

The crystal structure of kraisslite, $[^{41}\text{Zn}_3(\text{Mn,Mg})_{25}(\text{Fe}^{3+},\text{Al})(\text{As}^{3+}\text{O}_3)_2[(\text{Si},\text{As}^{5+})\text{O}_4]_{10}(\text{OH})_{16}$, from the Sterling Hill mine, Ogdensburg, Sussex County, New Jersey, USA

M. A. COOPER AND F. C. HAWTHORNE*

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

[Received 17 September 2012; Accepted 2 December 2012; Associate Editor: Andrew Christy]

ABSTRACT

The crystal structure of kraisslite, orthorhombic (pseudo-hexagonal), $a = 8.1821(1)$, $b = 14.1946(3)$, $c = 43.9103(8)$ Å, $V = 5099.8(2)$ Å³, $Z = 4$ and $d_{\text{calc}} = 4.083$ g cm⁻³, has been solved by direct methods and refined in the space group $C222_1$ to an R_1 index of 1.68% for 7432 observed ($|F_o| > 4\sigma|F|$) reflections. Electron-microprobe analysis gave the following chemical composition: As₂O₅ 10.86, As₂O₃ 6.18, SiO₂ 13.39, Al₂O₃ 0.25, Fe₂O₃ 2.06, MnO 51.14, ZnO 7.39, MgO 2.13, CaO 0.05, H₂O_{calc} = 4.50, sum 97.95 wt.%; and empirical formula: $\text{Zn}_{2.91}(\text{Mn}_{23.07}\text{Mg}_{1.69}\text{Ca}_{0.03})_{\Sigma=24.79}(\text{Fe}_{0.83}\text{Al}_{0.16})_{\Sigma=0.99}(\text{As}^{3+}\text{O}_3)_2[(\text{Si}_{0.71}\text{As}_{0.30}^{5+})\text{O}_4]_{10}(\text{OH})_{16}$ calculated on the basis of 62 anions with (OH) = 16 and $\text{As}^{3+}/(\text{As}^{3+} + \text{As}^{5+})$ taken from the refined crystal structure. The general formula, $[^{41}\text{Zn}_3(\text{Mn,Mg})_{25}(\text{Fe}^{3+},\text{Al})(\text{As}^{3+}\text{O}_3)_2[(\text{Si},\text{As}^{5+})\text{O}_4]_{10}(\text{OH})_{16}$, differs from those given previously.

There is one As³⁺ site with a <As–O> distance of 1.780 Å and a stereochemistry typical of a stereoactive lone-pair of electrons. There are five tetrahedrally coordinated *T* sites with <*T*–O> distances from 1.635 to 1.692 Å; the *T*(1) site is fully occupied by As⁵⁺, and the *T*(2)–*T*(5) sites are occupied by both Si and As⁵⁺. There are two tetrahedrally coordinated *Zn* sites with <*T*–O> distances of ~1.996 Å, both of which are occupied by dominant Zn and minor Mn²⁺. There are thirteen octahedrally coordinated *M* sites, twelve of which are occupied by dominant Mn²⁺ with lesser Mg and minor Zn; <*M*–O> distances are in the range 2.197–2.284 Å. The <*M*(13)–O> distance is 2.083 Å and its lower site scattering indicates occupancy by Fe³⁺, Mn²⁺, Mg and Al. The structure consists of five crystallographically distinct layers of polyhedra, labelled $m = 0$ –4. Layer $m = 0$ consists of corner-sharing Zn and (Si,As⁵⁺) tetrahedra, and layers $m = 1$ –4 each consist of trimers of Mn²⁺ octahedra linked by (Si,As⁵⁺) tetrahedra and intrasheet hydrogen bonds ($m = 1, 3$) or (Si,As⁵⁺) tetrahedra and (Fe³⁺,Al) octahedra ($m = 2$) or (As⁵⁺) tetrahedra and (As³⁺O₃) triangular pyramids and intrasheet hydrogen bonds ($m = 4$). The layers stack along [001] with reversals of the sequence $m = 1, 2, 3, 4$ at $z = 0, \frac{1}{4}, \frac{1}{2}$ and $\frac{3}{4}$. Kraisslite is a member of the mcgovernite family.

KEYWORDS: crystal structure, electron-microprobe analysis, mcgovernite family.

Introduction

KRAISSLITE was initially described as a hexagonal arseno-silicate from Sterling Hill mine, Ogdensburg, Sussex County, New Jersey, USA

(Moore and Ito, 1978). The space group was given as $P6_322$, with $a = 8.22(1)$ and $c = 43.88(5)$ Å, and the diffraction pattern showed significant streaking parallel to c^* . The chemical formula was given as $\text{Zn}_4(\text{Mn}_{21.36}\text{Mg}_{1.92}\text{Fe}_{0.72}^{2+})_{\Sigma=24}(\text{AsO}_4)_4(\text{SiO}_4)_8(\text{OH})_{12}$. A later chemical analysis of kraisslite revealed the presence of significant As³⁺ and Fe³⁺, and a new

* E-mail: frank_hawthorne@umanitoba.ca
DOI: 10.1180/minmag.2012.076.7.13

idealized formula was given as $Zn_3Mn_{22}Mg_2Fe^{3+}(AsO_3)_2(AsO_4)_3(SiO_4)_6(OH)_{18}$ (Dunn and Nelen, 1980). Moore and Ito (1978) stated that kraisslite is structurally related to hematolite (Moore and Araki, 1978) and mcgovernite (Palache and Bauer, 1927; Wuensch, 1960). As part of our general interest in the basic Mn arsenates (Cooper and Hawthorne, 1999, 2001), here we report on the crystal structure of kraisslite.

Experimental

The kraisslite used for this work is from the Sterling Hill mine, New Jersey, USA, and was provided by the Smithsonian National Museum of Natural History, sample number NMNH 83135. The majority of the kraisslite on the sample consists of pale pinkish orange bent ultra-thin sheets. Our earlier attempts to determine a structure using these bent sheets resulted in diffraction patterns with extensive streaking and multiple satellite diffractions, and the sample was relinquished to the 'nasty' drawer for over a decade. The sample was recently revisited, and careful inspection revealed rare dark orange plates 10–20 μm thick that were partly concealed within a white powdery fine-grained matrix. We initially thought that these plates might be something other than kraisslite, but unit-cell determinations showed that they are high-quality crystals of kraisslite. One crystal was selected for the collection of single-crystal X-ray diffraction data, and subsequent chemical characterization via electron-microprobe analysis.

The kraisslite crystal was attached to a tapered glass fibre and mounted on a Bruker D8 three-circle diffractometer equipped with a rotating-anode generator ($\text{MoK}\alpha$), multilayer optics and an APEX-II detector. A total of 140,897 reflections (29,422 within the Ewald sphere) was collected to $60^\circ 2\theta$ using 5 s per 0.2° frames with a crystal-to-detector distance of 8 cm. Empirical absorption corrections (*SADABS*; Sheldrick, 2008) were applied and equivalent reflections were then corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors. The unit-cell dimensions were obtained by least-squares refinement of the positions of 9679 reflections with $I > 10\sigma I$ and are given in Table 1, together with other information pertaining to data collection and structure refinement.

Structure solution and refinement

The X-ray diffraction pattern of the crystal selected possesses uniform sharp diffraction spots with no suggestion of streaking or additional satellite reflections. Although the observed diffraction pattern is metrically consistent with a hexagonal unit cell, the internal agreement index, R_{int} , for the Laue merging of reflection equivalents for hexagonal symmetry gives an R_{int} of 41.1% (Table 2), clearly indicating that the intensity distribution is not conformable with hexagonal symmetry. There are three possible C-centred orthorhombic cells conformable with the pseudo-hexagonal unit cell, but it is clear that only one

TABLE 1. Miscellaneous refinement data for kraisslite.

a (\AA)	8.1821(1)	Crystal size (μm)	$50 \times 60 \times 15$
b (\AA)	14.1946(3)	Radiation	$\text{MoK}\alpha$
c (\AA)	43.9103(8)	No. of reflections	140,897
V (\AA^3)	5099.8(2)	No. in Ewald sphere	29,422
Space group	$C222_1$	No. unique reflections	7496
Z	4	No. with ($F_o > 4\sigma F$)	7432
d_{calc} (g cm^{-3})	4.083	R_{merge} (%)	1.4
		R_1	1.7
		wR_2	4.2
		Fleck parameter	0.026(7)
Cell content: $Zn_3(\text{Mn},\text{Mg})_{25}(\text{Fe}^{3+}\text{Al})(\text{As}^{3+}\text{O}_3)_2[\text{Si}_7\text{As}_3^{5+}\text{O}_{40}](\text{OH})_{16}$			

$$R_1 = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}$$

$$wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}, w = 1/[\sigma^2(F_o^2) + (0.0105 P)^2 + 19.89 P]$$

where $P = (\max(F_o^2, 0) + 2F_c^2)/3$

THE CRYSTAL STRUCTURE OF KRAISSLITE

TABLE 2. Cell and R_{int} values for different Laue symmetries and cell orientations.

