Long-range and short-range cation order in the crystal structures of carlfrancisite and mcgovernite

Frank C. Hawthorne

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

ABSTRACT

The crystal structures of carlfrancisite, ideally $Mn_3^{2+}(Mn^{2+},Mg,Fe^{3+},Al)_{42}(As^{3+}O_3)_2(As^{5+}O_4)_4[(Si,As^{5+})O_4]_8(OH)_{42}$, hexagonal (rhombohedral), $R\bar{3}m$ with $Z = 6$, and unit-cell parameters: $a = 8.2238(2)$, $c = 205.113(6)$ Å and $V = 12013.5(4)$ Å^3, from the Kombat mine, Otavi Valley, Namibia, and mcgovernite, ideally $Zn_3(Mn^{2+},Mg,Fe^{3+},Al)_{42}(As^{3+}O_3)_2(As^{5+}O_4)_4[(Si,As^{5+})O_4]_8(OH)_{42}$, hexagonal (rhombohedral), $R\bar{3}m$ with $Z = 6$, and unit-cell parameters: $a = 8.2061(3)$, $c = 204.118(8)$ Å and $V = 11903.8(6)$ Å^3, from Sterling Hill, New Jersey, have been solved by direct methods and refined to R_1 values of 3.37 and 5.02% for 3837 and 3772 unique observed reflections, respectively; they are isostructural. Chemical analysis by electron microprobe and crystal-structure refinement gave the following compositions: carlfrancisite: As$_2$O$_5$ 12.89, As$_2$O$_3$ 3.33, P$_2$O$_5$ 0.50, V$_2$O$_5$ 0.74, SiO$_2$ 8.96, Al$_2$O$_3$ 0.78, FeO 0.22, MnO 53.25, MgO 9.37, H$_2$O (calc) 8.42, sum 98.50 wt.%; mcgovernite: As$_2$O$_5$ 13.06, As$_2$O$_3$ 3.71, SiO$_2$ 9.34, Al$_2$O$_3$ 0.20, FeO 1.38, MnO 44.58, ZnO 8.81, MgO 8.89, H$_2$O(calc) 8.24, sum 98.21 wt.%. The H$_2$O contents and the valence states of As were determined by crystal-structure analysis.

There are 18 crystallographically distinct cation sites in both carlfrancisite and mcgovernite. There are two [4]-coordinated *As* sites fully occupied by As^{5+}, and four *T* sites occupied by Si and As^{5+} in solid solution. The *As*(3) site has triangular pyramidal coordination with <*As*(3)–O> distances of 1.808 and 1.817 Å, typical of As^{3+}. The *Z*(1) site, occupied by Mn^{2+} in carlfrancisite and Zn in mcgovernite, has tetrahedral coordination, and the *Z*(2) site is only partly occupied by Mg and Mn^{2+} in both structures. There are nine *M* sites, all of which are octahedrally coordinated and contain dominantly Mn^{2+} and Mg, with minor Al and Fe. There are three cation sites with significant vacancies: *As*(3), *Z*(2), *M*(3), and there are complicated patterns of short-range order involving the cations and vacancies at these sites.

The carlfrancisite–mcgovernite structure contains 84 layers of approximately close-packed polyhedra along one translation on **c**. The anions in the structure are arranged in approximately close-packed layers orthogonal to the **c** axis. Fourteen layers stack along the **c** axis in the sequence |**hhchch•hchchh| (* denotes a layer of anions displaced from close packed). There are eight distinct layers of cation-centred polyhedra that repeat via a centre of symmetry at the origin, and via the *R*-centering to give 84 layers per unit-cell.

Introduction

MCGOVERNITE was described as a new species from Sterling Hill, New Jersey, by Palache and Bauer (1927), its nature as a very large structure was described by Wuensch (1960), and a preliminary description of its crystal structure was given by Cooper and Hawthorne (2001). Dunn *et al.* (1988) reported a mcgovernite-like mineral from the Kombat mine, Otavi Valley, Namibia, and Hawthorne *et al.* (2013) recently described this mcgovernite-like mineral as the new species carlfrancisite. Brugger *et al.* (2001) described turtmannite from manganoan ores filling paleokarst pockets in the Triassic marbles of the Barrhorn Unit in the Central Alps, Switzerland, and reported its

E-mail: frank_hawthorne@umanitoba.ca
https://doi.org/10.1180/minmag.2017.081.098

structure. Mcgovernite (Wuensch, 1960; Cooper and Hawthorne, 2001), ideally $Zn_3(Mn^{2+},Mg,Fe^{3+},Al)_{42}(As^{3+}O_3)_2(As^{5+}O_4)_4[(Si,As^{5+})O_4]_8(OH)_{42}$ is isostructural with carlfrancisite, ideally $Mn_3^{2+}(Mn^{2+},Mg,Fe^{3+},Al)_{42}(As^{3+}O_3)_2(As^{5+}O_4)_4[(Si,As^{5+})O_4]_8(OH)_{42}$, and both are related to turtmannite, ideally $(Mn,Mg)_{22.5}Mg_{3-3x}(V,AsO_4)_3(SiO_4)_3(AsO_3)_x O_{5-5x}(OH)_{20+x}$ (Brugger et al., 2001). All three structures have similar cell dimensions and consist of close-packed (and not-so-close-packed) layers of octahedra and tetrahedra stacked along the **c** direction. These structures are the most complicated of a family of minerals based on dominantly close-packed layers (Wuensch, 1968), including arakiite (Cooper and Hawthorne, 1999), dixenite (Araki and Moore, 1981), franciscanite (Pertlik, 1986), hematolite (Moore and Araki, 1978), kraisslite (Moore and Ito, 1978; Cooper and Hawthorne, 2012), örebroite (Dunn et al., 1986) and welinite (Moore, 1967). Here, I report the structures of mcgovernite and carlfrancisite and examine the similarities and differences between mcgovernite, carlfrancisite and turtmannite.

Sample provenance

The carlfrancisite crystals used in the present work were taken from the holotype sample. A sample of mcgovernite from Sterling Hill, New Jersey, was purchased from a mineral dealer and its identity was confirmed by X-ray diffraction.

Chemical composition

Crystals were mounted in epoxy, polished, and analysed using a Cameca SX-100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, and a beam diameter of 10 µm. The following standards were used: cobaltite: As; apatite: P; synthetic VP_2O_7: V; diopside: Si; andalusite: Al; fayalite: Fe; spessartine: Mn; gahnite Zn; forsterite: Mg. The data were reduced and corrected by the PAP method of Pouchou and Pichoir (1985) and the presence and quantity of (OH) groups were established by crystal-structure solution and refinement. Table 1 gives the resultant chemical compositions (each the mean of ten determinations).

Calculation of the chemical formulae

The empirical formulae were calculated on the basis of 96 anions with (OH) = 42 apfu (anions per

formula unit) as indicated by crystal-structure solution and refinement. Interatomic distances show that all Mn and Fe are in the divalent state. Both minerals contain significant As. The refined site-scattering and long <T–O> bond lengths indicate the presence of both trivalent and pentavalent As in mcgovernite and carlfrancisite. These valence states were used in the calculation of the empirical formulae, giving the following: carlfrancisite: $Mn_{33.59}^{2+}Mg_{10.40}Fe_{0.14}^{2+}Al_{0.69}As_{1.51}^{3+}Si_{6.77}P_{0.32}V_{0.36}^{5+}As_{5.02}^{5+}O_{54}(OH)_{42}$; mcgovernite: $Mn_{28.85}^{2+}Mg_{10.13}Fe_{0.88}^{2+}Al_{0.18}Zn_{4.97}Si_{7.14}As_{5.22}^{5+}O_{54}(OH)_{42}$.

X-ray data collection, crystal-structure solution and structure refinement

Each crystal was attached to a tapered glass fibre. X-ray-diffraction data for carlfrancisite were collected with MoKα X-radiation on a Bruker D8 three-circle diffractometer equipped with a rotating-anode generator, multilayer optics and an APEX-II CCD detector. Intensities were collected to 60°2θ using 5 s per 0.3° frame with a crystal-to-detector distance of 8 cm. An empirical absorption correction (SADABS; Sheldrick, 2008) was applied, and the data were corrected for Lorentz, polarization and background effects. X-ray-diffraction data for mcgovernite were collected with MoKα X-radiation on a Siemens P4 four-circle diffractometer. Cell dimensions were determined from the setting angles of 30 automatically aligned reflections in the range 14 < 2θ < 30°. The refined unit-cell parameters of both structures are given in Table 2, together with other information pertaining to data collection and structure refinement.

The structures were solved by direct methods and refined in the space groups $R\bar{3}m$ with the SHELXTL version 5.1 system of programs (Bruker, 1997). There are several scattering species to be distributed over a comparatively large number of sites, but this cannot be done unambiguously during refinement (Hawthorne, 1983). Hence I assigned what I considered to be the dominant scattering species at each site and refined the occupancies unconstrained. If the absorption corrections are accurate, the resulting site-scattering values (Hawthorne et al., 1995) should also be accurate, and one can combine these values with mean bond lengths and constituent-cation radii to derive site populations. The final models refined to R_1 indices of 3.56% for carlfrancisite and 5.02% for mcgovernite. Final atom parameters are given in Table 3, selected

TABLE 1. The chemical composition (wt.%) and unit formulae (apfu) of mcgovernite and carlfrancisite.

