

Kôzulite, an Mn-rich alkali amphibole

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{Si}-\text{O}) = 0.001$ Å; some non-H atoms missing; disorder in main residue; R factor = 0.023; wR factor = 0.067; data-to-parameter ratio = 17.8.

The crystal structure of kôzulite, an Mn-rich alkali amphibole with the ideal formula $\text{NaNa}_2[\text{Mn}_4^{2+}(\text{Fe}^{3+}, \text{Al})]\text{Si}_8\text{O}_{22}(\text{OH})_2$, trisodium tetramanganese iron/aluminium octasilicate dihydroxide, was refined from a natural specimen with composition $(\text{K}_{0.20}\text{Na}_{0.80})(\text{Na}_{1.60}\text{Ca}_{0.18}\text{Mn}_{2.22}^{2+})(\text{Mn}_{2.14}\text{Mn}_{0.25}^{3+}\text{Mg}_{2.20}\text{Fe}^{3+}_{0.27}\text{Al}_{0.14})(\text{Si}_{7.92}\text{Al}_{0.06}\text{Ti}_{0.02})\text{O}_{22}[(\text{OH})_{1.86}\text{F}_{0.14}]$. The site occupancies determined from the refinements are $M1 = 0.453$ (1) Mn + 0.547 (1) Mg, $M2 = 0.766$ (1) Mn + 0.234 (1) Mg, and $M3 = 0.257$ (1) Mn + 0.743 (1) Mg, where Mn and Mg represent (Mn+Fe) and (Mg+Al), respectively. The average $M-\text{O}$ bond lengths are 2.064 (1), 2.139 (1), and 2.060 (1) Å for the $M1$, $M2$, and $M3$ sites, respectively, indicating the preference of large Mn^{2+} for the $M2$ site. Four partially occupied amphibole A sites were revealed from the refinement, with $A(m) = 0.101$ (4) K, $A(m)' = 0.187$ (14) Na, $A(2) = 0.073$ (6) Na, and $A(1) = 0.056$ (18) Na, in accord with the result derived from microprobe analysis (0.20 K + 0.80 Na), considering experimental uncertainties.

Related literature

For more information on the geologic occurrence of kôzulite, see: Ashley (1986); Banno (1997); Hirtopanu (2006); Kawachi & Coombs (1993); Matsubara *et al.* (2002); Nambu *et al.* (1969, 1970, 1981); Watanabe *et al.* (1976). For the initial structural refinement of kôzulite, see: Fleischer & Nickel (1970); Kitamura & Morimoto (1972). For general background to the amphibole group, see: Hawthorne (1983); Hawthorne *et al.* (1995, 1996); Hawthorne & Harlow (2008). For background information on the amphibole group and nomenclature, see: Leake (1978); Leake *et al.* (1997, 2003); Mogessie *et al.* (2004).

Experimental

Crystal data

$\text{Na}_3[\text{Mn}_4(\text{FeAl})]\text{Si}_8\text{O}_{22}(\text{OH})_2$	$b = 18.1117$ (12) Å
$M_r = 897.29$	$c = 5.2992$ (4) Å
Monoclinic, $C2/m$	$\beta = 104.034$ (4)°
$a = 9.9024$ (7) Å	$V = 922.04$ (11) Å ³

$Z = 2$
Mo $K\alpha$ radiation
 $\mu = 2.87$ mm⁻¹

$T = 293$ K
 $0.06 \times 0.05 \times 0.04$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	7829 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008a)	1977 independent reflections
$T_{\min} = 0.847$, $T_{\max} = 0.894$	1656 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	1 restraint
$wR(F^2) = 0.067$	H-atom parameters not refined
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.58$ e Å ⁻³
1977 reflections	$\Delta\rho_{\text{min}} = -0.59$ e Å ⁻³
111 parameters	

Data collection: APEX2 (Bruker, 2003); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008b); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008b); molecular graphics: Xtal-Draw (Downs & Hall-Wallace, 2003); software used to prepare material for publication: SHELXTL (Sheldrick, 2008b).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2265).