Symmetry	Transformation	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	R_{int} (%)
Hexagonal- <i>P</i>	$[\frac{1}{2}\frac{1}{2}0 \bar{1}00 001]$	8.192	8.182	43.910	90.00	90.00	119.96	41.1
Orthorhombic- <i>C</i>	$[100 010 001]$	8.182	14.195	43.910	90.00	90.00	90.00	2.6
Orthorhombic- <i>C</i>	$[\frac{1}{2}\frac{1}{2}0 \frac{3}{2}\frac{1}{2}0 001]$	8.192	14.178	43.910	90.00	90.00	90.08	33.3
Orthorhombic- <i>C</i>	$[\frac{1}{2}\frac{1}{2}0 \frac{3}{2}\frac{1}{2}0 001]$	8.192	14.178	43.910	90.00	90.00	89.92	33.2

orthorhombic cell is compatible with the X-ray intensity data (Table 2). Systematic absences are consistent with the space groups *Cmmm*, *C222* and *Cmm2*. There were numerous weak to moderate intensity (up to 10σ) reflections ($00l$ with $l = \text{odd}$) that seemed to eliminate *C222*₁ as a possible space group. Moreover, the E statistic of 0.875 for the data falls midway between the ideal values of 0.968 (centric) and 0.736 (acentric). Structure solutions were tried in all four of the above orthorhombic space groups without success. A brute force direct-methods approach in space group *C1* ultimately gave the kraisslite structural arrangement. The complete *C1* structure was then evaluated on a site-by-site basis (refined electron scattering, cation coordination, bond lengths), and equivalent sites were grouped accordingly. These equivalent site groupings were then input into the *MISSYM* program (Le Page, 1988) and symmetry elements compatible with the space group *C222*₁ were identified by the program. The asymmetric

unit of the structure (for *C222*₁) was then constructed and an origin shift applied to the coordinates (so as to place the origin at $212\frac{1}{2}$). Successful subsequent structure-refinement in *C222*₁ seemed to confirm that *C222*₁ is the correct space group, in spite of the observed ($00l$, $l = \text{odd}$) reflections violating the extinction conditions of the 2_1 screw axis along $[001]$. We then returned to the raw data frames and constructed oriented precession slices to evaluate the significance of these apparent violating reflections. We saw no clear evidence of any ($00l$, $l = \text{odd}$) reflections on these precession slices, and conclude that *C222*₁ is the correct space group for the kraisslite crystal studied; presumably the intensities violating the ($00l$, $l = \text{even}$) condition are due to double diffraction. The final refinement included positional parameters for all atoms, anisotropic-displacement parameters for all non-H atoms, isotropic-displacement parameters for all H atoms, variable site scattering at the cation sites,

TABLE 3. Chemical formula and unit formula for kraisslite.

Constituent	Dunn and Nelen (1980)	This work, mean (wt.%)	— Cations (p.f.u) —	
As ₂ O ₃	6.69	6.18	As ³⁺	2.00
As ₂ O ₅	10.35	10.86(31)		
SiO ₂	12.9	13.39(14)	As ⁵⁺	3.03
MnO	52.0	51.14(33)	Si	7.13
ZnO	8.6	7.39(19)		10.16
Fe ₂ O ₃	2.0	2.06(10)		
MgO	2.6	2.13(3)	Mn ²⁺	23.07
Al ₂ O ₃	0.2	0.25(3)	Zn	2.91
CaO	—	0.05(1)	Mg	1.69
H ₂ O	3.68*	4.50	Ca	0.03
Total	99.02	97.95	Fe ³⁺	0.83
			Al	0.16
				28.69

* H₂O value from Moore and Ito (1978).

TABLE 4. Atom coordinates and displacement parameters (\AA^2) for kraisslite.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
As(1)	0.12685(4)	0.33013(2)	0.21500(1)	0.01052(13)	0.00924(12)	0.00743(11)	-0.00048(10)	0.00039(10)	0.00010(11)	0.00906(6)
T(1)	0.36021(4)	0.17724(2)	0.29370(1)	0.00921(13)	0.00914(12)	0.00987(11)	0.00014(10)	-0.00034(11)	-0.00022(11)	0.00941(6)
T(2)	0.37360(7)	0.16654(4)	0.48735(1)	0.0075(3)	0.0071(3)	0.0056(2)	0.00001(17)	0.00015(18)	-0.0001(2)	0.00669(16)
T(3)	0.12655(7)	-0.00001(4)	0.04514(1)	0.0074(3)	0.0074(3)	0.0066(3)	0.00022(19)	-0.0001(2)	-0.0001(2)	0.00713(17)
T(4)	0.12574(9)	0.33338(5)	0.09945(1)	0.0080(3)	0.0075(3)	0.0067(6)	-0.0002(2)	-0.0001(3)	-0.0005(3)	0.0074(2)
T(5)	0.12740(9)	0.00039(6)	0.15588(2)	0.0074(4)	0.0082(4)	0.0066(4)	-0.0003(3)	0.0003(3)	0.0003(3)	0.0074(2)
Zn(1)	0.14487(7)	0	$\frac{1}{2}$	0.0132(3)	0.0155(3)	0.0133(3)	-0.00286(19)	0	0	0.01403(16)
Zn(2)	0.23800(5)	0.36425(3)	0.50000(1)	0.01495(18)	0.01365(18)	0.01278(18)	0.00125(14)	-0.00254(14)	-0.00091(13)	0.01380(11)
M(1)	0.02100(5)	0.22186(3)	0.33883(1)	0.00959(19)	0.00955(19)	0.01018(19)	0.00073(16)	-0.00126(16)	0.00010(15)	0.00978(8)
M(2)	0.02540(6)	0.22262(3)	0.44770(1)	0.0105(2)	0.01091(19)	0.0123(2)	0.00125(16)	-0.00085(16)	0.00056(16)	0.01122(9)
M(3)	0.03620(6)	0.46448(3)	0.05230(1)	0.0110(2)	0.01039(19)	0.0119(2)	0.00124(16)	-0.00063(17)	-0.00002(16)	0.01109(8)
M(4)	0.03715(6)	0.45962(3)	0.16205(1)	0.0093(2)	0.0125(2)	0.0130(2)	0.00386(17)	-0.00091(17)	-0.00003(16)	0.01161(9)
M(5)	0.10924(5)	0.00933(3)	0.39255(1)	0.0092(2)	0.0110(2)	0.0106(2)	-0.00024(17)	-0.00157(17)	-0.00037(16)	0.01027(14)
M(6)	0.10941(5)	0.00750(3)	0.28318(1)	0.0096(2)	0.0117(2)	0.0092(2)	0.00110(16)	-0.00007(16)	0.00075(18)	0.01017(14)
M(7)	0.25716(6)	0.11308(3)	0.10685(1)	0.0099(2)	0.0098(2)	0.0110(2)	0.00033(17)	0.00148(17)	-0.00080(16)	0.01023(14)
M(8)	0.25848(6)	0.11432(3)	0.21986(1)	0.0134(3)	0.0105(2)	0.0123(2)	0.00276(16)	-0.00176(17)	0.00030(17)	0.01205(15)
M(9)	0.26996(6)	0.37826(3)	0.39286(1)	0.0101(2)	0.0092(2)	0.0105(2)	0.00109(16)	0.00025(17)	-0.00067(16)	0.00997(14)
M(10)	0.27731(6)	0.38450(3)	0.28114(1)	0.01036(19)	0.0125(2)	0.0135(2)	0.00242(16)	0.00122(16)	-0.00117(16)	0.01210(9)
M(11)	0.36630(6)	0.31424(3)	0.16118(1)	0.00965(18)	0.00945(18)	0.01071(18)	-0.00090(15)	0.00163(17)	-0.00027(16)	0.00993(8)
M(12)	0.36792(6)	0.31303(3)	0.05229(1)	0.0105(2)	0.01079(19)	0.01224(18)	-0.00020(15)	0.00126(17)	0.00000(17)	0.01119(8)
M(13)	0.37342(6)	0.16641(3)	0.39146(1)	0.0088(2)	0.0087(2)	0.0109(2)	0.00000(18)	-0.00023(19)	-0.00002(18)	0.00945(14)
O(1)	0.0597(3)	0.35285(16)	0.30455(5)	0.0094(10)	0.0160(10)	0.0137(10)	-0.0014(8)	0.0002(8)	-0.0010(8)	0.0130(4)
O(2)	0.1831(3)	0.22906(15)	0.19354(5)	0.0150(10)	0.0098(10)	0.0086(9)	-0.0024(8)	-0.0016(7)	0.0020(8)	0.0111(4)
O(3)	0.2443(3)	0.41020(15)	0.19261(5)	0.0114(10)	0.0106(9)	0.0096(9)	-0.0003(7)	0.0016(8)	-0.0019(8)	0.0105(4)
O(4)	0.1867(3)	0.13288(15)	0.30945(5)	0.0104(10)	0.0108(10)	0.0154(10)	-0.0020(8)	0.0024(8)	-0.0028(8)	0.0122(4)
O(5)	0.3240(3)	0.20671(18)	0.25743(5)	0.0263(13)	0.0234(12)	0.0102(10)	0.0034(9)	-0.0040(9)	-0.0035(10)	0.0200(5)
O(6)	0.4111(3)	0.28196(15)	0.30995(5)	0.0140(10)	0.0100(9)	0.0135(10)	-0.0023(8)	-0.0031(8)	-0.0019(8)	0.0125(4)
O(7)	0.5066(3)	0.09615(17)	0.30123(6)	0.0111(10)	0.0146(11)	0.0257(12)	0.0040(9)	0.0021(9)	0.0040(8)	0.0172(5)
O(8)	0.1264(3)	0.33338(15)	0.02492(4)	0.0116(9)	0.0139(10)	0.0078(8)	0.0005(8)	-0.0005(8)	0.0007(9)	0.0111(4)
O(9)	0.2477(3)	0.24754(15)	0.47414(5)	0.0102(9)	0.0118(10)	0.0112(9)	-0.0010(7)	-0.0034(8)	0.0009(8)	0.0110(4)
O(10)	0.3145(3)	0.06353(15)	0.47404(5)	0.0121(10)	0.0094(10)	0.0095(9)	-0.0036(8)	0.0022(7)	-0.0010(7)	0.0103(4)
O(11)	0.5882(3)	0.18868(15)	0.47408(5)	0.0079(9)	0.0119(10)	0.0104(9)	0.0014(7)	0.0009(7)	-0.0009(7)	0.0101(4)
O(12)	0.0962(3)	0.10684(15)	0.03156(5)	0.0157(10)	0.0093(9)	0.0105(9)	0.0012(8)	0.0019(8)	0.0025(8)	0.0118(4)
O(13)	0.1268(3)	0.00047(16)	0.08255(4)	0.0123(9)	0.0123(9)	0.0063(8)	-0.0002(7)	-0.0002(7)	-0.0002(9)	0.0103(4)
O(14)	0.1988(3)	0.46215(16)	0.46857(5)	0.0091(9)	0.0147(10)	0.0108(10)	0.0003(8)	0.0000(8)	-0.0011(8)	0.0116(4)
O(15)	0.4811(3)	0.43160(15)	0.03151(5)	0.0126(10)	0.0101(10)	0.0130(10)	0.0016(8)	-0.0027(8)	-0.0033(8)	0.0119(4)
O(16)	0.0535(3)	0.35184(15)	0.41611(4)	0.0084(9)	0.0126(10)	0.0076(9)	-0.0010(7)	-0.0006(7)	-0.0005(7)	0.0095(4)