Oxide	Carlfrancisite	Mcgovernite	Ion	Carlfrancisite	Mcgovernite
As_2O_5	16.76(28)	17.37			
As_2O_5*	12.89	13.06	As^{5+}	5.02	5.22
As_2O_3*	3.33	3.71	As^{3+}	1.51	1.72
P_2O_5	0.50(5)	n.d.	P	0.32	–
V_2O_5	0.74(4)	n.d.	V^{5+}	0.36	–
SiO_2	8.96(8)	9.34	Si	6.77	7.14
Al_2O_3	0.78(3)	0.20	Al	0.69	0.18
FeO	0.22(3)	1.38	Fe^{2+}	0.14	0.88
MnO	53.25(26)	44.58	Mn^{2+}	33.59	28.85
ZnO	n.d.	8.81	Zn	–	4.97
MgO	9.37(11)	8.89	Mg	10.40	10.13
H_2O	8.42	8.24	(OH)	42	42
Total	98.50	98.21			

*The $As^{3+}/(As^{3+} + As^{5+})$ ratio was derived from the crystal structure; n.d. not detected.

interatomic distances in Table 4, and refined site-scattering values and site populations in Tables 5 and 6; a bond-valence table for carlfrancisite was calculated using the parameters of Gagné and Hawthorne (2015) and is given in Table 7; crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine*, and are available as Supplementary material (see below).

TABLE 2. Miscellaneous information for mcgovernite and carlfrancisite.

	Mcgovernite	Carlfrancisite
Unit-cell dimensions		
a (Å)	8.2061(3)	8.2238(2)
c	204.118(8)	205.113(6)
V (Å^3)	11,903.8(12)	12,013.4(11)
Space group	$R\bar{3}m$	$R\bar{3}m$
Z	6	6
Crystal size (μm)	~100 × 100 × 10	~100 × 100 × 10
Radiation/ monochromator	Mo$K\alpha$/ Graphite	Mo$K\alpha$/ Graphite
Total reflections	109,205	111,218
Ewald sphere	33,085	33,645
No. unique reflections	3912	3947
No. $I_o > 2\sigma I$	3772	3837
R_{sigma} %	2.07	1.25
R_{int} %	4.55	2.41
R_{1obs} %	5.02	3.37
wR_2 %	12.40	9.79
GoF	1.229	1.106

Assignment of site populations

There are 18 crystallographically distinct cation sites, and the site occupancies were assigned using the refined site-scattering values (Table 5), the observed local stereochemistry, the unit formula derived by electron-microprobe analysis (Table 1), and the constraints exerted by cation sites that are too close for simultaneous local occupancy. Inspection of the interatomic distances in both structures (Table 4) shows that three sites are involved in short (long-range) interatomic separations such that both sites in each local pair of sites cannot each be occupied, and this forces the occurrence of vacancies at each of these sites. This is the case for the $As(3)$, $Z(2)$ and $M(3)$ sites. I will first consider the site populations for the sites not involved in such short separations.

Sites not involving vacancies

There are two As sites, $As(1)$ and $As(2)$, that are [4]-coordinated with site-scattering values of 66 epfu (electrons per formula unit) and grand $<As–O>$ distances of 1.694 and 1.698 Å, in carlfrancisite and mcgovernite, respectively. These values are slightly larger than the grand $<^{[4]}As^{5+}–\varphi>$ distances ($\varphi = O^{2-}$, $(OH)^-$) in well-refined arsenate structures (1.687 Å, Majzlan et al., 2014), which is in accord with the presence of a small amount of V^{5+} in the

1103

TABLE 3. Atom coordinates and displacement parameters for carlfrancisite and mcgovernite.

Site	x	y	z	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	U_{eq}
						Carlfrancisite				
As(1)	⅓	⅔	0.01445(2)	0.01227(16)	0.01227(16)	0.0201(3)	0	0	0.00614(8)	0.01488(12)
As(2)	0	0	0.03838(2)	0.01027(15)	0.01027(15)	0.0182(3)	0	0	0.00514(8)	0.01293(12)
As(3)	⅔	⅓	0.02398(2)	0.0115(2)	0.0115(2)	0.0170(3)	0	0	0.00573(12)	0.0133(2)
Z(1)	0	0.25789(8)	¼	0.0212(4)	0.0140(3)	0.0230(4)	−0.00343(12)	−0.0069(3)	0.01060(18)	0.0186(2)
Z(2)	0.4716(6)	0.0861(5)	0.02384(2)	0.0164(19)	0.0158(19)	0.028(2)	0.0005(14)	0.0001(14)	0.0082(15)	0.0200(13)
M(1)	0.68709(6)	0.10960(6)	0.06004(2)	0.0112(2)	0.0100(2)	0.0201(3)	0.00034(15)	−0.00018(16)	0.00568(17)	0.01361(16)
M(2)	0.21486(7)	0.25881(7)	0.02367(2)	0.0181(3)	0.0142(2)	0.0223(3)	−0.00315(17)	−0.00341(17)	0.00939(19)	0.01760(17)
M(3)	0.64649(8)	0.55508(8)	0.03530(2)	0.0117(3)	0.0117(3)	0.0214(3)	−0.00146(18)	−0.00027(19)	0.0065(2)	0.01460(18)
M(4)	0	0	0.05968(2)	0.0119(4)	0.0119(4)	0.0227(7)	0	0	0.0059(2)	0.0155(4)
M(5)	0.10709(6)	0.40024(6)	0.07178(2)	0.0107(2)	0.0118(2)	0.0210(2)	0.00199(15)	0.00203(15)	0.00582(16)	0.01444(12)
M(6)	0	0	0.01029(2)	0.0194(4)	0.0194(4)	0.0199(5)	0	0	0.00968(18)	0.0195(3)
M(7)	0.11707(6)	0.41594(6)	0.04879(2)	0.0110(2)	0.0112(2)	0.0228(2)	0.00191(15)	0.00005(15)	0.00599(16)	0.01480(12)
M(8)	⅓	⅔	0.03497(2)	0.0128(6)	0.0128(6)	0.0189(8)	0	0	0.0064(3)	0.0148(5)
M(9)	0.13869(12)	0.42033(12)	0.00011(2)	0.0086(4)	0.0100(4)	0.0220(5)	0.0006(3)	−0.0005(3)	0.0050(3)	0.0133(3)
T(1)	⅔	⅓	0.07322(2)	0.0084(5)	0.0084(5)	0.0152(7)	0	0	0.0042(2)	0.0107(4)
T(2)	⅔	⅓	0.04910(2)	0.0095(4)	0.0095(4)	0.0263(6)	0	0	0.0047(2)	0.0151(4)
T(3)	⅓	⅔	0.06197(2)	0.0084(5)	0.0084(5)	0.0157(7)	0	0	0.0042(2)	0.0108(4)
T(4)	0	0	0.08053(2)	0.0085(3)	0.0085(3)	0.0167(4)	0	0	0.00426(14)	0.0113(3)
O(1)	⅓	⅔	0.00608(2)	0.0172(11)	0.0172(11)	0.0126(15)	0	0	0.0086(5)	0.0157(7)
O(2)	0.1357(3)	0.6302(3)	0.06513(2)	0.0098(8)	0.0135(9)	0.0187(9)	0.0005(7)	0.0000(7)	0.0064(7)	0.0138(4)
O(3)	0.3802(3)	0.4809(3)	−0.00480(2)	0.0143(9)	0.0148(10)	0.0241(11)	0.0000(8)	0.0001(8)	0.0064(8)	0.0181(4)
O(4)	0.4667(3)	0.3072(3)	0.02861(2)	0.0227(11)	0.0159(10)	0.0206(10)	−0.0011(8)	−0.0021(8)	0.0118(9)	0.0188(4)
O(5)	0.5177(3)	0.1279(3)	0.07632(2)	0.0113(9)	0.0093(8)	0.0199(9)	0.0017(7)	−0.0023(7)	0.0022(7)	0.0148(4)
O(6)	0.2150(3)	0.0535(3)	0.04126(2)	0.0110(9)	0.0217(10)	0.0201(10)	−0.0007(8)	−0.0010(8)	0.0085(8)	0.0175(4)
O(7)	0.1489(3)	0.4350(3)	0.02948(2)	0.0145(9)	0.0166(10)	0.0213(10)	−0.0031(8)	−0.0014(8)	0.0092(8)	0.0168(4)
O(8)	0.3955(3)	0.5056(3)	0.04157(2)	0.0213(11)	0.0129(9)	0.0239(11)	−0.0010(8)	−0.0052(8)	0.0087(9)	0.0192(4)
O(9)	0.2140(3)	0.0406(3)	0.01800(2)	0.0180(10)	0.0131(9)	0.0212(10)	0.0007(8)	0.0021(8)	0.0080(8)	0.0173(4)
O(10)	⅔	⅓	0.04143(2)	0.0217(12)	0.0217(12)	0.025(2)	0	0	0.0108(6)	0.0228(8)
O(11)	0.1837(3)	0.2310(3)	0.05357(2)	0.0141(9)	0.0124(9)	0.0207(10)	−0.0005(7)	−0.0023(8)	0.0077(8)	0.0152(4)
O(12)	0.3874(3)	0.5042(3)	0.01706(2)	0.0192(10)	0.0166(10)	0.0252(11)	0.0016(8)	−0.0006(8)	0.0109(9)	0.0194(4)
O(13)	⅔	⅓	0.06525(2)	0.0120(9)	0.0120(9)	0.0136(15)	0	0	0.0060(5)	0.0126(6)
O(14)	0.2361(3)	0.0728(3)	0.06569(2)	0.0126(9)	0.0126(9)	0.0197(9)	0.0017(7)	0.0007(7)	0.0067(8)	0.0148(4)
O(15)	⅓	⅔	0.07806(2)	0.0169(11)	0.0169(11)	0.0151(16)	0	0	0.0084(5)	0.0163(7)
O(16)	0.2033(3)	0.2537(3)	0.00570(2)	0.0168(10)	0.0147(9)	0.0227(11)	0.0004(8)	0.0000(8)	0.0070(8)	0.0185(4)
O(17)	0.6382(3)	0.4995(3)	0.05278(2)	0.0136(9)	0.0097(8)	0.0189(9)	0.0011(7)	0.0006(7)	0.0071(7)	0.0135(4)