References

- Ashley, P. M. (1986). *Aust. J. Earth Sci.* **33**, 441–456.
 Banno, Y. (1997). *J. Miner. Petrol. Econ. Geol.* **92**, 189–194.
 Bruker (2003). SMART. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2005). SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
 Downs, R. T. & Hall-Wallace, M. (2003). *Am. Mineral.* **88**, 247–250.
 Fleischer, M. & Nickel, E. H. (1970). *Am. Mineral.* **55**, 1810–1818.
 Hawthorne, F. C. (1983). *Can. Mineral.* **21**, 173–480.
 Hawthorne, F. C. & Harlow, G. E. (2008). *Can. Mineral.* **46**, 151–162.
 Hawthorne, F. C., Oberti, R., Cannillo, E., Sardone, N. & Zanetti, A. (1995). *Am. Mineral.* **80**, 165–172.
 Hawthorne, F. C., Oberti, R., Ungaretti, L. & Grice, J. D. (1996). *Am. Mineral.* **81**, 995–1002.
 Hirtopanu, P. (2006). *Acta Miner. Petrog. Abstr. Ser.* **5**, 38.
 Kawachi, Y. & Coombs, D. S. (1993). *Mineral. Mag.* **57**, 533–538.
 Kitamura, M. & Morimoto, N. (1972). *Acta Cryst.* **A28**, S71.
 Leake, B. E. (1978). *Am. Mineral.* **63**, 1023–1052.
 Leake, B. E., Wooley, A. R., Arps, C. E. S., Birch, W. D., Gilbert, M. C., Grice, J. D., Hawthorne, F. C., Kato, A., Kisch, H. J., Krivovichev, V. G., Linthout, K., Laird, J. & Mandarino, J. (1997). *Mineral. Mag.* **61**, 295–321.
 Leake, B. E., Woolley, A. R., Birch, W. D., Burke, E. A. J., Ferraris, G., Grice, J. D., Hawthorne, F. C., Kisch, H. J., Krivovichev, V. G., Schumacher, J. C., Stephenson, N. C. N. & Whittaker, E. J. W. (2003). *Can. Mineral.* **41**, 1355–1362.
 Matsubara, S., Miyawaki, R., Kurosawa, M. & Suzuki, Y. (2002). *J. Miner. Petrol. Sci.* **97**, 177–184.
 Mogessie, A., Ettinger, K. & Leake, B. E. (2004). *Mineral. Mag.* **68**, 825–830.
 Nambu, M. K., Tanida K., Kitamura, T. (1969). *J. Jpn Assoc. Miner. Petrol. Econ. Geol.* **62**, 311–328.
 Nambu, M., Tanida, K. & Kitamura, T. (1970). *Am. Mineral.* **55**, 1815–1816.
 Nambu, M., Tanida, K. & Kitamura, T. (1981). *Bul. Res. Inst. Miner. Dres. Met. Tohoku Univ.* **37**, 205–212.
 Sheldrick, G. M. (2008a). SADABS. University of Göttingen, Germany.
 Sheldrick, G. M. (2008b). *Acta Cryst.* **A64**, 112–122.
 Watanabe, T., Kato, A., Nambu, M., Tanida, K. & Kitamura, T. (1976). *Bul. Res. Inst. Miner. Dres. Met. Tohoku Univ.* **31**, 2–13.

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Comment

Kôzulite, with the ideal formula $\text{NaNa}_2[\text{Mn}_4^{2+}(\text{Fe}^{3+}, \text{Al})]\text{Si}_8\text{O}_{22}(\text{OH})_2$, is an Mn-rich alkali member of the rock-forming amphibole family and was first described by Nambu *et al.* (1969). Kitamura and Morimoto (1972), in a meeting abstract, presented the structure refinement of a kôzulite crystal with the composition $(\text{Na}_{2.54}\text{K}_{0.27}\text{Ca}_{0.19})(\text{Mn}_{3.69}\text{Mg}_{0.63}\text{Fe}^{3+}_{0.33}\text{Al}^{3+}_{0.31})\text{Si}_{8.00}\text{O}_{21.78}[(\text{OH})_{2.18}\text{F}_{0.04}]$. However, they did not report its detailed structure information, such as atomic coordinates and displacement parameters. This study presents the first reported structure of kôzulite based on single-crystal X-ray diffraction data, as a part of our effort to build an integrated, web-based database of Raman spectra, X-ray diffraction, and chemistry data for all minerals (<http://rruff.info>).