THE CRYSTAL STRUCTURE OF KRAISSLITE

O(17)	0.1248(3)	0.33267(15)	0.13628(4)	0.0129(10)	0.0116(9)	0.0075(8)	0.0016(7)	-0.0009(8)	-0.0007(8)	0.0107(4)
O(18)	0.1884(3)	0.23446(15)	0.08393(5)	0.0140(10)	0.0078(9)	0.0114(10)	-0.0009(8)	-0.0002(8)	0.0016(8)	0.0111(4)
O(19)	0.2438(3)	0.41399(14)	0.08413(5)	0.0114(10)	0.0115(10)	0.0072(9)	0.0003(7)	0.0003(7)	-0.0024(8)	0.0100(4)
O(20)	0.4879(3)	0.41815(15)	0.35938(5)	0.0109(10)	0.0100(9)	0.0119(10)	-0.0012(7)	-0.0000(8)	0.0015(7)	0.0109(4)
O(21)	0.0630(3)	0.09830(15)	0.14020(5)	0.0123(10)	0.0108(9)	0.0090(9)	0.0003(8)	0.0011(8)	0.0019(8)	0.0107(4)
O(22)	0.1229(3)	0.00186(16)	0.19298(4)	0.0127(9)	0.0126(9)	0.0047(8)	0.0016(7)	-0.0000(8)	0.0014(9)	0.0100(4)
O(23)	0.1900(3)	0.48342(15)	0.35819(5)	0.0093(9)	0.0120(10)	0.0121(10)	-0.0016(8)	-0.0003(7)	-0.0009(7)	0.0111(4)
OH(1)	0.1768(3)	0.13016(15)	0.41875(5)	0.0146(10)	0.0108(10)	0.0108(9)	-0.0011(8)	-0.0015(8)	0.0013(8)	0.0121(4)
OH(2)	0.1962(3)	0.49748(16)	0.25168(5)	0.0136(9)	0.0114(9)	0.0131(10)	-0.0035(9)	0.0002(8)	-0.0006(9)	0.0127(4)
OH(3)	0.2355(3)	0.25616(15)	0.36447(5)	0.0114(10)	0.0144(10)	0.0101(10)	-0.0015(8)	-0.0001(8)	-0.0029(8)	0.0120(4)
OH(4)	0.3111(3)	0.05324(16)	0.36331(5)	0.0116(10)	0.0127(10)	0.0117(10)	0.0010(8)	0.0012(8)	0.0021(8)	0.0120(4)
OH(5)	0.4195(3)	0.28349(16)	0.41901(5)	0.0094(10)	0.0170(10)	0.0118(10)	0.0012(8)	-0.0014(7)	0.0001(8)	0.0127(4)
OH(6)	0.4231(3)	0.18940(15)	0.13633(5)	0.0143(10)	0.0106(10)	0.0130(10)	-0.0012(8)	-0.0037(8)	0.0007(8)	0.0126(4)
OH(7)	0.5266(3)	0.08603(15)	0.41902(5)	0.0153(10)	0.0113(10)	0.0114(10)	0.0001(8)	0.0009(8)	-0.0007(8)	0.0127(4)
OH(8)	0	0.0982(2)	$\frac{1}{4}$	0.030(2)	0.0110(15)	0.0254(18)	0	-0.0156(15)	0	0.0220(8)
OH(9)	$\frac{1}{2}$	0.3958(2)	$\frac{1}{4}$	0.0128(15)	0.0115(14)	0.0163(15)	0	0.0023(12)	0	0.0135(6)
H(1)	0.253(5)	0.113(4)	0.4350(9)							0.051(6)*
H(2)	0.090(3)	0.486(4)	0.2422(11)							0.051(6)*
H(3)	0.297(6)	0.274(4)	0.3462(7)							0.051(6)*
H(4)	0.252(6)	0.077(4)	0.3456(8)							0.051(6)*
H(5)	0.349(6)	0.281(4)	0.4371(8)							0.051(6)*
H(6)	0.434(7)	0.135(2)	0.1500(10)							0.051(6)*
H(7)	0.539(7)	0.120(4)	0.4384(7)							0.051(6)*
H(8)	0	0.1672(3)	$\frac{1}{4}$							0.051(6)*
H(9)	$\frac{1}{2}$	0.3268(2)	$\frac{1}{4}$							0.051(6)*

* Constrained to be equal during refinement.

TABLE 5. Selected interatomic distances (Å) for kraisslite.