O(18)	⅓	⅔	0.05398(2)	0.0122(9)	0.0122(9)	0.0125(15)	0	0	0.0061(5)	0.0123(6)
O(19)	0.1602(3)	0.2078(3)	0.07772(2)	0.0118(9)	0.0113(9)	0.0190(9)	0.0013(7)	−0.0010(7)	0.0049(8)	0.0145(4)
O(20)	0	0	0.03011(2)	0.0181(11)	0.0181(11)	0.0127(15)	0	0	0.0090(5)	0.0163(7)
X	⅔	⅓	0.01822(11)	0.048(7)						
Mcgovernite										
$As(1)$	⅓	⅔	0.01451(2)	0.0147(3)	0.0147(3)	0.0190(4)	0	0	0.00736(13)	0.0161(2)
$As(2)$	0	0	0.03846(2)	0.0134(3)	0.0134(3)	0.0173(4)	0	0	0.00669(13)	0.01469(19)
$As(3)$	⅔	⅓	0.02403(2)	0.0154(4)	0.0154(4)	0.0166(5)	0	0	0.00770(19)	0.0158(3)
$Z(1)$	0	0.27384(11)	¼	0.0195(5)	0.0177(4)	0.0229(5)	−0.00138(16)	−0.0028(3)	0.0097(2)	0.0198(3)
$Z(2)$	0.4727(15)	0.0857(14)	0.02385(5)	0.022(5)	0.015(5)	0.020(5)	0.000(3)	0.000(3)	0.008(4)	0.019(3)
$M(1)$	0.68743(11)	0.10966(11)	0.06029(2)	0.0139(4)	0.0134(4)	0.0203(4)	0.0008(3)	−0.0004(3)	0.0069(3)	0.0159(3)
$M(2)$	0.21647(12)	0.25938(12)	0.02374(2)	0.0194(4)	0.0162(4)	0.0208(4)	−0.003(3)	−0.0029(3)	0.0098(3)	0.0184(3)
$M(3)$	0.64752(13)	0.55621(13)	0.03537(2)	0.0148(5)	0.0153(5)	0.0216(5)	−0.0015(3)	0.0001(3)	0.0083(4)	0.0169(3)
$M(4)$	0	0	0.06005(2)	0.0137(6)	0.0137(6)	0.0201(8)	0	0	0.0068(3)	0.0158(5)
$M(5)$	0.11057(11)	0.40352(11)	0.07208(2)	0.0147(4)	0.0138(4)	0.0203(4)	0.0011(3)	0.0010(3)	0.0066(3)	0.0165(3)
$M(6)$	0	0	0.01041(2)	0.0202(6)	0.0202(6)	0.0203(8)	0	0	0.0101(3)	0.0203(5)
$M(7)$	0.11596(11)	0.41598(11)	0.04901(2)	0.0148(4)	0.0150(4)	0.0242(4)	0.0020(3)	−0.0009(3)	0.0075(3)	0.01799(19)
$M(8)$	⅓	⅔	0.03506(2)	0.0152(10)	0.0152(10)	0.0192(14)	0	0	0.0076(5)	0.0165(8)
$M(9)$	0.1383(2)	0.4194(2)	0.00010(2)	0.0110(7)	0.0121(7)	0.0215(8)	0.0006(5)	0.0001(5)	0.0061(5)	0.0147(4)
$T(1)$	⅔	⅓	0.07367(2)	0.0116(6)	0.0116(6)	0.0159(8)	0	0	0.0058(3)	0.0131(5)
$T(2)$	⅔	⅓	0.04934(2)	0.0125(7)	0.0125(7)	0.0237(10)	0	0	0.0063(3)	0.0163(6)
$T(3)$	⅓	⅔	0.06202(2)	0.0111(8)	0.0111(8)	0.0143(11)	0	0	0.0056(4)	0.0122(7)
$T(4)$	0	0	0.08066(2)	0.0113(6)	0.0113(6)	0.0153(8)	0	0	0.0057(3)	0.0127(5)
O(1)	⅓	⅔	0.00613(3)	0.0210(19)	0.0210(19)	0.014(3)	0	0	0.0105(10)	0.0186(12)
O(2)	0.1349(5)	0.6293(5)	0.06517(2)	0.0147(16)	0.0192(17)	0.0183(16)	0.0018(13)	0.0014(13)	0.0089(14)	0.0172(7)
O(3)	0.3799(5)	0.4806(5)	−0.00484(2)	0.0176(17)	0.0178(17)	0.0212(17)	−0.0017(13)	0.0002(13)	0.0091(14)	0.0188(7)
O(4)	0.4682(6)	0.3073(6)	0.02872(2)	0.0220(19)	0.0192(18)	0.0238(18)	−0.0008(14)	−0.0023(14)	0.0115(15)	0.0211(7)
O(5)	0.5319(5)	0.1195(5)	0.07658(2)	0.0125(15)	0.0117(15)	0.0223(16)	0.0012(13)	−0.0016(13)	0.0025(13)	0.0170(7)
O(6)	0.2153(5)	0.0551(6)	0.04136(2)	0.0143(17)	0.0249(19)	0.0220(17)	−0.0018(14)	−0.0025(14)	0.0101(15)	0.0203(7)
O(7)	0.1494(5)	0.4350(6)	0.02954(2)	0.0185(17)	0.0215(18)	0.0204(17)	−0.0022(14)	−0.0006(14)	0.0117(15)	0.0194(7)
O(8)	0.4001(6)	0.5083(6)	0.04161(2)	0.0249(19)	0.0188(18)	0.0253(18)	−0.0014(14)	−0.0048(15)	0.0127(16)	0.0222(8)
O(9)	0.2116(6)	0.0395(5)	0.01799(2)	0.0241(19)	0.0161(17)	0.0220(18)	0.0006(14)	0.0031(14)	0.0103(15)	0.0206(7)
O(10)	⅔	⅓	0.04158(3)	0.022(2)	0.022(2)	0.026(3)	0	0	0.0112(10)	0.0235(14)
O(11)	0.1834(5)	0.2313(5)	0.05373(2)	0.0202(18)	0.0188(17)	0.0209(17)	−0.0003(14)	−0.0013(14)	0.0110(15)	0.0194(7)
O(12)	0.3880(6)	0.5048(6)	0.01713(2)	0.0246(19)	0.0200(18)	0.0251(19)	0.0027(14)	−0.0007(15)	0.0146(16)	0.0217(8)
O(13)	⅔	⅓	0.06555(3)	0.0173(18)	0.0173(18)	0.017(3)	0	0	0.0086(9)	0.0172(12)
O(14)	0.2387(5)	0.0742(5)	0.06600(2)	0.0155(16)	0.0156(16)	0.0212(17)	0.0027(13)	0.0005(13)	0.0073(14)	0.0177(7)
O(15)	⅓	⅔	0.07789(3)	0.0172(18)	0.0172(18)	0.015(3)	0	0	0.0086(9)	0.0165(12)
O(16)	0.1996(6)	0.2492(5)	0.00582(2)	0.0193(18)	0.0191(18)	0.0236(18)	−0.0004(14)	−0.0008(14)	0.0100(15)	0.0205(7)

(continued)

TABLE 3. (*contd.*)

Site	x	y	z	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	U_{eq}
O(17)	0.6382(5)	0.4990(5)	0.05299(2)	0.0178(17)	0.0143(16)	0.0190(16)	0.0001(13)	0.0008(13)	0.0095(14)	0.0164(7)
O(18)	⅓	⅔	0.05401(3)	0.0174(17)	0.0174(17)	0.013(2)	0	0	0.0087(9)	0.0159(11)
O(19)	0.1609(5)	0.2067(5)	0.07781(2)	0.0137(15)	0.0132(15)	0.0177(16)	0.0016(12)	−0.0018(12)	0.0052(13)	0.0155(7)
O(20)	0	0	0.03018(3)	0.0227(19)	0.0227(19)	0.011(2)	0	0	0.0114(10)	0.0187(12)
LP	⅔	⅓	0.0186(2)	0.032(14)						

chemical analysis (Table 1). The observed equivalent isotropic-displacement parameters U_{eq} in each refinement (Table 3) are in accord with these site-scattering values which match with the presence of As (plus minor V^{5+} and P) in the chemical compositions determined by electron-microprobe analysis (Table 1).

There is one Z(1) site that is [4]-coordinated with refined site-scattering values of 75.7 and 87.1 epfu. From the refined site-scattering values, the possibilities for occupancy of this site are Mn^{2+} in carlfrancisite and (Mn^{2+},Zn) in mcgovernite (Table 1). The <Z(1)–O> distances are 2.091 Å in carlfrancisite and 1.989 Å in mcgovernite, in accord with occupancy by Mn^{2+} and Zn, respectively.

The T(1), T(2), T(3) and T(4) sites in both structures are [4]-coordinated and the <T–O> distances range from ~1.632 to 1.656 Å (Table 4). The refined site-scattering values range from 27.1 to 49.6 epfu (Table 5) which, in combination with the chemical formulae (Table 1), indicate that these sites contain Si in solid solution with a heavier cation. The refined site-scattering values constrain the second cation to be As, and the coordination number and observed <T–O> distances indicate that it is As^{5+}. This being the case, the Si and As site-populations were derived from the refined site-scattering values and the resultant values are given in Table 5. The mean bond-lengths should be related to the site populations, and this is shown to be the case for the T and As sites in both structures in Fig. 1.

There are nine M sites, all of which are octahedrally coordinated and contain dominantly Mn^{2+} and Mg as indicated by the unit formulae calculated from the electron-microprobe analyses (Table 1). Site-scattering refinement shows that that six M sites have dominant Mn^{2+}, and the remaining M sites have dominant Mg (Table 5). As indicated by the unit formulae (Table 5), the M sites also contain minor Al and Fe. The <M–O> distances range from ~2.09 to 2.25 Å (Table 4), and comparison of the observed mean incident bond-valences suggests that the minor Al and Fe may occur at the M(8) and M(9) sites. The Mg and Mn site-populations were initially assigned from the refined site-scattering values.