The site occupancies determined from the refinements are $M1 = 0.453(1) \text{ Mn} + 0.547(1) \text{ Mg}$, $M2 = 0.766(1) \text{ Mn} + 0.234(1) \text{ Mg}$, and $M3 = 0.257(1) \text{ Mn} + 0.743(1) \text{ Mg}$, where Mn and Mg represent (Mn + Fe) and (Mg + Al), respectively. These results should be compared to those given by Kitamura and Morimoto (1972) for their kôzulite crystal: $M1 = 0.78 \text{ Mn} + 0.22 \text{ Mg}$, $M2 = 0.95 \text{ Mn} + 0.05 \text{ Mg}$, and $M3 = 0.58 \text{ Mn} + 0.42 \text{ Mg}$. The average M—O bond lengths are 2.064(1), 2.139(1), and 2.060(1) Å for the $M1$, $M2$, and $M3$ sites, respectively. These values indicate that the $M2$ site is dominantly occupied by larger Mn^{2+} , whereas the $M1$ and $M3$ sites should have similar amounts of $(\text{Mn}^{3+} + \text{Fe}^{3+})$ and Mg. The relatively short average $M3$ —O distance (*versus*. $M1$ —O) suggests that Al^{3+} is preferentially ordered into the $M3$ site. Our results on kôzulite are very similar to those observed by Hawthorne *et al.* (1995) for ungarrettiite with the composition $(\text{K}_{0.15}\text{Na}_{0.82})(\text{Na}_{1.97}\text{Ca}_{0.03})(\text{Mn}^{2+}_{1.66}\text{Mn}^{3+}_{2.97}\text{Mg}_{0.34}\text{Fe}^{3+}_{0.03}\text{Zn}_{0.01})(\text{Si}_{7.99}\text{Al}_{0.01})\text{O}_{22}\text{O}_2$. The average M—O distances in ungarrettiite are 2.03, 2.17, and 2.01 Å for the $M1$, $M2$, and $M3$ sites, respectively, pointing to the strong ordering of larger Mn^{2+} into the $M2$ site and smaller Mn^{3+} into $M1$ and $M3$.

Four partially occupied amphibole A sites [$A(m)$, $A(m)'$, $A(2)$, and $A(1)$] were revealed from the structure refinements. The refinement shows that K prefers the $A(m)$ site, whereas Na is distributed among the other three sites. The refined A site occupancies are 0.208 K + 0.764 Na [$A(m) = 0.208(4) \text{ K}$, $A(m)' = 0.374(14) \text{ Na}$, $A(2) = 0.146(6) \text{ Na}$, and $A(1) = 0.224(18) \text{ Na}$], consistent with the result derived from microprobe analysis (0.20 K + 0.80 Na), considering experimental uncertainties. The presence of two distinct A sites on the mirror plane, $A(m)$ and $A(m)'$ has also been observed in many other alkali amphiboles (*e.g.*, Hawthorne *et al.* 1996; Hawthorne and Harlow 2008).

Experimental

The kôzulite specimen used in this study is from the type locality Tanohata Mine, Iwate Prefecture, Tohoku Region, Honshu Island, Japan and is in the collection of the RRUFF project (deposition No. R070122; <http://rruff.info>). The crystal chemistry was determined with a CAMECA SX50 electron microprobe (<http://rruff.info>) on the same single-crystal used for the collection of X-ray intensity data. The av-

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verage composition (10 point analyses) yielded a chemical formula (normalized on the basis of 23 oxygen): $(K_{0.20}Na_{0.80})(Na_{1.60}Ca_{0.18}Mn^{2+}_{0.22})\sim Mn^{2+}_{2.14}Mn^{3+}_{0.25}Mg_{2.20}Fe^{3+}_{0.27}Al_{0.14})\sim Si_{7.92}Al_{0.06}Ti_{0.02}O_{22}[(OH)_{1.86}F_{0.14}]$.

Refinement

The chemical analysis and crystal-chemical considerations show that the C-group cations consist of Mn^{2+} , Mn^{3+} , Fe^{3+} , Mg, and Al^{3+} . Because of similar X-ray scattering powers, Fe and Mn were grouped together (represented by the scattering factor for Mn) and Mg and Al together (represented by Mg) throughout the structure refinements. No refinement was made for the cations in the M4 site ($= Na_{0.80}Ca_{0.09}Mn^{2+}_{0.11}$); they were assigned based on crystal-chemical considerations and previous studies on amphiboles (Hawthorne 1983). The total Mn and Mg in the M1 + M2 + M3 sites were fixed to those from the chemical analysis. To dampen the extreme correlations that would otherwise occur among the refined A-site variables, the isotropic displacement factors of these A sites were constrained to be equal (Hawthorne & Harlow 2008).