As(1)-O(1)a	1.781(2)	Zn(2)-O(9)	2.010(2)	T(1)-O(4)	1.700(2)	T(2)-O(8)g	1.650(2)
As(1)-O(2)	1.777(2)	Zn(2)-O(11)f	2.006(2)	T(1)-O(5)	1.673(2)	T(2)-O(9)	1.649(2)
As(1)-O(3)	1.783(2)	Zn(2)-O(12)g	1.982(2)	T(1)-O(6)	1.701(2)	T(2)-O(10)	1.647(2)
<As(1)-O>	1.780	Zn(2)-O(14)	1.985(2)	T(1)-O(7)	1.694(2)	T(2)-O(11)	1.649(2)
Zn(1)-O(10)e	2.009(2) × 2	<Zn(2)-O>	1.996	<T-O>	1.692	<T(2)-O>	1.649
Zn(1)-O(15)b,g	1.980(2) × 2						
<Zn(1)-O>	1.995						
T(3)-O(12)	1.648(2)	T(4)-O(16)a	1.639(2)	T(5)-O(20)b	1.644(2)	M(1)-O(1)	2.413(2)
T(3)-O(13)	1.643(2)	T(4)-O(17)	1.617(2)	T(5)-O(21)	1.638(2)	M(1)-O(2)a	2.195(2)
T(3)-O(14)b	1.641(2)	T(4)-O(18)	1.643(2)	T(5)-O(22)	1.630(2)	M(1)-O(4)	2.258(2)
T(3)-O(15)h	1.649(2)	T(4)-O(19)	1.642(2)	T(5)-O(23)b	1.635(2)	M(1)-O(17)a	2.257(2)
<T(3)-O>	1.645	<T(4)-O>	1.635	<T(5)-O>	1.637	M(1)-O(21)a	2.097(2)
M(2)-O(8)a	2.337(2)	M(3)-O(8)	2.335(2)	M(4)-O(1)a	2.253(2)	M(1)-OH(3)	2.141(2)
M(2)-O(9)	2.187(2)	M(3)-O(10)d	2.193(2)	M(4)-O(3)	2.273(2)	<M(1)-φ>	2.227
M(2)-O(12)a	2.126(2)	M(3)-O(14)a	2.130(2)	M(4)-O(7)d	2.546(2)	M(5)-O(13)a	2.223(2)
M(2)-O(16)	2.311(2)	M(3)-O(16)a	2.240(2)	M(4)-O(17)	2.245(2)	M(5)-O(19)b	2.080(2)
M(2)-O(18)a	2.240(2)	M(3)-O(19)	2.314(2)	M(4)-O(23)a	2.087(2)	M(5)-O(20)h	2.187(2)
M(2)-OH(1)	2.208(2)	M(3)-OH(7)d	2.197(2)	M(4)-OH(4)d	2.133(2)	M(5)-O(21)a	2.377(2)
<M(2)-φ>	2.235	<M(3)-φ>	2.235	<M(4)-φ>	2.256	M(5)-OH(1)	2.138(2)
M(6)-O(3)b	2.115(2)	M(7)-O(13)	2.198(2)	M(8)-O(2)	2.090(2)	M(5)-OH(4)	2.183(2)
M(6)-O(4)	2.213(2)	M(7)-O(18)	2.073(2)	M(8)-O(5)	2.175(2)	<M(5)-φ>	2.198
M(6)-O(22)a	2.172(2)	M(7)-O(21)	2.171(2)	M(8)-O(7)c	2.149(2)	M(9)-O(13)d	2.211(2)
M(6)-OH(2)b	2.212(2)	M(7)-O(23)b	2.435(2)	M(8)-O(22)	2.274(2)	M(9)-O(16)	2.078(2)
M(6)-OH(8)	2.140(2)	M(7)-OH(6)	2.166(2)	M(8)-OH(2)b	2.110(2)	M(9)-O(20)	2.379(2)
M(6)-OH(9)h	2.332(2)	M(7)-OH(7)c	2.137(2)	M(8)-OH(8)	2.505(2)	M(9)-O(23)	2.230(2)
<M(6)-φ>	2.197	<M(7)-φ>	2.197	<M(8)-φ>	2.217	M(9)-OH(3)	2.154(2)
M(10)-O(1)	2.105(2)	M(11)-O(2)	2.393(2)	M(12)-O(8)	2.331(2)	M(9)-OH(5)	2.150(2)
M(10)-O(5)	2.757(2)	M(11)-O(3)	2.181(2)	M(12)-O(11)c	2.196(2)	<M(9)-φ>	2.200
M(10)-O(6)	2.218(2)	M(11)-O(6)c	2.266(2)	M(12)-O(15)	2.126(2)	M(13)-OH(1)	2.071(2)
M(10)-O(22)d	2.176(2)	M(11)-O(17)	2.273(2)	M(12)-O(18)	2.309(2)	M(13)-OH(4)	2.074(2)
M(10)-OH(2)	2.165(2)	M(11)-O(20)c	2.101(2)	M(12)-O(19)	2.245(2)	M(13)-OH(5)	2.090(2)
M(10)-OH(9)	2.284(2)	M(11)-OH(6)	2.132(2)	M(12)-OH(5)c	2.189(2)	M(13)-OH(6)c	2.090(2)
<M(10)-φ>	2.284	<M(11)-φ>	2.224	<M(12)-φ>	2.233	M(13)-OH(7)	2.083(2)
						<M(13)-OH>	2.083

OH(1)–H(1)	0.98	H(1)···O(10)	1.92(2)	OH(1)–O(10)	2.838(3)	OH(1)–H(1)–O(10)	155(5)
OH(2)–H(2)	0.98	H(2)···OH(2)a	2.36(3)	OH(2)–OH(2)a	3.214(4)	OH(2)–H(2)–OH(2)a	145(4)
OH(3)–H(3)	0.98	H(3)···O(6)	1.848(11)	OH(3)–O(6)	2.816(3)	OH(3)–H(3)–O(6)	169(5)
OH(4)–H(4)	0.98	H(4)···O(4)	1.849(13)	OH(4)–O(4)	2.812(3)	OH(4)–H(4)–O(4)	167(5)
OH(5)–H(5)	0.98	H(5)···O(9)	1.888(15)	OH(5)–O(9)	2.845(3)	OH(5)–H(5)–O(9)	165(5)
OH(6)–H(6)	0.98	H(6)···O(7)c	2.26(3)	OH(6)–O(7)c	3.098(3)	OH(6)–H(6)–O(7)c	142(4)
OH(7)–H(7)	0.98	H(7)···O(11)	1.856(4)	OH(7)–O(11)	2.835(3)	OH(7)–H(7)–O(11)	177(5)
OH(8)–H(8)	0.98	H(9)···O(5)	2.225(4)	OH(9)–O(5)	3.063(4)	OH(9)–H(9)–O(5)	139.10(9)
OH(9)–H(9)	0.98	H(9)···O(5)c	2.225(4)	OH(9)–O(5)c	3.063(4)	OH(9)–H(9)–O(5)c	139.10(9)

a: \bar{x} , y , $\bar{z} + \frac{1}{2}$; b: $\bar{x} + \frac{1}{2}$, $y - \frac{1}{2}$, $\bar{z} + \frac{1}{2}$; c: $\bar{x} + \frac{1}{2}$, $y, \bar{z} + \frac{1}{2}$; d: $\bar{x} + \frac{1}{2}$, $y + \frac{1}{2}$, $\bar{z} + \frac{1}{2}$; e: $x, \bar{y}, \bar{z} + \frac{1}{2}$; f: $x - \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2}$; g: $\bar{x} + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2}$; h: $x - \frac{1}{2}, y - \frac{1}{2}, \bar{z}$.

and all H-atoms were constrained to be 0.98 Å from their donor anions. The Flack parameter refined to 0.026(7), indicating that the structure model has the correct absolute configuration. The refinement converged to a final R_1 index of 1.68% for 7432 observed ($|F_o| > 4\sigma|F|$) reflections and 1.70% for all 7496 data; this very small discrepancy index is a further testament to the surprising crystal quality for a mineral belonging to the family of complex layered mcgovernite-like minerals. Refined atom coordinates and anisotropic-displacement parameters are listed in Table 4, selected interatomic distances are given in Table 5, refined site-scattering values (Hawthorne *et al.*, 1995) and assigned site populations are given in Table 6, and bond valences, calculated with the parameters of Brown and Altermatt (1985), are given in Table 7.

Electron microprobe analysis

After the structure refinement was completed, the kraisslite crystal was removed from the glass fibre and immersed in epoxy, polished and carbon coated for subsequent chemical analysis by electron microprobe. It was analysed using a Cameca SX-100 electron microprobe operating in wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 20 nA and a beam size of 5 µm. The following standards were used: forsterite (Mg), andalusite (Al), cobaltite (As), diopside (Ca, Si), spessartine (Mn), gahnite (Zn) and fayalite (Fe), and the data were reduced using the method of Pouchou and Pichoir (1985). The chemical composition of the kraisslite crystal (mean of 10 points) is given in Table 3. The unit formula was calculated on the basis of 62 anions, with (OH) = 16, $As^{3+} = 2$ and all Fe as Fe_2O_3 . We have also listed the chemical analysis of Dunn and Nelen (1980) in Table 3 for comparison; the results of the two studies are very similar. Our empirical formula, $Zn_{2.91}(Mn_{23.07}Mg_{1.69}Ca_{0.03})_{\Sigma=24.79}(Fe_{0.83}^{3+}Al_{0.16})_{\Sigma=0.99}(As^{3+}O_3)_2[(Si_{0.71}As_{0.30}^{5+})O_4]_{10}(OH)_{16}$, leads to the simplified formula, $[^{44}Zn_3(Mn,Mg)_{25}(Fe^{3+},Al)(As^{3+}O_3)_2[(Si,As^{5+})O_4]_{10}(OH)_{16}]$, in which five tetrahedrally coordinated sites contain $(Si_7As_3^{5+})$ a.p.f.u. (atoms per formula unit) to maintain overall electroneutrality.

Cation coordination

The As^{3+} site

The $As(1)$ site is coordinated by three O atoms to one side of the As position, forming a triangular

pyramid with $As(1)-O$ distances in the range 1.777–1.783 Å (Table 5); this stereochemistry is typical of As^{3+} with a stereoactive lone pair of electrons. The $As(1)$ site is fully occupied by As^{3+} .