Sites involving vacancies

As noted above, the As(3), Z(2) and M(3) sites are involved in short interatomic separations such that both sites in each local pair of sites cannot each be occupied, forcing the occurrence of vacancies at each of these sites.

1106

TABLE 4. Selected interatomic distances (Å) in carlfrancisite and mcgovernite.

	Carlfrancisite	Mcgovernite		Carlfrancisite	Mcgovernite
$T(1)$–O(5),b,c	1.640(2)	1.647(4)	$T(2)$–O(17),b,c	1.677(2)	1.667(4)
$T(1)$–O(13)	<u>1.635(4)</u>	<u>1.659(7)</u>	$T(2)$–O(10)	<u>1.572(5)</u>	<u>1.584(7)</u>
$<T(1)$–O>	1.639	1.650	$<T(2)$–O>	1.651	1.646
$T(3)$–O(2),e,f	1.633(2)	1.630(4)	$T(4)$–O(19),a,d	1.654(2)	1.649(4)
$T(3)$–O(18)	<u>1.638(4)</u>	<u>1.635(6)</u>	$T(4)$–O(15),j	<u>1.657(4)</u>	<u>1.656(6)</u>
$<T(3)$–O>	1.634	1.632	$<T(4)$–O>	1.655	1.651
$As(1)$–O(12),e,f	1.692(2)	1.688(4)	$As(2)$–O(6),a,d	1.700(2)	1.696(4)
$As(1)$–O(1)	<u>1.716(4)</u>	<u>1.709(7)</u>	$As(2)$–O(20)	<u>1.697(4)</u>	<u>1.691(7)</u>
$<As(1)$–O>	1.698	1.694	$<As(2)$–O>	1.699	1.695
$As(3)$–O(4),b,c	1.817(3)	1.807(4)	$Z(1)$–O(5),i	2.070(2)	1.978(4)
$As(3)$–X	1.18(2)	1.11(5)	$Z(1)$–O(19)b,h	<u>2.112(2)</u>	<u>1.999(4)</u>
			$<Z(1)$–O>	2.091	1.989
$Z(2)$–O(4)	2.083(5)	2.089(11)	$As(3)$–Z(2),b,c	1.857(4)	1.852(10)
$Z(2)$–O(4),b	1.879(5)	1.874(11)			
$Z(2)$–O(7),d	2.110(5)	2.113(11)	$Z(2)$–As(3)	1.856(5)	1.852(10)
$Z(2)$–O(9)	2.296(5)	2.315(11)	$Z(2)$–Mn(3)	2.364(5)	2.365(10)
$Z(2)$–O(12),b	<u>2.256(5)</u>	<u>2.233(11)</u>	$Z(2)$–X	2.185(13)	2.14(3)
$<Z(2)$–O>	2.125	2.125			
$M(1)$–O(2),d	2.115(2)	2.086(4)	$M(2)$–O(4)	2.156(2)	2.154(4)
$M(1)$–O(11),b	2.178(2)	2.184(4)	$M(2)$–O(7)	2.145(2)	2.139(4)
$M(1)$–O(13)	2.206(2)	2.205(3)	$M(2)$–O(9)	2.136(2)	2.136(4)
$M(1)$–O(14),b	2.137(2)	2.123(4)	$M(2)$–O(9),a	2.188(2)	2.191(4)
$M(1)$–O(17),b	2.235(2)	2.233(4)	$M(2)$–O(12)	2.251(2)	2.242(4)
$M(1)$–O(17),c	<u>2.366(3)</u>	<u>2.362(4)</u>	$M(2)$–O(20)	<u>2.373(2)</u>	<u>2.373(4)</u>
$<M(1)$–O>	2.206	2.199	$<M(2)$–O>	2.208	2.206
$M(3)$–O(4)	2.283(2)	2.275(4)	$M(3)$–Z(2)	2.364(4)	2.369(11)
$M(3)$–O(4),c	2.179(2)	2.162(4)			
$M(3)$–O(6),c	2.139(2)	2.131(4)	$M(4)$–O(11),a,d	2.142(2)	2.162(4)
$M(3)$–O(7),e	2.111(2)	2.107(4)	$M(4)$–O(14),a,d	<u>2.118(2)</u>	<u>2.118(4)</u>
$M(3)$–O(8)	2.289(3)	2.259(4)	$<M(4)$–O>	2.130	2.140
$M(3)$–O(10)	<u>2.288(3)</u>	<u>2.294(4)</u>			
$<M(3)$–O>	2.215	2.205			
$M(5)$–O(2)	2.246(2)	2.257(4)	$M(6)$–O(16),a,d	2.133(2)	2.096(4)
$M(5)$–O(2),e	2.325(2)	2.336(4)	$M(6)$–O(9),a,d	<u>2.262(2)</u>	<u>2.225(5)</u>
$M(5)$–O(5),a	2.108(2)	2.133(4)	$<M(6)$–O>	2.197	2.161
$M(5)$–O(14),a	2.160(2)	2.171(4)			
$M(5)$–O(15)	2.418(2)	2.337(3)	$M(8)$–O(7),e,f	2.075(2)	2.072(4)
$M(5)$–O(19)	<u>2.207(2)</u>	<u>2.195(4)</u>	$M(8)$–O(8),e,f	<u>2.128(2)</u>	<u>2.118(4)</u>
$<M(5)$–O>	2.244	2.238	$<M(8)$–O>	2.102	2.095

(continued)

TABLE 4. (*contd.*)

	Carlfrancisite	Mcgovernite		Carlfrancisite	Mcgovernite
$M(7)$–O(6),a	2.408(2)	2.423(4)	$M(9)$–O(1)	2.219(2)	2.225(4)
$M(7)$–O(8)	2.508(3)	2.554(4)	$M(9)$–O(3)	2.054(2)	2.050(4)
$M(7)$–O(8),f	2.166(2)	2.159(4)	$M(9)$–O(3),f	2.078(2)	2.082(4)
$M(7)$–O(11)	2.100(2)	2.090(4)	$M(9)$–O(3),g	2.065(2)	2.062(4)
$M(7)$–O(17),f	2.087(2)	2.076(4)	$M(9)$–O(16)	2.050(2)	2.067(4)
$M(7)$–O(18)	2.209(2)	2.188(3)	$M(9)$–O(16),g	2.061(3)	2.076(4)
<$M(7)$–O>	2.246	2.249	<$M(9)$–O>	2.088	2.094

a: –*y*, *x*–*y*, *z*; b: 1–*y*, *x*–*y*, *z*; c: 1–*x* + *y*, 1–*x*, *z*; d: *y*–*x*, –*x*, *z*; e: 1–*y*, 1 + *x*–*y*, *z*; f: *y*–*x*, 1–*x*, *z*; g: *x*–*y*, *x*, –*z*; h: *y* + 1/3, *x*–1/3, –*z* + 1/6; i: 4/3–*x*, 2/3–*x* + *y*, 1/6–*z*; j: *y*–2/3, *x*–1/3, –*z* + 1/6.

As(3) site

The $As(3)$ site has triangular pyramidal coordination with <$As(3)$–O> distances of 1.817 and 1.808 Å typical of As^{3+} (Majzlan *et al.*, 2014). The only constituent in either structure that is compatible with the observed stereochemistry is As^{3+}. Moreover, a weak peak is observed in each structure (labelled X in Tables 3 and 4) ~1.1–1.2 Å from the $As(3)$ site. One may interpret X in two ways: [1] X lies on the opposite side of the $As(3)$ site to the anions bonded to the As^{3+} cation, and is characteristic of the stereoactive lone-pair of electrons expected for As^{3+}. The refined site-scattering values (Table 5) for both structures indicate only partial occupancy by As^{3+} and the rest of the site must be vacant as there is no other constituent in the structure that is compatible with the local stereochemistry. [2] X lies 2.14–2.18 Å from the $Z(2)$ site and its occupancy when considered as an O anion equals that of the $Z(2)$ cation, with a $Z(2)$–X distance of ~2.16 Å. Whichever interpretation is correct, it does not affect the cation order in the rest of the structure. Hence the site populations of Table 5 were so assigned.

Z(2) site

Additional scattering ~2.3 Å from the $As(3)$ site was located in the difference-Fourier maps of both structures. This was designated the $Z(2)$ site, and the site-scattering values at both the $As(3)$ and $Z(2)$ sites were refined independently, initially using As and Mn scattering factors. The arrangement of the $Z(2)$ and $As(3)$ sites in adjacent layers of the structure are shown in Fig. 2. The $(As^{3+}O_3)$ group shares three O–O edges with adjacent $Z(2)$ octahedra, with $As(3)$–$Z(2)$ distances of ~1.85 Å, precluding simultaneous local occupancy of one $As(3)$ site and three $Z(2)$ sites. The site populations

of the $As(3)$ site in carlfrancisite and mcgovernite are 1.62 As^{3+} + 0.38 □ and 1.70 As^{3+} + 0.30 □, respectively. Thus the $Z(2)$ sites in carlfrancisite and mcgovernite must have a minimum of 1.62 × 3 = 4.86 □ and 1.70 × 3 = 5.10 □ pfu, respectively.

There are two possibilities as to the occupancy of the $Z(2)$ site in each structure: [1] there are 1.14 and 0.90 pfu of cations occupying $Z(2)$; in this case, the cations give scattering corresponding to 15.2 and 12.4 electrons per cation, i.e. dominantly Mg in each case, with a small amount of Mn^{2+}. [2] There are additional vacancies at the $Z(2)$ site in each structure, and $Z(2)$ is occupied by cations of a higher scattering power than Mg. The possible cations occupying $Z(2)$ in this case are Mn^{2+} in carlfrancisite and (Mn^{2+}, Zn) in mcgovernite. In this case, the refined scattering values at $Z(2)$ correspond to 0.69 Mn^{2+} + 0.45 □ in carlfrancisite and 0.45 Mn^{2+} + 0.45 □ or 0.37 Zn + 0.53 □ pfu in mcgovernite (Table 6). The $Z(2)$ site is surrounded by five O anions in a square-pyramidal arrangement, with <$Z(2)$–O> distances of 2.126 and 2.125 Å (Table 4) in carlfrancisite and mcgovernite, respectively. As the $Z(2)$ site is dominantly vacant in each structure, these distances are dictated primarily by the arrangement where $Z(2)$ is vacant rather than where it is occupied by cations. The site populations for the two models are given in Table 6.

