGANOKUKISVUMITE

Kukisvumite (calc. pattern) †					Kukisvumite*			Manganokukisvumite		
h	*k*	*l*	*d* calc	I	*d* calc	*d* obs	I	*d* calc	*d* obs	I
2	**0**	**0**	**14.52**	**100**	14.45	14.49	90	14.52	14.47	100
1	**1**	**0**	**8.241**	**8**	8.244	8.25	13	8.257	8.18	<10
4	0	0	7.257	<1	7.226	7.24	3	-------	-----	
3	**1**	**0**	**6.426**	**19**	6.416	6.42	60	6.435	6.43	20
6	**0**	**0**	**4.838**	**6**	4.817	} 4.815	80	4.841	} 4.83	10
5	**1**	**0**	**4.811**	**8**	4.798			4.816		
1	**1**	**1**	**4.403**	**10**	-------	-------		4.412	4.42	<10
0	**2**	**0**	**4.298**	**9**	4.300	4.302	47	-------	-------	
2	**1**	**1**	**4.259**	**6**	-------	-------		4.267	4.273	<10
7	**1**	**0**	**3.735**	**9**	3.722	3.722	65	3.738	3.743	10
8	**0**	**0**	**3.629**	**12**	3.613	3.614	28	-------	-------	
9	**1**	**0**	**3.020**	**22**	3.009	} 3.009	100	3.022	} 3.025	40
4	**2**	**1**	**3.015**	**27**	3.015			3.021		
5	**2**	**1**	**2.879**	**25**	2.878	2.878	25	2.884	2.881	20
1	3	0	2.851	<1	2.853	2.855	10	-------	-------	
8	2	0	2.773	<1	2.766	} 2.758	5	-------	-------	
3	3	0	2.747	<1	2.748			-------	-------	
7	**2**	**1**	**2.589**	**12**	2.586	2.584	3	2.593	2.591	10
5	3	0	2.569	1	2.568	} 2.567	5	-------	-------	
2	0	2	2.564	2	2.566			-------	-------	
3	**0**	**2**	**2.515**	**5**	2.517	2.511	5	-------	-------	
1	**3**	**1**	**2.501**	**4**	-------	-------		2.506	2.501	<10
2	**3**	**1**	**2.474**	**5**	-------	-------		-------	-------	
4	**0**	**2**	**2.451**	**9**	-------	-------		2.456	2.458	10
12	0	0	2.419	<1	2.409	} 2.406	12	-------	-------	
10	2	0	2.406	1	2.399			-------	-------	
6	**3**	**1**	**2.228**	**2**	-------	-------		2.232	} 2.225	<10
6	**1**	**2**	**2.216**	**4**	-------	-------		2.220		
10	**2**	**1**	**2.184**	**5**	-------	-------		2.187	2.186	<10
9	**3**	**0**	**2.142**	**4**	2.139	} 2.139	12	2.145	2.146	10
7	**1**	**2**	**2.136**	**3**	2.136			2.140	-------	
12	2	0	2.108	<1	2.101	2.102	6	-------	-------	
8	**3**	**1**	**2.065**	**2**	2.063	} 2.061	6	2.068	} 2.075	<10
11	**2**	**1**	**2.065**	**2**	2.060			2.067		
9	**0**	**2**	**2.026**	**7**	2.024	2.026	3	2.030	2.028	<10
1	4	1	1.982	1	1.983	1.984	2	1.986	} 1.981	<10
9	**3**	**1**	**1.981**	**3**	1.979	1.976	3	1.984		
0	**3**	**2**	**1.927**	**2**	1.929	} 1.934	3	1.931	} 1.933	<10
1	**3**	**2**	**1.923**	**2**	1.925			1.927		
15	1	0	1.888	<1	1.880	} 1.880	10	-------	-------	
5	4	1	1.879	1	1.880			-------	-------	
11	0	2	1.854	<1	1.851			-------	-------	
8	4	0	1.849	1	1.848	} 1.848	5	-------	-------	
13	2	1	1.852	<1	1.847			-------	-------	
11	3	1	1.819	1	-------	-------		1.821	1.822	<10
11	1	2	1.812	<1	1.809	} 1.806	25	-------	-------	
16	0	0	1.814	1	1.806			-------	-------	
10	4	0	1.727	1	1.725	1.725	5	-------	-------	
1	5	0	1.716	1	1.717	1.718	4	-------	-------	
3	5	0	1.693	1	1.693			-------	-------	
2	1	3	1.690	<1	1.692	1.691	8	-------	-------	
13	0	2	1.695	1	1.692			-------	-------	
13	**3**	**1**	**1.668**	**5**	-------	-------		1.671	1.676	<10
1	4	2	1.655	1	1.656	1.655	6	-------	-------	
5	**5**	**0**	**1.648**	**2**	1.649	} 1.648	8	1.651	} 1.649	<10
2	**4**	**2**	**1.647**	**2**	1.648			1.650		
18	**0**	**0**	**1.613**	**2**	-------	-------		1.614	} 1.612	<10
1	**2**	**3**	**1.607**	**2**	-------	-------		1.611		
12	4	0	1.607	1	1.604	1.604	35	-------	-------	
2	**2**	**3**	**1.600**	**3**	1.602	-------		1.603	} 1.601	<10
14	**3**	**1**	**1.599**	**4**	-------	-------		1.601		
15	**0**	**2**	**1.553**	**4**	-------	-------		1.555	1.553	<10
9	5	0	1.517	1	1.516	1.514	4	1.520	1.522	<10
16	0	2	1.489	<1	1.485	} 1.485	5	-------	-------	
1	**3**	**3**	**1.483**	**2**	1.484			-------	-------	
16	**3**	**1**	**1.471**	**3**	-------	-------		1.472	1.474	<10
a			29.029			28.90(1)			29.05(2)	Å
b			8.595			8.601(3)			8.612(6)	
c			5.209			5.215(3)			5.220(4)	

† structural parameters of Merlino *et al.* (2000); * Yakovenchuk *et al.* (1991)
- the strongest reflections in the calculated pattern are shown in bold

unit-cell volume (1305.9 Å^3) than either kukisvumite (1296 Å^3) or lintisite (1283 Å^3), as r_i (Mn) > r_i (Zn) > r_i (Li) for tetrahedral coordination.

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