The T sites

There are five tetrahedrally coordinated T sites with $\langle T-O \rangle$ distances from 1.635 to 1.692 Å (Table 5) and refined site-scattering values (Hawthorne *et al.*, 1995) ranging from ~28 to 66 electrons per formula unit (e.p.f.u.) (Table 7). Site-occupancy refinement at the $T(1)$ site showed full occupancy using the As scattering factor, and in combination with the observed $\langle T(1)-O \rangle$ distance of 1.692 Å indicates that the $T(1)$ site is fully occupied by As^{5+} . Site-occupancy refinement and observed $\langle T-O \rangle$ distances for the $T(2)$ to $T(5)$ sites show that these sites are occupied predominantly by Si. We attribute the excess scattering (i.e. greater than 14 electrons per site) to the presence of As^{5+} at these sites, and the Si and As site-populations were assigned accordingly. The aggregate assignment is in good agreement with the Si and As^{5+} contents derived from electron-microprobe analysis (cf. Tables 3 and 6)

The Zn sites

There are two additional tetrahedrally coordinated sites (the Zn sites) with $\langle Zn-O \rangle$ distances of 1.995 and 1.996 Å, respectively. Both the $Zn(1)$ and $Zn(2)$ sites show a slight deficiency in the refined site scattering (i.e. less than 30 electrons per site) relative to full occupancy by Zn. The coordinating O atoms are each linked to three cations and have a mean ionic radius of ~1.36 Å (Shannon, 1976). The mean ionic radius of the $Zn(1)$ and $Zn(2)$ cation constituents is then ~0.64 Å (i.e. $2.00 - 1.36 = 0.64$ Å). Shannon (1976) gives the ionic radius of $^{[4]}Zn$ as 0.60 Å, and those of the remaining possible constituents are $^{[4]}Mn^{2+} = 0.66$, $^{[4]}Al = 0.39$, $^{[4]}Fe^{3+} = 0.49$, and $^{[4]}Mg = 0.57$ Å; only $^{[4]}Mn^{2+}$ is larger than $^{[4]}Zn$. Although Mn^{2+} is a large cation, it has been found in tetrahedral coordination in minerals, e.g. in akatoreite (Burns and Hawthorne, 1993). We therefore assume a simple binary occupancy of the $Zn(1)$ and $Zn(2)$ sites by Zn and Mn^{2+} and have assigned Zn and Mn^{2+} to each site as indicated by the refined site scattering (Table 6). Both Zn sites are dominated by Zn, with 25% and 28.5% $^{[4]}Mn^{2+}$ at $Zn(1)$ and $Zn(2)$, respectively.

The M sites

There are thirteen M sites, octahedrally coordinated by a combination of O atoms and (OH) groups. Twelve M sites have $\langle M-O \rangle$ distances in the range 2.197–2.284 Å; the $\langle M(13)-O \rangle$ distance is shorter: 2.083 Å (Table 5). The lower refined scattering at the $M(13)$ site, in combination with the shorter $\langle M(13)-O \rangle$ distance, suggests that smaller and lighter octahedrally coordinated cations order at $M(13)$. We therefore assigned all of the smaller octahedrally coordinated cations (i.e. $Fe^{3+} = 0.645$, $Al = 0.535$ Å) to the $M(13)$ site, and partitioned the Mn^{2+} and Mg content such that the site is full and the assigned electron total is in accord with the observed site scattering (Table 6). This strategy results in an $M(13)$ site that is dominated by Fe^{3+} and is 50% occupied by trivalent cations. We note that the four sites in the preliminary $C1$ structure model (that correspond to the single $M(13)$ site in the final $C222_1$ model) all gave the same site-scattering values and bond lengths, suggesting that Mn^{2+} , Mg, Al and Fe^{3+} are completely disordered at the $M(13)$ site in $C222_1$. For the $M(1)-M(4)$ and $M(10)-M(12)$ sites, the observed $\langle M-O \rangle$ distances range from 2.224–2.284 Å and the refined site-scattering values suggest full occupancy by Mn^{2+} . For the $M(5)-M(9)$ sites, the observed $\langle M-O \rangle$ distances range from 2.197–2.217 Å, and the refined site-scattering values are all slightly deficient relative to full occupancy by Mn. This suggests that the $M(5)-M(9)$ sites contain significant amounts of lighter and smaller cations relative to Mn^{2+} . The octahedrally coordinated cations available are Mn^{2+} ($r = 0.83$ Å), Zn ($r = 0.74$ Å) and Mg ($r = 0.72$ Å), and partial occupancy by minor Zn and/or Mg would reduce the mean aggregate radius relative to complete occupancy by Mn^{2+} . Zinc is a slightly stronger X-ray scatterer than Mn, and Mg has approximately half the X-ray scattering power of Mn, and hence any Zn assigned to these $M(5)-M(9)$ sites must be accompanied by Mg such that the aggregate electron count will sum to less than 25 electrons per site. There is no direct solution for three scattering species distributed over several sites in a structure (Hawthorne, 1983), and we have approximated a solution to the site assignment over the $M(5)-M(9)$ sites by assuming that minor Zn (remaining after Zn was assigned to the Zn sites) is disordered over the $M(5)-M(9)$ sites, and then

THE CRYSTAL STRUCTURE OF KRAISSLITE

TABLE 6. Refined site scattering (e.p.f.u.) and site assignments (a.p.f.u.) for kraisslite.

	SREF*	As ³⁺	As ⁵⁺	Si	Zn	Mn ²⁺	Mg	Fe ³⁺	Al	e ⁻
As(1)	66	2.00								66
T(1)	66		2.00							66
T(2)	36.89(14)		0.47	1.53						36.9
T(3)	34.60(14)		0.35	1.65						34.6
T(4)	29.68(14)		0.09	1.91						29.7
T(5)	28.12(14)		0.01	1.99						28.2
Zn(1)	28.75(8)				0.75	0.25				28.8
Zn(2)	57.15(11)				1.43	0.57				57.2
M(1)	50					2.00				50
M(2)	50					2.00				50
M(3)	50					2.00				50
M(4)	50					2.00				50
M(5)	47.54(12)				0.15	1.57	0.28			47.1
M(6)	48.66(12)				0.15	1.66	0.19			48.3
M(7)	47.08(12)				0.15	1.54	0.31			46.7
M(8)	49.24(13)				0.15	1.70	0.15			48.8
M(9)	47.47(12)				0.15	1.57	0.28			47.1
M(10)	50					2.00				50
M(11)	50					2.00				50
M(12)	50					2.00				50
M(13)	43.10(11)					0.55	0.45	0.84	0.16	43.1
	980.3	2.00	2.92	7.08	2.93	23.41	1.66	0.84	0.16	978.5

* Site-scattering values from structure refinement.

assigned Mn²⁺ and Mg such that the aggregate electron count is in accord with the observed scattering (in all cases, the assigned electron site sums are slightly less than the respective observed site scattering) (Table 6). In the overall site assignment, there is extremely close agreement between total refined site scattering (980.3 e.p.f.u.) and the number of electrons (978.5 e.p.f.u.) for the cations from the electron-microprobe analysis (cf. Tables 3 and 6).

Mean bond lengths

Figure 1 shows the observed mean bond lengths as a function of the aggregate constituent cation radii for the seven tetrahedrally coordinated sites and the thirteen octahedrally coordinated sites in kraisslite, as well as for the three tetrahedrally and fourteen octahedrally coordinated sites in the structurally related mineral arakiite (Cooper and Hawthorne, 1999). The relation shown in Fig. 1 has $r^2 = 0.99$ and the slope of ~ 1.0 , indicating agreement with a simple hard-sphere model, and supporting the assigned site occupancies in

Table 6 for kraisslite. The departure of the *M*(4) and *M*(10) sites in kraisslite from the least-squares line in Fig. 1 is related to the single unusually long bonds in each octahedron (i.e. *M*(4)–O(7) = 2.546, *M*(10)–O(5) = 2.757 Å; Table 5).

The anion sites

Examination of the bond-valence table (Table 7) shows that all anions bonded to triangular-pyramidally or tetrahedrally coordinated cations are O²⁻, i.e. their incident bond-valence sums (excluding any contributions from H atoms; see Σ' column in Table 7) exceed 1.7 vu (valence units). All anions not bonded to triangular-pyramidally or tetrahedrally coordinated cations have incident bond-valence sums (excluding any contributions from H atoms; see Σ' column in Table 7) in the range 0.96–1.16 vu, indicating that these anions must be (OH)⁻ groups. Hydrogen bonds were assigned on the basis of local stereochemistry and anion bond-valence requirements, and the resultant arrangement of atoms accords with the valence-sum rule (Brown, 2002).

TABLE 7. Bond-valence (vu) table for kraisslite.