M(3) site

The $Z(2)$ square pyramid links to three $M(3)$ octahedra (Fig. 3). It shares an edge with one $M(3)$ octahedron (shown as a thick dashed line in Fig. 3) and a vertex with two other $M(3)$ octahedra. The $Z(2)$–$M(3)$ distance across this shared edge is ~2.365 Å in both structures and precludes simultaneous local occupancy of these two sites. Thus each occupied $Z(2)$ must be locally associated with a

TABLE 5. Site-scattering values and assigned site-populations in carlfrancisite and mcgovernite.

	Refined site-scattering (epfu)		Coordination number, mean bond length (Å)		Assigned site-populations (apfu)	
	Carlfrancisite	Mcgovernite	Carlfrancisite	Mcgovernite	Carlfrancisite	Mcgovernite
$As(1)*$	66	66	[4] 1.698	[4] 1.694	2 As^{5+}	2 As^{5+}
$As(2)*$	66	66	[4] 1.699	[4] 1.695	2 As^{5+}	2 As^{5+}
$As(3)$	53.6(2)	56.1(4)	[3] 1.817	[3] 1.807	1.62 As^{3+} + 0.38 □	1.70 As^{3+} + 0.30 □
$Z(1)$	75.7(3)	87.1(5)	[4] 2.091	[4] 1.989	3.00 Mn^{2+}	2.90 Zn
$Z(2)$	17.3(4)	11.2(6)	[5] 2.125	[5] 2.125	See Table 6	See Table 6
$T(1)*$	28.9(2)	35.8(3)	[4] 1.639	[4] 1.650	1.95 Si + 0.05 As^{5+}	1.59 Si + 0.41 As^{5+}
$T(2)*$	34.9(2)	33.6(3)	[4] 1.651	[4] 1.646	1.56 Si + 0.44 As^{5+}	1.71 Si + 0.29 As^{5+}
$T(3)*$	28.3(2)	27.5(3)	[4] 1.634	[4] 1.632	1.98 Si + 0.02 As^{5+}	2.00 Si
$T(4)*$	44.8(2)	36.5(3)	[4] 1.655	[4] 1.651	1.12 Si + 0.88 As^{5+}	1.55 Si + 0.45 As^{5+}
$M(1)$	145.0(4)	140.6(7)	[6] 2.206	[6] 2.199	5.62 Mn^{2+} + 0.48 Mg	5.28 Mn^{2+} + 0.72 Mg
$M(2)$	145.1(5)	144.1(7)	[6] 2.208	[6] 2.206	5.62 Mn^{2+} + 0.48 Mg	5.55 Mn^{2+} + 0.45 Mg
$M(3)$	123.3(5)	129.1(7)	[6] 2.215	[6] 2.205	See Table 6	See Table 6
$M(4)$	33.0(2)	40.3(4)	[6] 2.130	[6] 2.140	0.69 Mn^{2+} + 1.31 Mg	1.25 Mn^{2+} + 0.75 Mg
$M(5)$	154.1(6)	147.5(7)	[6] 2.244	[6] 2.238	6 Mn^{2+}	5.81 Mn^{2+} + 0.19 Mg
$M(6)$	48.9(2)	44.7(4)	[6] 2.197	[6] 2.161	1.92 Mn^{2+} + 0.08 Mg	1.59 Mn^{2+} + 0.41 Mg
$M(7)$	150	150	[6] 2.246	[6] 2.249	6 Mn^{2+}	6 Mn^{2+}
$M(8)**$	28.2(3)	27.5(4)	[6] 2.102	[6] 2.095	0.32 Mn^{2+} + 1.68 Mg	0.27 Mn^{2+} + 1.73 Mg
$M(9)**$	79.7(4)	86.3(7)	[6] 2.088	[6] 2.094	0.41 Mn^{2+} + 5.59 Mg	1.10 Mn^{2+} + 4.90 Mg

*includes minor V^{5+} and P;
**includes minor Al.

TABLE 6. Site occupancies for the $As(3)$, $Z(2)$ and $M(3)$ sites.

	Refined site-scattering	Site occupancy	Model [1][1]	Model [2][1]
			Carlfrancisite	
$As(3)$	53.6(2)	1.62 As^{3+} + 0.38 $\square$		
$Z(2)$	17.3(4)		0.86 Mg + 0.28 Mn^{2+} + 4.86 $\square$	0.69 Mn^{2+} + 5.31 $\square$
$M(3)$	123.3(5)		4.93 Mn^{2+} + 1.07 $\square$	0.73 Mg + 4.58 Mn^{2+} + 0.69 $\square$
			Mcgovernite	
$As(3)$	56.1(4)	1.70 As^{3+} + 0.30 $\square$		
$Z(2)$	11.2(6)		0.87 Mg + 0.03 Mn^{2+} + 5.10 $\square$	0.45 Mn^{2+} + 5.55 $\square$
				0.37 Zn + 5.63 $\square$
$M(3)$	129.1(7)		5.16 Mn^{2+} + 0.84 $\square$	0.90 Mg + 4.73 Mn^{2+} + 0.37 $\square$

[1]see text

vacant $M(3)$ site across the edge shared between the constituent polyhedra. The ranges of cation content at $Z(2)$ from the two models described above are as follows: 0.69–1.14 for carlfrancisite and 0.37–0.90 apfu for mcgovernite (Table 6). As each cation at $Z(2)$ must be locally associated with a vacancy at $M(3)$, the ranges of vacancy content at $M(3)$ for carlfrancisite and mcgovernite are 0.69–1.14 and 0.37–0.90 pfu, respectively.

There are two ways to assign cations to the $M(3)$ site: [1] we may calculate the Mn^{2+} content from the refined site-scattering value and compare the resulting vacancy content with the range dictated by the occupancy of the $Z(2)$ site; [2] we may fix the vacancy content at the minimum value allowed by the occupancy of the associated $Z(2)$ site and calculate the Mn^{2+} and Mg contents from the refined site-scattering values. These two sets of values are given in Table 6. The chemical composition of the two models are the same, they just have a different distribution of cations and vacancies over the $Z(2)$ and $M(3)$ sites.

Anion sites

For the long-range structure, all anions coordinating the cations at the As and T sites are oxygen (O^{2-}) and all anions not coordinating the cations at the As and T sites are $(OH)^-$ groups, as indicated by the bond valences incident at each anion (Table 7).

Short-range order

Short-Range Order (SRO) involves the local occupancies of individual (i.e. non-averaged) sites over a scale of a few Å in a crystal structure. Information on disorder and local structure can, in

principle, be derived from diffuse (non-Bragg) scattering or via several spectroscopic techniques. However, this information is not easy to extract from the diffuse scattering as the weak intensities involved may not easily be distinguished from background noise, particularly where the disorder is complicated (Hawthorne, 2016). An alternative approach is to apply bond-valence theory (Brown, 2002, 2016) to local atomic-arrangements in minerals (Hawthorne 1996, 1997, 2016; Hawthorne et al., 1993, 1996), and that is what I shall do now.

There are three sites involved in SRO of cations: $As(3)$, $Z(2)$, $M(3)$, and their coordinating anions will be greatly affected by the presence of vacancies and/or cations at these three sites. Inspection of Table 6 shows that there are two distinct arrangements in the local structure around these three sites: [1] $Z(3)$ occupied, $As(3)$ and $M(3)$ vacant; [2] $Z(3)$ vacant, $As(3)$ and $M(3)$ occupied. The O(4) anion is of particular importance with regard to incident bond-valence as it is close to the $As(3)$, $Z(2)$, $M(3)$ ×2 and $M(2)$ sites. The environment of the O(4) anion is shown in Table 8. Where the $Z(2)$ site is vacant, the bond valence incident at O(4) sums to 1.90 and 1.94 valence units (vu), in carlfrancisite and mcgovernite respectively, indicating that the O(4) site is occupied by O^{2-} in this arrangement. Where the $Z(2)$ site is occupied, there are two $Z(2)$ sites adjacent to the O(4) site. The site population at the (long-range) $Z(2)$ site is ~1(Mn^{2+},Mg) + 5 $\square$ pfu, and hence the two $Z(2)$ sites locally adjacent to O(4) are unlikely to both be occupied if they show a random distribution. In this case, the incident bond valence at O(4) is 1.04 and 1.02 vu. if the closer $Z(2)$ site is occupied, and O(4) is an (OH) group. If the closer $Z(2)$ site is vacant, the further $Z(2)$ site is occupied by Mg and the $M(2)$ site is

TABLE 7. Bond-valence table for carlfrancisite.