Figures

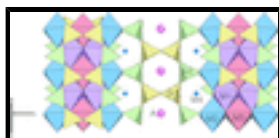


Fig. 1. The crystal structure of kôzultite. Green and yellow tetrahedra represent $[Si_1O_4]$ and $[Si_2O_4]$ groups, respectively. Purple, blue, and red octahedra represent the M1, M2, and M3 octahedra, respectively. The small blue and large pink spheres represent the M4 and A cations, respectively.

trisodium tetramanganese iron/aluminium octasilicate dihydroxide

Crystal data

$Na_3[Mn_4(Fe)]Si_8O_{22}(OH)_2$

$M_r = 897.29$

Monoclinic, $C2/m$

Hall symbol: $-C 2y$

$a = 9.9024 (7) \text{ \AA}$

$b = 18.1117 (12) \text{ \AA}$

$c = 5.2992 (4) \text{ \AA}$

$\beta = 104.034 (4)^\circ$

$V = 922.04 (11) \text{ \AA}^3$

$Z = 2$

$F(000) = 954$

$D_x = 3.232 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2537 reflections

$\theta = 4.0\text{--}34.7^\circ$

$\mu = 2.87 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Euhedral, brown

$0.06 \times 0.05 \times 0.04 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2008a)

$T_{\min} = 0.847$, $T_{\max} = 0.894$

7829 measured reflections

1977 independent reflections

1656 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 34.4^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -15 \rightarrow 15$

$k = -28 \rightarrow 28$

$l = -8 \rightarrow 7$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.023$	H-atom parameters not refined
$wR(F^2) = 0.067$	$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 1.2008P]$
$S = 1.08$	where $P = (F_o^2 + 2F_c^2)/3$
1977 reflections	$(\Delta/\sigma)_{\max} < 0.001$
111 parameters	$\Delta\rho_{\max} = 0.58 \text{ e } \text{\AA}^{-3}$
1 restraint	$\Delta\rho_{\min} = -0.59 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
M1	0.0000	0.08447 (2)	0.5000	0.00933 (11)	0.4529 (19)
M1A	0.0000	0.08447 (2)	0.5000	0.00933 (11)	0.5471 (19)
M2	0.0000	0.182241 (18)	0.0000	0.00935 (9)	0.766 (2)
M2A	0.0000	0.182241 (18)	0.0000	0.00935 (9)	0.234 (2)
M3	0.0000	0.0000	0.0000	0.00682 (19)	0.256 (4)
M3A	0.0000	0.0000	0.0000	0.00682 (19)	0.744 (4)
M4A	0.0000	0.27152 (4)	0.5000	0.02191 (15)	0.79
M4B	0.0000	0.27152 (4)	0.5000	0.02191 (15)	0.09
M4C	0.0000	0.27152 (4)	0.5000	0.02191 (15)	0.11
Si1	0.28233 (4)	0.084285 (19)	0.28706 (7)	0.00858 (8)	
Si2	0.28734 (4)	0.16909 (2)	0.79054 (7)	0.00908 (8)	
O1	0.11555 (10)	0.08452 (5)	0.2127 (2)	0.01077 (18)	
O2	0.11918 (11)	0.16575 (6)	0.7170 (2)	0.01460 (19)	
O3	0.10330 (15)	0.0000	0.7118 (3)	0.0131 (3)	
O4	0.35819 (12)	0.24732 (6)	0.7901 (2)	0.0179 (2)	
O5	0.34710 (10)	0.12714 (6)	0.0742 (2)	0.01335 (19)	
O6	0.34473 (10)	0.11704 (6)	0.57692 (19)	0.01358 (19)	
O7	0.34279 (16)	0.0000	0.2884 (3)	0.0154 (3)	
AM	0.5211 (9)	0.0000	0.053 (2)	0.0149 (9)*	0.104 (4)