	$As(1)$	$Zn(1)$	$Zn(2)$	$T(1)$	$T(2)$	$T(3)$	$T(4)$	$T(5)$	$M(1)$	$M(2)$	$M(3)$	$M(4)$	$M(5)$	$M(6)$	$M(7)$	$M(8)$	$M(9)$	$M(10)$	$M(11)$	$M(12)$	$M(13)$	Σ	
O(1)	1.02								0.19			0.29						0.43					1.93
O(2)	1.03								0.33							0.43			0.20				1.99
O(3)	1.02											0.27		0.40					0.35				2.04
O(4)				1.20					0.28					0.31									1.79
O(5)				1.29																			1.70
O(6)				1.20												0.34		0.07					1.79
O(7)				1.22														0.31					1.72
O(8)					1.04					0.23	0.23										0.23		1.73
O(9)			0.47		1.04					0.34													1.85
O(10)		0.47^{*2}			1.04						0.34												1.85
O(11)			0.48		1.04																0.33		1.85
O(12)			0.51			1.01			0.40														1.92
O(13)						1.03																	1.95
O(14)			0.50			1.03				0.40													1.93
O(15)		0.51^{*2}				1.01															0.40		1.92
O(16)							0.98			0.24	0.30	0.29								0.27			1.96
O(17)							1.04		0.28														1.88
O(18)							0.97			0.30											0.25		1.96
O(19)							0.97				0.24				0.44					0.29			1.93
O(20)								0.95					0.43										1.90
O(21)								0.96	0.44				0.33							0.43			1.93
O(22)								0.98					0.19										1.93
O(23)								0.97						0.34									1.88
OH(1)												0.45			0.17								1.11
OH(2)										0.32											0.42		1.08
OH(3)									0.39					0.31									1.16
OH(4)												0.40											1.13
OH(5)													0.33										1.13
OH(6)																					0.34		1.14
OH(7)																							1.10
OH(8)											0.33										0.40		1.10
OH(9)																							1.02
Σ	3.07	1.96	1.96	4.91	4.16	4.08	3.96	3.86	1.91	1.83	1.84	1.83	1.95	1.95	1.97	1.95	1.95	1.78	1.93	1.84	1.84	2.43	0.96

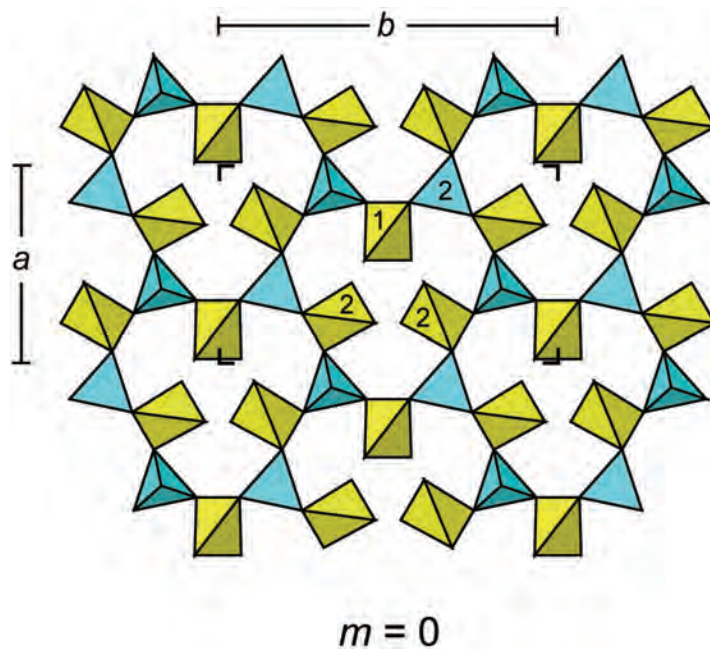


FIG. 2. Polyhedron layer ($m = 0$) in kraisslite projected down [001]; Zn-dominant $Zn(1,2)$ tetrahedra are yellow; Si-dominant $T(2)$ tetrahedron are blue; numbers identify site-specific cations; black corners mark unit-cell boundaries.

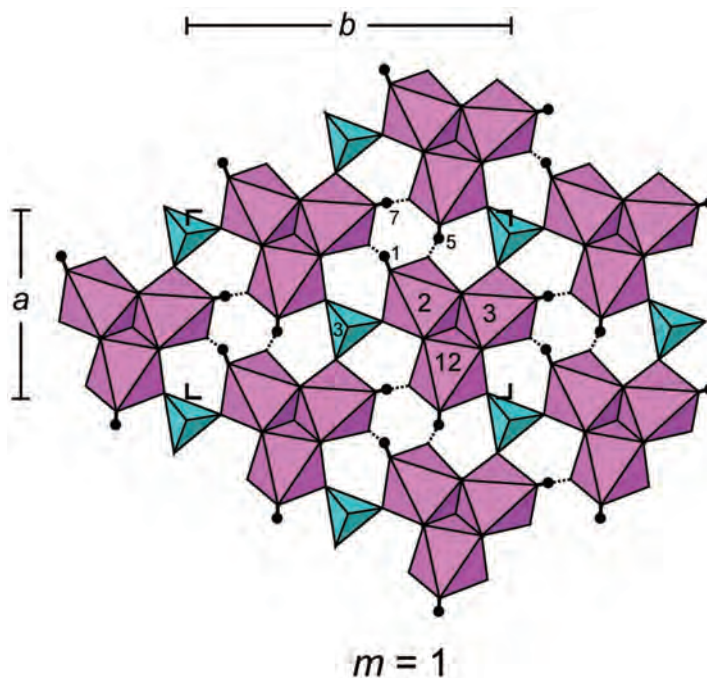


FIG. 3. Polyhedron layer ($m = 1$) in kraisslite projected down [001]; Mn-dominant $M(2)$, $M(3)$ and $M(12)$ octahedra are pink; Si-dominant $T(3)$ tetrahedron is blue; H atoms are black circles; hydrogen bonds are dashed lines; black corners mark unit-cell boundaries.

Structure topology

We have recently discovered two new minerals in the mcgovernite family, and also have to publish a description of the crystal structure of mcgovernite itself. When this additional information is available, we will consider the general crystal-chemistry and structure topology of this family in detail. Herein we confine ourselves to a description of the structure of kraisslite.

The kraisslite structure is based on five distinct layers of polyhedra stacked along the c axis; these layers are labelled $m = 0$ to $m = 4$. The $m = 0$ layer consists of tetrahedra that share vertices to form twelve-membered rings of alternating Zn and $T(2)$ tetrahedra (Fig. 2). Within a given ring, the $T(2)$ tetrahedra alternately point up and down, and the Zn tetrahedra alternately project inward and outward. The result is that the Zn cations of $m =$

0 layer lie at the vertices of a 12^3 plane net. The $m = 1$ layer consists of trimers of edge-sharing octahedra [$M(2)-M(3)-M(12)$] that share vertices with $T(3)$ tetrahedra that all point in the same direction (Fig. 3). Additional linkage between these trimers occurs via hydrogen bonding. The $m = 2$ layer also contains a trimer of edge-sharing octahedra [$M(5)-M(7)-M(9)$] that similarly link via $T(4)$ tetrahedra that all point in the same direction (Fig. 4). An additional octahedron [$M(13)$] occurs at the junction of three [$M(5)-M(7)-M(9)$] trimers, sharing edges with octahedra of each trimer. The $M(13)$ octahedron is coordinated by six (OH) groups and occupied by 50% divalent and 50% trivalent cations (Tables 5 and 6). The $m = 3$ layer contains an [$M(1)-M(4)-M(11)$] trimer of octahedra and the $T(5)$ tetrahedron, and has the same general topology as the $m = 1$ layer. However, the O_D-O_A relations

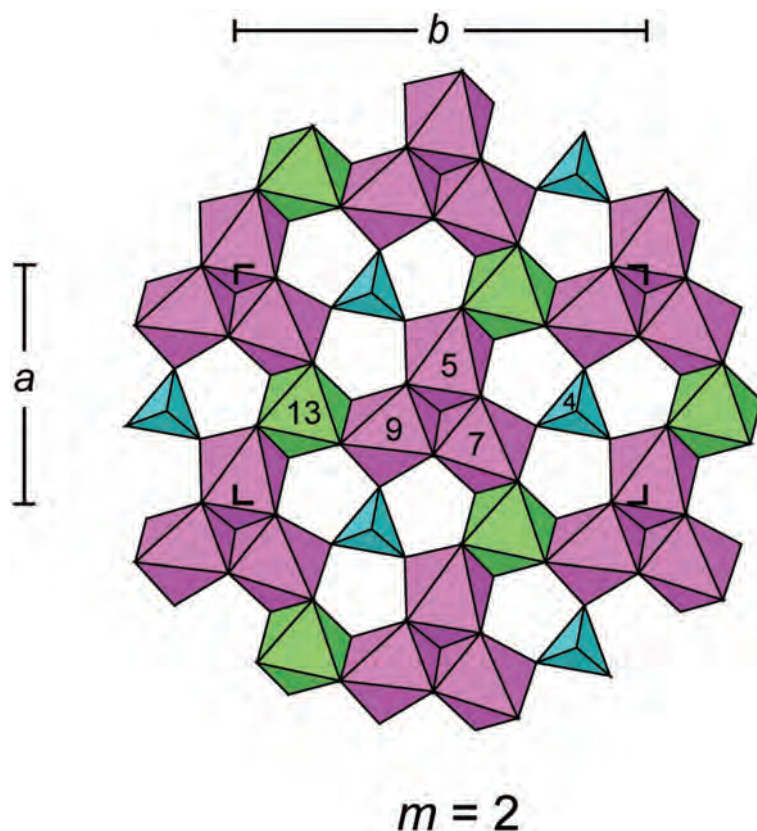


FIG. 4. Polyhedron layer ($m = 2$) in kraisslite projected down $[001]$; Mn-dominant $M(5)$, $M(7)$ and $M(9)$ octahedra are pink; $Fe^{3+}(Al)$ -bearing $M(13)$ octahedron is green; Si-dominant $T(4)$ tetrahedron is blue; black corners mark unit-cell boundaries.