	As(1)	As(2)	As(3)	Z(1)	Z(2)	M(1)	M(2)	M(3)	M(4)	M(5)	M(6)	M(7)	M(8)	M(9)	T(1)	T(2)	T(3)	T(4)	Σ
O(1)	1.15													**0.26$^{\times3}$**					1.93
O(2)						0.41				0.30, 0.25							0.98$^{\times3}$		1.94
O(3)														0.37, 0.35, 0.36					1.08
O(4)			*0.73$^{\times3}$*		*0.20, 0.31*		0.37	*0.22, 0.28*											
O(5)				0.45						0.41					0.97$^{\times3}$				1.83
O(6)		1.20$^{\times3}$						*0.31*				0.20							
O(7)						*0.18*	0.38	*0.33*					0.36$^{\times3}$						
O(8)								*0.22*				0.16, 0.36	0.32$^{\times3}$						
O(9)					*0.12*		0.38, 0.34				0.28$^{\times3}$								
O(10)								*0.22$^{\times3}$*								1.27			
O(11)						0.35			0.33$^{\times3}$			0.42							1.10
O(12)	1.23$^{\times3}$				*0.13*		0.29												
O(13)						**0.33$^{\times3}$**										0.98			1.97
O(14)						0.39			0.35$^{\times3}$	0.37									1.11
O(15)										**0.20$^{\times3}$**								1.11	1.71
O(16)											0.39$^{\times3}$		0.38, 0.37						1.14
O(17)						0.31, 0.22						0.44					0.96$^{\times3}$		1.93
O(18)												**0.33$^{\times3}$**						0.97	1.96
O(19)				0.41$^{\times3}$						0.33								1.12$^{\times3}$	1.86
O(20)		1.21					**0.22$^{\times3}$**												1.87
Σ	4.84	4.81	2.20	1.68	0.94	2.00	1.99	1.58	2.02	1.86	2.01	1.91	2.04	2.09	3.90	4.15	3.92	4.48	
Cation charge	5.00	5.00	2.43	2.00	1.14	2.00	2.00	1.62	2.00	2.00	2.00	2.00	2.00	2.00	4.03	4.22	4.00	4.44	

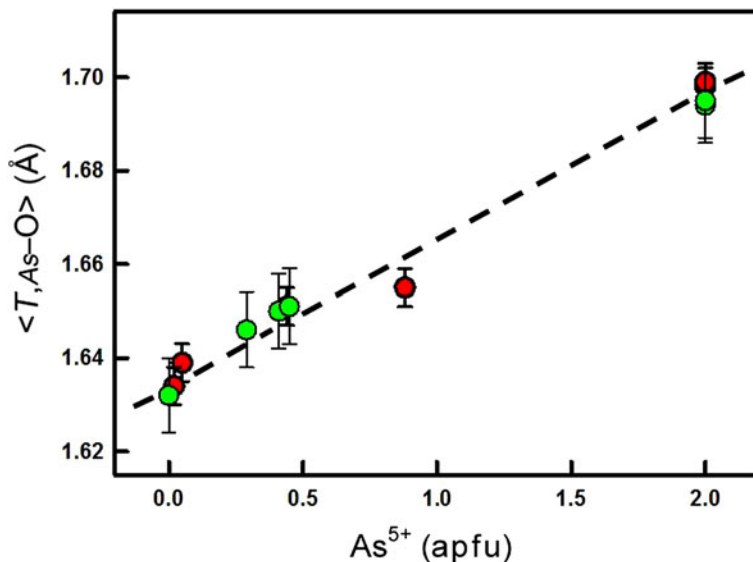Bold font indicates that the bond-valence sum is included in the sum to the right; italics indicates vacancies.

FIG. 1. Variation in $<T,^{[4]}As–O>$ as a function of the site population of As^{5+} in mcgovernite (green) and carlfrancisite (red).

occupied by Mg, the bond valence incident at O(4) is 0.69 and 0.63 vu in carlfrancisite and mcgovernite, respectively. In this case, O(4) must be (locally) an (H_2O) group. If both Z(2) sites are occupied, the incident bond valence at O(4) is ~1.5 vu, indicating that it is unlikely that both these sites
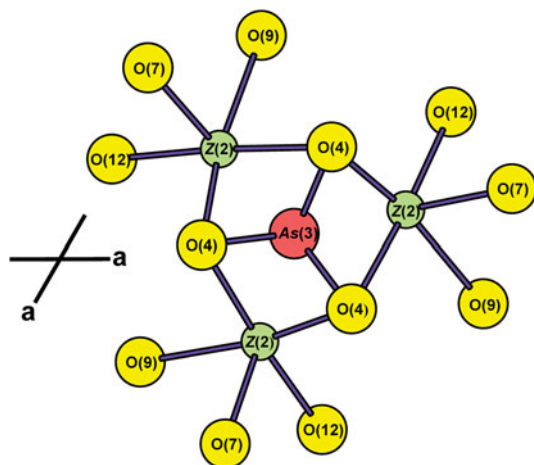

FIG. 2. The arrangement of Z(2) and As(3) sites in adjacent layers of the mcgovernite structure; these involve a Z(2)–As(3) approach of ~1.86 Å across common polyhedron edges, and polyhedra sharing these edges cannot both be locally occupied. Red circle: As(3); green circle: Z(2); yellow circles: anions.
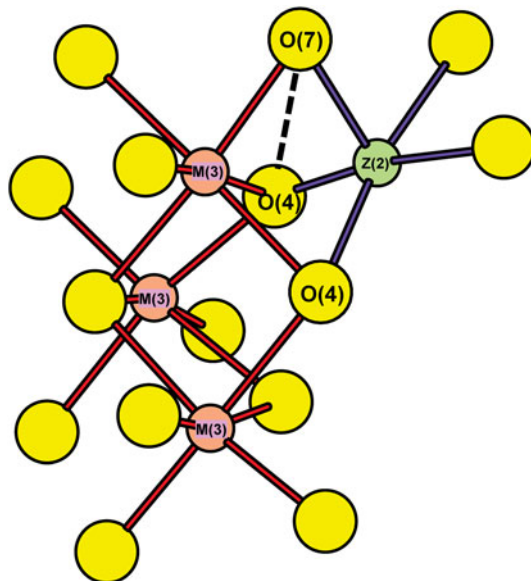
FIG. 3. The arrangement of Z(2) and M(3) sites in the mcgovernite structure: these involve a Z(2)–M(3) approach of 2.36 Å across a shared edge (one of which is shown by a thick dashed line) and the polyhedra across these edges cannot both be locally occupied. Pink circles: M(3), legend as in Fig. 2.

1112

TABLE 8. The short-range environment around O(4) in carlfrancisite and mcgovernite.

	Distance (Å)	Bond valence (vu)			
		Z(2) vacant	Z(2) occupied		
Carlfrancisite					
O(4)–As(3)	1.817	0.91			□
O(4)–Z(2)	1.879	□	0.67		□
O(4)–Z(2)′	2.083	□	□		0.44
O(4)–M(2)	2.156	0.37		0.29	
O(4)–M(3)	2.179	0.35		□	
O(4)–M(3)′	2.283	0.27		□	
Sum		1.90	1.04		0.69
Mcgovernite					
O(4)–As(3)	1.807	0.93			□
O(4)–Z(2)	1.874	□	0.73		□
O(4)–Z(2)′	2.089	□	□		0.34
O(4)–M(2)	2.154	0.37		0.29	
O(4)–M(3)	2.162	0.36		□	
O(4)–M(3)′	2.275	0.28		□	
Sum		1.94	1.02		0.63

are locally occupied. Thus the O(4) anion may be O^{2-} where the Z site is vacant and As(3) and M(3) are occupied, and either (OH) or (H_2O) or both where the Z site is occupied. The presence of (H_2O) is not apparent when considering only the long-range structure, but local bond-valence theory (Hawthorne, 1997) shows that (H_2O) is present.

The Raman spectrum of carlfrancisite (Hawthorne et al., 2013) has an intense envelope of absorption centred on $\sim$3550 cm^{-1} (Fig. 4) that has extensive fine-structure with numerous sharp bands characteristic of O–H stretching modes, in accord with the presence of numerous (OH) groups in the structure. However, there is a peak at $\sim$1600 cm^{-1} that is
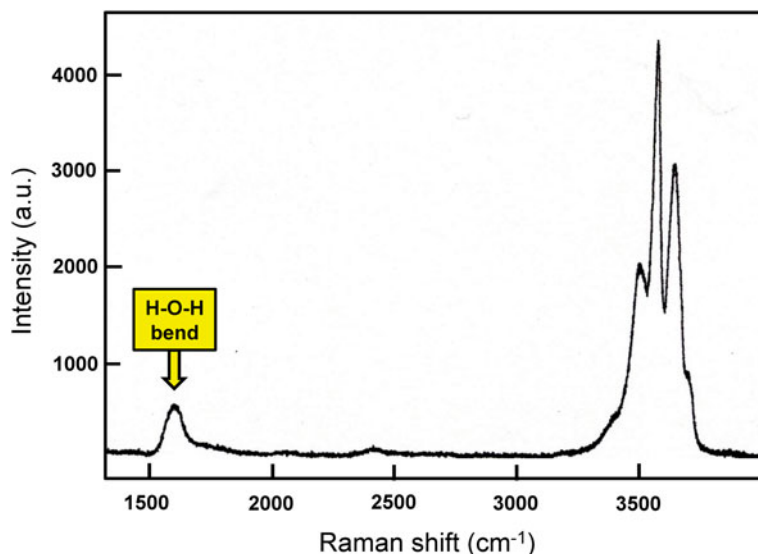
FIG. 4. The Raman spectrum of carlfrancisite; after Hawthorne et al. (2013).

1113

characteristic of the H–O–H bend of an (H_2O) group, in accord with the short-range arrangement of one $Z(2)$ cation and one $M(2)$ cation around (H_2O) at O(4) in carlfrancisite. The Raman spectrum of mcgovernite from RRUFF (Lafuente, 2015, http://rruff.info/mcgovernite/) contains only the faintest suggestion of intensity at ~1600 cm^{-1}, suggesting that the local order around O(4) in mcgovernite is somewhat different to that in carlfrancisite. Possibly the small amount of Fe in mcgovernite is trivalent rather than divalent (as I have assumed); in this case, possible ordering of Fe^{3+} at $Z(2)$ [or even $M(8)$ where Fe^{3+} would provide increased bond valence to O(7), allowing the $Z(2)$ cation to move toward O(4)] would provide sufficient incident bond valence to obviate the need for H_2O at O(4).

Bond topology

The carlfrancisite–mcgovernite structure contains 84 layers of approximately close-packed polyhedra that comprise one translation along **c**, giving this structure type the distinction of possessing the largest unit-cell parameter of any mineral. The anions in the structure are arranged in (generally close-packed) layers orthogonal to the **c**-axis. Fourteen layers stack along the **c**-axis in the sequence |**hhchch•hchchh| (* denotes a layer of anions displaced from close packed). The first eight anion layers (Fig. 5) repeat via a centre of symmetry (•) at the origin (within the layer $m = 0$). There are eight distinct layers of cation-centred polyhedra labelled $m = 0$–7 in Fig. 5, and these layers are shown in plan in Figs 6 and 7.

At $m = 0$ (Fig. 6a), the layer consists of an interrupted sheet of edge-sharing $M(9)$ octahedra that are occupied dominantly by Mg with

significant (~0.4–1.1 apfu) Mn^{2+}. The vacant octahedra in the sheet lie on the **c** axis. At $m = 1$ (Fig. 6b), the layer consists of a rather sparsely occupied sheet of unconnected (within the $m = 1$ sheet) $As(1)$ tetrahedra and $M(6)$ octahedra where $M(6)$ is occupied predominantly by Mn^{2+} but also contains significant (0.1–0.4 apfu) Mg. The $m = 2$ layer contains significant disorder (Fig. 7). There is a trimer of edge-sharing $M(2)$ octahedra occupied predominantly by Mn^{2+} but also containing significant (0.46 apfu) Mg, and this trimer is centred on the **c** axis in both arrangements of the $m = 2$ layer. In layer $m = 2A$ (Fig. 7a), the trimers are linked into a sheet by $As(3)$ trigonal pyramids that are present 1.66 / 2 × 100 = 83%, whereas in layer $m = 2B$ (Fig. 7b), the trimers are linked into a sheet by sharing edges with trimers of edge-sharing $Z(2)$ octahedra occupied by Mg, Mn^{2+} and Zn. At $m = 3$ (Fig. 6c), the layer consists of trimers of edge-sharing $M(3)$ octahedra occupied predominantly by Mn^{2+} but also containing significant (~2 apfu) Mg, linked into a sheet by sharing edges with M(8) octahedra, occupied predominantly by Mg but also containing some (~0.30 apfu) Mn^{2+}, and sharing corners with $As(2)$ tetrahedra completely occupied by As^{5+} in both carlfrancisite and mcgovernite. At $m = 4$ (Fig. 6d), the layer consists of trimers of edge-sharing $M(7)$ octahedra occupied by Mn^{2+} and linked by sharing corners with $T(2)$ tetrahedra occupied predominantly by Si with minor (~0.29–0.44 apfu) As^{5+}. At $m = 5$ (Fig. 6e), the layer consists of trimers of edge-sharing $M(1)$ octahedra occupied by Mn^{2+} (with significant Mg in mcgovernite) and linked by sharing edges with $M(4)$ octahedra that lie on the **c** axis and $T(3)$ tetrahedra that are dominated by Si; the $M(4)$
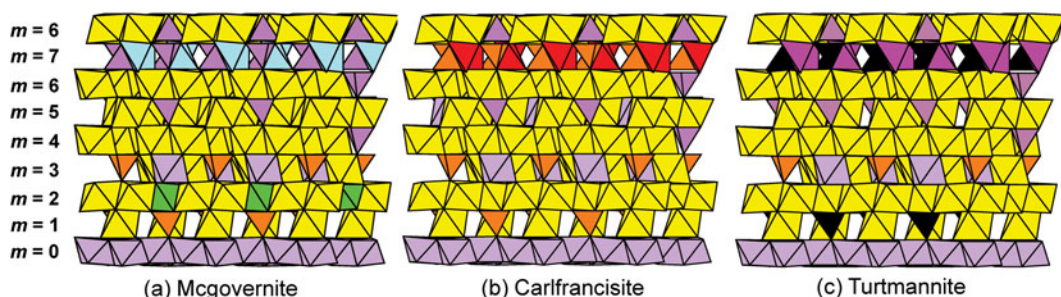

FIG. 5. Part of the crystal structures of mcgovernite, carlfrancisite and turtmannite projected along [100], showing the first eight distinct layers of cation-centred polyhedra labelled $m = 0$–7; note that the stacking sequence reverses at layer 7 (via a centre of symmetry) and the resulting 14-layer stacking comprises ⅙ of the **c**-axis repeat. The following cations and cation-centred coordination polyhedra correspond to the following colours in this and the following figures: Mn^{2+}: yellow, red at $Z(2)$ in carlfrancisite; As^{5+}: orange; Si^{4+}: purple; As^{3+}: dull green; Zn^{2+}: pale blue at $Z(1)$, bright green at $Z(2)$ in mcgovernite; Mg^{2+}: pale mauve; and V^{5+}: black. Layers are designated by the letter m where m = 0–7.
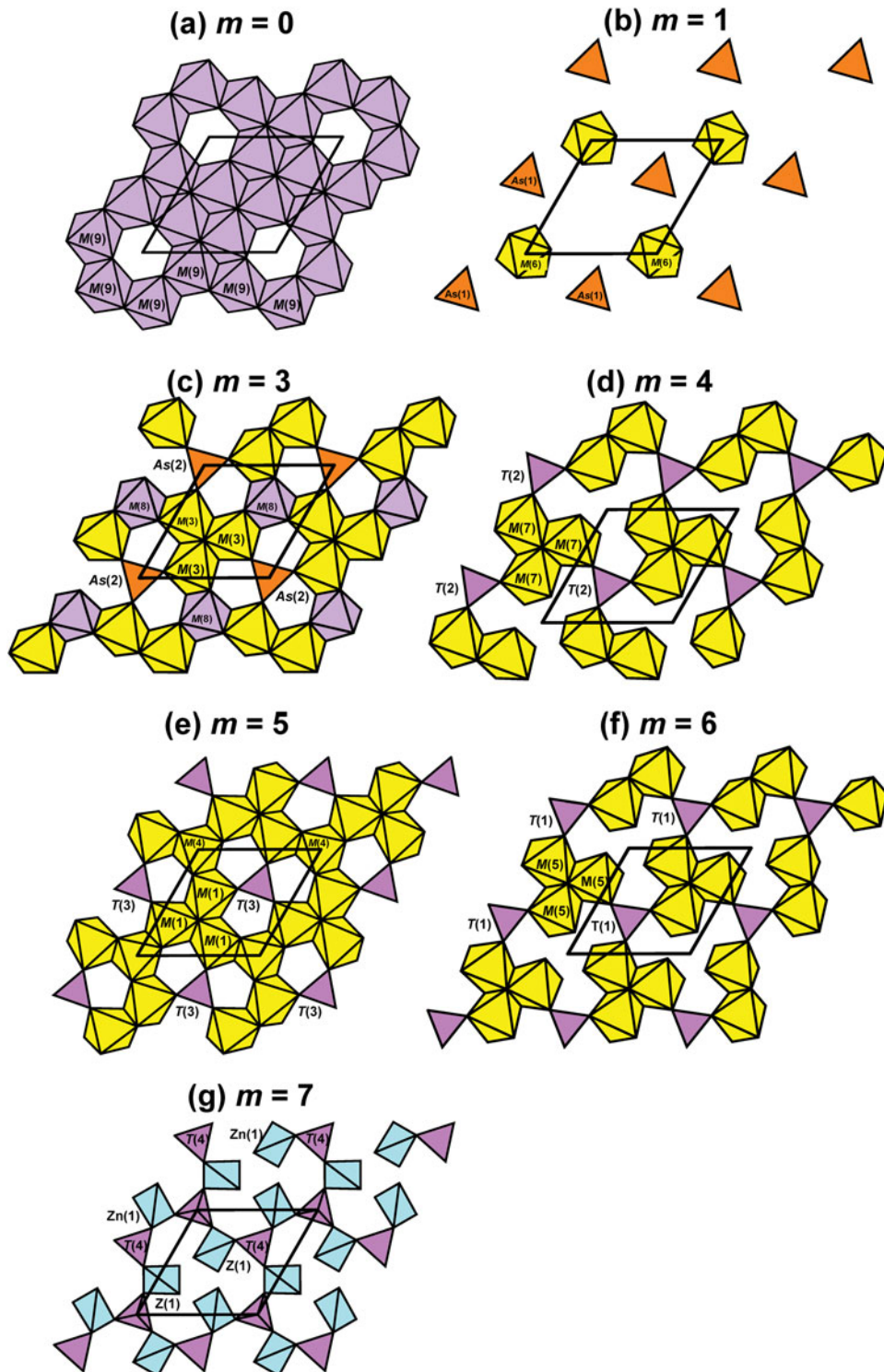
FIG. 6. The layers of polyhedra in mcgovernite. Legend as in Fig. 5; the unit cell is shown by the black lines.
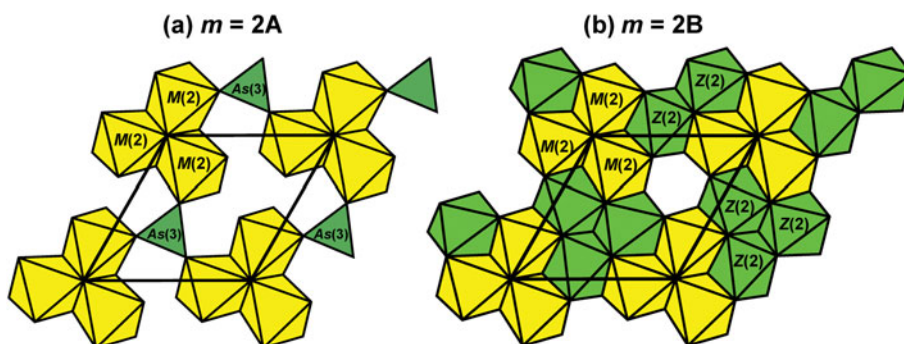
1115

FIG. 7. The two local variants of the $m = 2$ layer in mcgovernite. Legend as in Fig. 5; the unit cell is shown by the black lines. In (b), the $Z(2)$ octahedron is dominated by □ (vacancy) with minor Mg or Mn^{2+} (see Table 6).