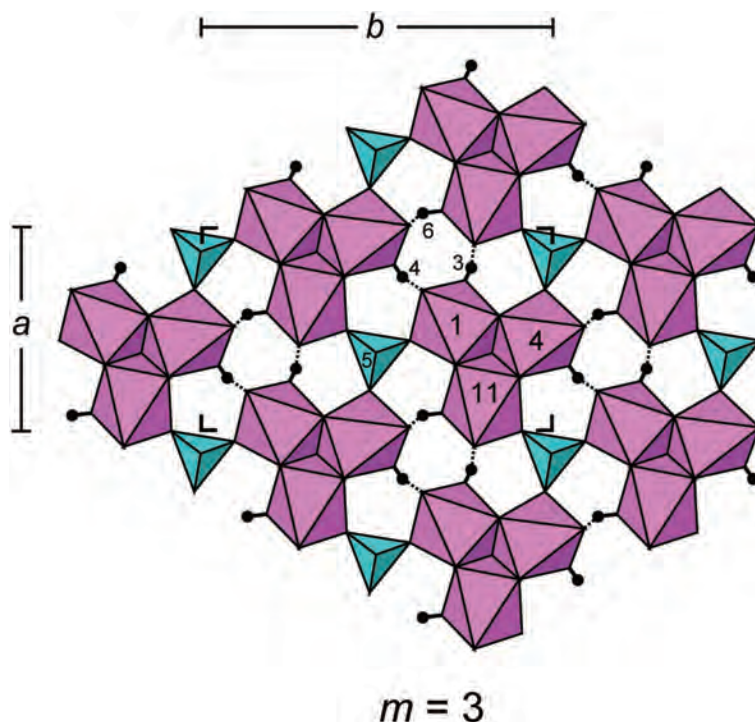


FIG. 5. Polyhedron layer ($m = 3$) in kraisslite projected down $[001]$; Mn-dominant $M(1)$, $M(4)$ and $M(11)$ octahedra are pink; Si-dominant $T(5)$ tetrahedron is blue; H atoms are black circles; hydrogen bonds are dashed lines; black corners mark unit-cell boundaries.

and associated hydrogen-bond directions are reversed (cf. Figs 3 and 5). The $m = 4$ layer contains trimers $[M(6)-M(8)-M(10)]$ of edge-sharing octahedra that connect via (1) $As^{3+}-O$ linkages, (2) edge and vertex sharing with $T(1)$ tetrahedra, and (3) hydrogen bonding (Fig. 6). The five layers of polyhedra ($m = 0$ to 4) stack along $[001]$ with a reversal in the sequence about the twofold axis at $z = 1/4$ (Fig. 7), $1/2$, $3/4$ and 1.

Kraisslite belongs to the mcgovernite family of arseno-silicates. Mcgovernite has the space group $R\bar{3}c$ (Wuensch, 1960) and kraisslite was originally thought to possess the space group $P6_322$ (Moore and Ito, 1978). Pseudo-threefold symmetry is present in each of the individual layers of polyhedra in kraisslite (Figs 2–6). This approximate threefold symmetry is contiguous through a single ($m = 0 \rightarrow m = 4$) packet of polyhedron layers; the pseudo-threefold axis passes through $x \approx 0.61$, $y \approx 0.5$ parallel to $[001]$ for the level $z = 0-1/4$. However, the true symmetry of kraisslite is $C222_1$, and 2_1 screw axes extend along $[001]$ at the corners and

through the midpoints of the unit cell. In Figs 2 to 6, we see that the pseudo-threefold axes (lying off the 2_1 screw axes) do not mutually coincide along $[001]$ as a function of the 2_1 screw operation. Lateral offsets in the (001) plane of the ($m = 0 \rightarrow m = 4$) packets in kraisslite offset the pseudo-threefold axes of each individual packet from each other. Thus these pseudo-threefold axes do not correspond with each other from one packet to another, and result in an overall reduction in symmetry to $C222_1$. It seems likely that general stacking disorder has led to the observed streaking parallel to $[001]$ in the X-ray diffraction pattern and the apparent hexagonal symmetry in the initial study of Moore and Ito (1978).

Cation order

In kraisslite, Zn preferentially orders at the Zn tetrahedra of the $m = 0$ layer, where it is disordered over the $Zn(1)$ and $Zn(2)$ sites, along with subordinate Mn^{2+} (Table 6; Fig. 2). Arsenic

THE CRYSTAL STRUCTURE OF KRAISSLITE

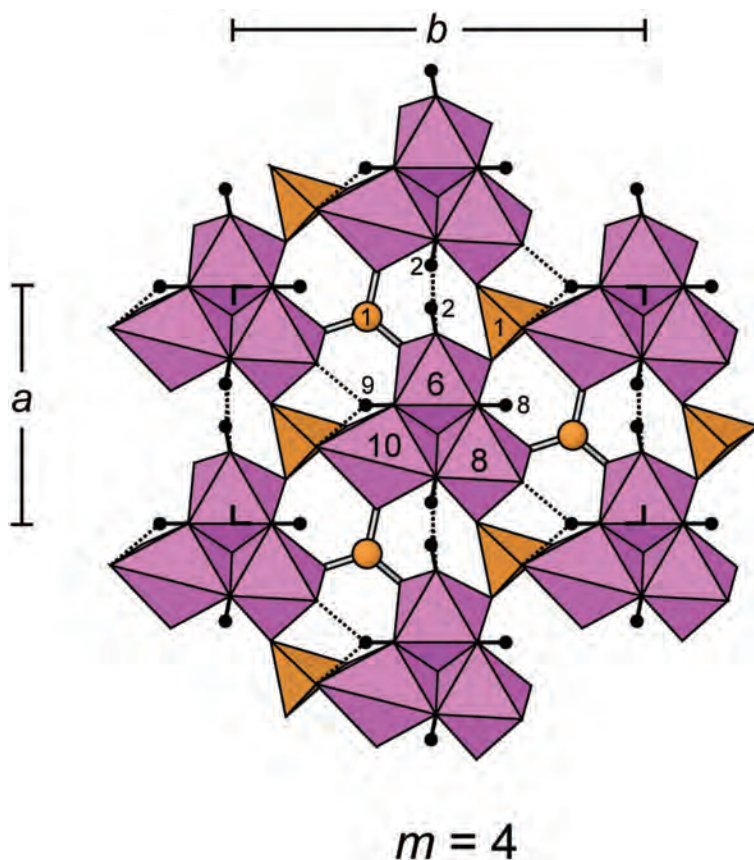


Fig. 6. Polyhedron layer ($m = 4$) in kraisslite projected down [001]; Mn-dominant $M(6)$, $M(8)$ and $M(10)$ octahedra are pink; As^{3+} -bearing $As(1)$ site are orange circles; As^{5+} -bearing $T(1)$ tetrahedron is orange; H atoms are black circles; hydrogen bonds are dashed lines; black corners mark unit-cell boundaries.

preferentially orders onto the $m = 4$ layer (Fig. 6), midway between successive $m = 0$ layers (Fig. 7), as (1) As^{3+} in pyramidal coordination at the $As(1)$ site, and as (2) As^{5+} in tetrahedral coordination at the $T(1)$ site (Tables 5, 6). The $m = 2$ layer (Fig. 7) occurs between the As-rich $m = 4$ layer and the Zn-rich $m = 0$ layer, and contains the octahedrally coordinated trivalent cations Fe^{3+} and Al at the $M(13)$ site (Table 6; Fig. 4). Magnesium in kraisslite occurs predominantly within the $m = 2$ layer at the $M(5)$, $M(7)$ and $M(9)$ sites of the trimer of octahedra. The Si-dominant tetrahedra $T(2)$ – $T(5)$ occur on the $m = 0$ through $m = 3$ layers in the following order: $T(2)$ at $m = 0$, $T(3)$ at $m = 1$, $T(4)$ at $m = 2$ and $T(5)$ at $m = 3$ (Figs 2–5). There is a progressive decrease in the As^{5+} content of these Si-dominant tetrahedra from $T(2)$ to $T(5)$ (Table 6).

Hydrogen bonds

The hydrogen-bonding environments associated with H(1) and H(3)–H(7) are all similar in that O_D is tetrahedrally coordinated by three cations and a H atom, and O_A is coordinated by three cations and also receives a single hydrogen bond (Table 7). These H atoms are involved in hydrogen bonding between neighbouring clusters of octahedra in the $m = 1$ and $m = 3$ layers (Figs 3 and 5). The O_D anion OH(2) is coordinated by three cations in addition to the H(2) atom, and also accepts a hydrogen bond from a neighbouring H(2) atom belonging to an adjacent OH(2) group (Fig. 6; Table 7). Both the OH(8) and OH(9) anions are each coordinated by four cations in addition to their respective H atoms [H(8) and H(9)]. The H(8) atom projects into a

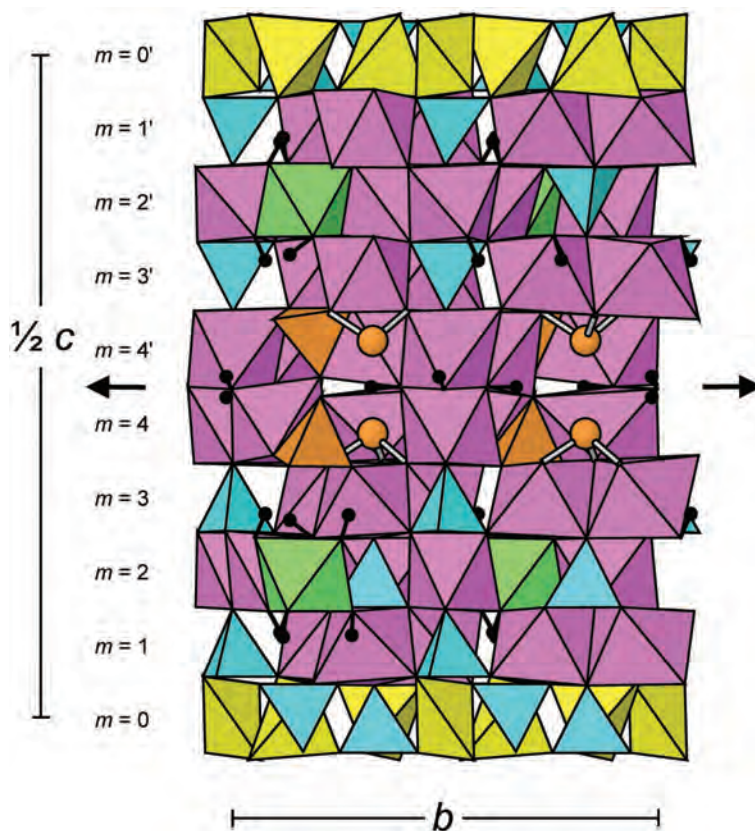


FIG. 7. Stacking of polyhedron layers ($m = 0$ through $m = 4$) along $[001]$ in kraisslite, projected down $[100]$; twofold rotation axis at $z = \frac{1}{4}$ is shown by black arrows. The As^{3+} -bearing $\text{As}(1)$ sites are orange circles; As^{5+} -bearing tetrahedra are orange; $\text{Fe}^{3+}(\text{Al})$ -bearing octahedra are green; Mn-dominant octahedra are pink; Si-dominant tetrahedra are blue; Zn-dominant tetrahedra are yellow; H atoms are black circles; black corners mark unit-cell boundaries.

void between two opposing $(\text{As}^{3+}\text{O}_3)$ pyramids, and seems to be a terminal H atom for which there is no suitable acceptor anion. The O(2), O(4) and O(5) anions are $<3.2 \text{ \AA}$ from H(8), which on its own does not preclude weak hydrogen bonding (Brown, 1977). However, the $\text{O}_D\text{--H}(8)\text{--O}_A$ angles of such hydrogen bonds would be $<110^\circ$, and would involve hydrogen bonding along edges of coordination polyhedra, both unrealistic conditions for hydrogen bonding. The anion OH(9) and its associated H(9) atom lie along a twofold rotation axis with two O_A anions [O(5) and O(5)'], suggesting a bifurcated hydrogen bond from H(9) to two equidistant O(5) acceptor anions. The OH(9)–H(9)···O(5) arrangement subtends an edge [OH(9)–O(5)] of the $M(10)$ octahedron; however, $M(10)\text{--O}(5)$ is very long (Tables 5 and

7), suggesting that such a hydrogen bond is feasible.

X-ray powder diffraction pattern

The published powder-diffraction pattern for kraisslite lists only data for reflections of type $0\ 0\ l$ (Moore and Ito, 1978). We have changed the symmetry and cell of kraisslite relative to previous work, and give a simulated powder-diffraction pattern obtained by collapsing the single-crystal diffraction data into two dimensions; reflections at low 2θ values are not present as they were obscured by the beam stop, and a large number of weak reflections ($I < 5$) have been omitted (Table 8). Comparison with the pattern of Moore and Ito (1978) shows that the accord

THE CRYSTAL STRUCTURE OF KRAISSLITE

TABLE 8. Simulated X-ray powder-diffraction data ($\lambda = 1.54178 \text{ \AA}$) for kraisslite.

<i>I</i>	<i>d</i> (Å)	<i>h k l</i>	<i>d</i> (Å), <i>I</i> *	<i>I</i>	<i>d</i> (Å)	<i>h k l</i>	<i>d</i> (Å), <i>I</i> *
2	7.318	0 0 6	7.266, 1	8	2.440	0 0 18	2.437, 55
10	4.391	0 0 10	4.385, 45	13	2.410	1 5 8	
7	4.342	0 2 8		15	2.407	3 1 8	
6	4.340	1 1 8		11	2.366	0 6 0	
21	4.096	1 3 0		13	2.363	3 3 0	
5	4.073	2 0 1		8	2.360	3 3 1	
8	3.944	1 3 3		37	2.350	1 5 9	
5	3.940	2 0 3		35	2.349	2 4 9	
6	3.838	1 3 4		28	2.348	3 1 9	
6	3.834	2 0 4		8	2.288	2 4 10	
6	3.659	0 0 12	3.651, 35	8	2.196	0 0 20	2.194, 55
7	3.479	0 2 11		7	2.185	1 3 17	
8	3.478	1 1 11		5	2.184	2 0 17	
5	3.430	1 3 7		5	2.081	3 3 10	
6	3.427	2 0 7		7	1.861	1 5 17	
19	3.283	1 3 8		8	1.859	3 1 17	
24	3.280	2 0 8		5	1.805	1 5 18	
6	3.252	1 1 12		27	1.804	2 4 18	
32	3.137	1 3 9		5	1.804	3 1 18	
3	3.136	0 0 14	3.130, 20	23	1.751	1 5 19	
6	3.135	2 0 9		5	1.750	2 4 19	
9	3.086	2 2 7		20	1.750	3 1 19	
87	2.995	1 3 10	2.993, 2	5	1.699	2 4 20	
42	2.993	2 0 10		5	1.697	3 3 18	
8	2.980	0 4 8		7	1.652	3 3 19	
9	2.978	2 2 8		7	1.649	1 5 21	
100	2.868	2 2 9		8	1.648	3 1 21	
5	2.859	1 3 11		6	1.643	4 4 10	
35	2.760	0 4 10		11	1.549	1 9 0	
10	2.744	0 0 16	2.740, 100	8	1.548	1 9 1	
11	2.729	1 3 12		18	1.547	4 6 0	
19	2.681	2 4 0		6	1.547	5 3 0	
19	2.677	1 5 1		11	1.546	5 3 1	
22	2.673	3 1 1		10	1.544	2 8 9	
6	2.650	2 2 11		10	1.544	3 7 9	
5	2.638	1 5 3		6	1.544	4 6 2	
7	2.466	1 5 7		13	1.542	5 1 9	
6	2.465	2 4 7		5	1.512	1 3 27	
5	2.463	3 1 7		5	1.465	1 3 28	1.460, 1

* The *d* (Å) and *I* values are taken from Moore and Araki (1978).

Acknowledgements

between *d*-values is almost exact [*c* = 43.88, Moore and Ito (1978); *c* = 43.9103, this work]. However, there is no correspondence between reflection intensities. In the experimental pattern, there is major enhancement of the (0 0 *l*) reflections, presumably due to preferred orientation caused by the platy nature of kraisslite.

This work was supported by a Canada Research Chair in Crystallography and Mineralogy and by Natural Sciences and Engineering Research Council of Canada Discovery, Equipment and Major Installation grants of the Natural Sciences and Engineering Research Council of Canada, and by Innovation grants from the Canada Foundation for Innovation to FCH.

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