TABLE 9. Principal compositional differences between mcgovernite, carlfrancisite and turtmannite.

Site	$Z(1)$	$M(4)$	$T(4)$	$As(1)$	$As(3)$
Layer	7	5	7	1	
Mcgovernite	Zn	$Mn^{2+} > Mg$	$Si > As^{5+}$	As^{5+}	$As^{3+} > □$
Carlfrancisite	Mn^{2+}	$Mg > Mn^{2+}$	$Si > As^{5+}$	As^{5+}	$As^{3+} > □$
Turtmannite	Mn^{2+}	Mn^{2+}	V^{5+}	V^{5+}	$□ \gg As^{3+}$

octahedron contains substantial Mg and Mn^{2+}, but is dominated by Mg in carlfrancisite and Mn^{2+} in mcgovernite. At $m = 6$ (Fig. 6f), the layer consists of trimers of edge-sharing $M(5)$ octahedra occupied by Mn^{2+} (with minor Mg in mcgovernite) that are linked by sharing corners with $T(1)$ tetrahedra that are dominated by Si (with significant As^{5+} in mcgovernite). The $m = 7$ layer (Fig. 6g) is substantially different from the other layers, consisting of 12-membered rings of 3-connected $T(4)$ tetrahedra and 2-connected $Z(1)$ tetrahedra, where $T(4)$ is occupied by dominant Si and substantial As^{5+} (0.45–0.88 apfu).

Principal chemical differences between mcgovernite, carlfrancisite and turtmannite

The principal compositional differences between each mineral are summarized in Table 9 and may be seen in Fig. 5. In layer $m = 1$, the $As(1)$ site is occupied by As^{5+} in carlfrancisite and mcgovernite, and by V^{5+} in turtmannite. In layer $m = 5$, the $M(4)$ site is occupied by dominant Mn^{2+} with minor Mg in mcgovernite and turtmannite, and by dominant Mg with minor Mn^{2+} in carlfrancisite. In layer $m = 7$, the $Z(1)$ site is occupied by Zn in mcgovernite,

and by Mn^{2+} in carlfrancisite and turtmannite, and the $T(4)$ site is occupied by dominant Si with minor As^{5+} in carlfrancisite and mcgovernite, and V^{5+} in turtmannite.

Related minerals

We will discuss the detailed structural relations between the minerals of the mcgovernite family following the formal description of two additional (new) minerals. However, it is notable that of the eight distinct layers of polyhedra in this structure type, four contiguous layers form a slab the topology of which is identical to that in arakiite (Cooper and Hawthorne, 1999) and hematolite (Moore and Araki, 1978). This four-layer unit interleaves with a unit of three [6]mangano-[4]silicate layers and a [4]zinco-[4]silicate layer in mcgovernite, a unit of four [6]mangano-[4]silicate layers in carlfrancisite.

Acknowledgements

1116

Supplementary material

To view supplementary material for this article, please visit https://doi.org/10.1180/minmag.2017.081.098

References

Araki, T. and Moore, P.B. (1981) Dixenite, $Cu^{1+}Mn_{14}^{2+}Fe^{3+}$ $(OH)_6(As^{3+}O_3)_5(Si^{4+}O_4)_5(As^{5+}O_4)$: metallic $[As_4^{3+}$ $Cu^{1+}]$ clusters in an oxide matrix. *American Mineralogist*, **66**, 1263–1273.

Brown, I.D. (2002) *The Chemical Bond in Inorganic Chemistry. The Bond Valence Model*. Oxford University Press, Oxford, UK.

Brown, I.D. (2016) *The Chemical Bond in Inorganic Chemistry. The Bond Valence Model*. 2nd edition. Oxford University Press, Oxford, UK.

Brugger, J., Armbruster, T., Meisser, N., Hejny, C. and Grobety, B. (2001) Description and crystal structure of turtmannite, a new mineral with a 68 Å period related to mcgovernite. *American Mineralogist*, **86**, 1494–1505.

Bruker (1997) SHELXTL Reference Manual 5.1., Bruker AXS Inc., Madison, WI, USA.

Cooper, M.A. and Hawthorne, F.C. (1999) The effect of differences in coordination on ordering of polyvalent cations in close-packed structures: the crystal structure of arakiite and comparison with hematolite. *The Canadian Mineralogist*, **37**, 1471–1482.

Cooper, M.A. and Hawthorne, F.C. (2001) The biggest mineral: The crystal structure of mcgovernite. *Eleventh Annual V.M. Goldschmidt Conference*, Abstract No. 3446. Available at https://www.lpi.usra.edu/meetings/gold2001/pdf/3446.pdf

Cooper, M.A. and Hawthorne, F.C. (2012) The crystal structure of kraisslite, $^{[4]}Zn_3(Mn,Mg)_{25}(Fe^{3+},Al)(As^{3+}$ $O_3)_2[(Si,As^{5+})O_4]_{10}(OH)_{16}$, from the Sterling Hill mine, Ogdensburg, Sussex County, New Jersey, USA. *Mineralogical Magazine*, **76**, 2819–2836.

Dunn, P.J., Peacor, D.R., Erd, R.C. and Ramik, R.A. (1986) Franciscanite and örebroite, two minerals from California and Sweden, related to redefined welinite. *American Mineralogist*, **71**, 1522–1526.

Dunn, P.J., Francis, C.A. and Innes, J. (1988) A mcgovernite-like mineral and leucophoenicite from the Kombat mine, Namibia. *American Mineralogist*, **73**, 1182–1185.

Gagné, O. and Hawthorne, F.C. (2015) Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Crystallographica*, **B71**, 562–578.

Hawthorne, F.C. (1983) Quantitative characterization of site occupancies in minerals. *American Mineralogist*, **68**, 287–306.

Hawthorne, F.C. (1996) Structural mechanisms for light-element variations in tourmaline. *Canadian Mineralogist*, **34**, 123–132.

Hawthorne, F.C. (1997) Short-range order in amphiboles: a bond-valence approach. *Canadian Mineralogist*, **35**, 203–218.

Hawthorne, F.C. (2016) Short-range atomic arrangements in minerals. I: The minerals of the amphibole, tourmaline and pyroxene supergroups. *European Journal of Mineralogy*, **28**, 513–536.

Hawthorne, F.C., Ungaretti, L., Oberti, R., Caucia, F. and Callegari, A. (1993) The crystal chemistry of staurolite. III. Local order and chemical composition. *The Canadian Mineralogist*, **31**, 597–616.

Hawthorne, F.C., Ungaretti, L. and Oberti, R. (1995) Site populations in minerals: terminology and presentation of results of crystal-structure refinement. *The Canadian Mineralogist*, **33**, 907–911.

Hawthorne, F.C., Della Ventura, G. and Robert, J.-L. (1996) Short-range order of (Na,K) and Al in tremolite: An infrared study. *American Mineralogist*, **81**, 782–784.

Hawthorne, F.C., Abdu, Y.A., Ball, N.A. and Pinch, W.W. (2013) Carlfrancisite: $Mn_3^{2+}(Mn^{2+},Mg,Fe^{3+},Al)_{42}$ $[As^{3+}O_3]_2(As^{5+}O_4)_4[(Si,As^{5+})O_4]_6$ $[(As^{5+},si)O_4]_2$ $(OH)_{42}$, a new arseno-silicate mineral from the Kombat mine, Otavi valley, Namibia. *American Mineralogist*, **98**, 1693–1696.

Lafuente, B., Downs, R.T., Yang, H. and Stone, N. (2015) The power of databases: the RRUFF project. Pp 1–30 in: *Highlights in Mineralogical Crystallography* (T. Armbruster and R.M. Danisi, editors). De Gruyter, Berlin, Germany.

Majzlan, J., Drahota, P. and Filippi, M. (2014) Paragenesis and crystal chemistry of arsenic minerals. Pp. 17–184 in: *Arsenic: Environmental Geochemistry, Mineralogy, and Microbiology* (R.J. Bowell, C.N. Alpers, H.E. Jamieson, D.K. Nordstrom and J. Majzlan, editors) Reviews in Mineralogy and Geochemistry, **79**. Mineralogical Society of America and the Geochemical Society, Chantilly, Virginia, USA.

Moore, P.B. (1967) The crystal structure of welinite, $(Mn^{+4},W)_{<1}(Mn^{+2},W,Mg)_{<3}Si(O,OH)_7$. *Arkiv för mineralogi och geologi*, **24**, 459–466.

Moore, P.B. and Araki, T. (1978) Hematolite: a complex dense-packed sheet structure. *American Mineralogist*, **63**, 150–159.

Moore, P.B. and Ito, J. (1978) Kraisslite, a new platy arsenosilicate from Sterling Hill, New Jersey. *American Mineralogist*, **63**, 938–940.

Palache, C. and Bauer, L.H. (1927) Mcgovernite, a new mineral from Sterling Hill, New Jersey. *American Mineralogist*, **12**, 373–374.

Pertlik, F. (1986) The crystal structure of franciscanite, $Mn_3(V_x\square_{1-x})(SiO_4)(O,OH)_3$, [x = 0.5]. *Neues Jahrbuch für Mineralogie, Monathefte*, **1986**, 493–499.

Pouchou, J.L. and Pichoir, F. (1985) 'PAP' ($\varphi\rho Z$) procedure for improved quantitative microanalysis. Pp. 104–106 in: *Microbeam Analysis* (J.T. Armstrong, editor). San Francisco Press, San Francisco, California, USA.

Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112–122.

Wuensch, B.J. (1960) The crystallography of mcgovernite, a complex arsenosilicate. *American Mineralogist*, **45**, 937–945.

Wuensch, B.J. (1968) Comparison of the crystallography of dixenite, mcgovernite and hematolite. *Zeitschrift für Kristallographie*, **127**, 309–318.

1118