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AM'	0.5562 (10)	0.0000	0.1298 (17)	0.0149 (9)*	0.187 (11)
A2	0.5000	-0.0215 (15)	0.0000	0.0149 (9)*	0.073 (6)
A1	0.5386 (18)	-0.0192 (18)	0.103 (4)	0.0149 (9)*	0.056 (6)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
M1	0.00812 (19)	0.01278 (19)	0.00693 (19)	0.000	0.00151 (14)	0.000
M1A	0.00812 (19)	0.01278 (19)	0.00693 (19)	0.000	0.00151 (14)	0.000
M2	0.00981 (15)	0.00801 (14)	0.01081 (16)	0.000	0.00360 (11)	0.000
M2A	0.00981 (15)	0.00801 (14)	0.01081 (16)	0.000	0.00360 (11)	0.000
M3	0.0078 (3)	0.0059 (3)	0.0063 (3)	0.000	0.0009 (2)	0.000
M3A	0.0078 (3)	0.0059 (3)	0.0063 (3)	0.000	0.0009 (2)	0.000
M4A	0.0226 (4)	0.0251 (4)	0.0224 (4)	0.000	0.0139 (3)	0.000
M4B	0.0226 (4)	0.0251 (4)	0.0224 (4)	0.000	0.0139 (3)	0.000
M4C	0.0226 (4)	0.0251 (4)	0.0224 (4)	0.000	0.0139 (3)	0.000
Si1	0.00867 (16)	0.00776 (15)	0.00854 (16)	-0.00068 (11)	0.00063 (12)	0.00007 (11)
Si2	0.00895 (16)	0.00906 (15)	0.00918 (16)	-0.00125 (11)	0.00213 (12)	0.00087 (11)
O1	0.0088 (4)	0.0112 (4)	0.0115 (4)	-0.0013 (3)	0.0009 (3)	-0.0005 (3)
O2	0.0093 (4)	0.0202 (5)	0.0138 (5)	0.0015 (4)	0.0018 (3)	0.0031 (4)
O3	0.0139 (6)	0.0114 (6)	0.0133 (6)	0.000	0.0021 (5)	0.000
O4	0.0236 (5)	0.0115 (4)	0.0186 (5)	-0.0056 (4)	0.0054 (4)	0.0012 (4)
O5	0.0112 (4)	0.0171 (5)	0.0114 (4)	0.0000 (3)	0.0021 (3)	0.0049 (3)
O6	0.0115 (4)	0.0184 (5)	0.0099 (4)	0.0004 (3)	0.0006 (3)	-0.0039 (3)
O7	0.0149 (7)	0.0076 (5)	0.0227 (7)	0.000	0.0022 (5)	0.000

Geometric parameters (\AA , $^\circ$)

M1—O3 ⁱ	2.0223 (10)	M4A—O5 ^{ix}	3.0160 (12)
M1—O3	2.0223 (10)	Si1—O1	1.6022 (11)
M1—O2	2.0551 (11)	Si1—O6	1.6226 (11)
M1—O2 ⁱⁱ	2.0551 (11)	Si1—O5	1.6240 (10)
M1—O1	2.1148 (10)	Si1—O7	1.6391 (7)
M1—O1 ⁱⁱ	2.1148 (10)	Si2—O4	1.5814 (11)
M2—O4 ⁱⁱⁱ	2.0197 (11)	Si2—O2	1.6166 (11)
M2—O4 ^{iv}	2.0197 (11)	Si2—O5 ^x	1.6598 (11)
M2—O2 ^v	2.1425 (11)	Si2—O6	1.6748 (11)
M2—O2 ⁱⁱ	2.1425 (11)	AM—O7 ^{xi}	2.506 (7)
M2—O1 ^{vi}	2.2554 (10)	AM—O5 ^{xii}	2.809 (3)
M2—O1	2.2554 (10)	AM—O5 ^{xi}	2.809 (3)
M3—O3 ⁱ	2.0339 (15)	AM—O5 ^{viii}	2.894 (4)
M3—O3 ^v	2.0339 (15)	AM ['] —O7 ^{xi}	2.643 (7)
M3—O1	2.0730 (10)	AM ['] —O6 ^{xiii}	2.671 (6)
M3—O1 ^{vi}	2.0730 (10)	AM ['] —O6 ^{xiv}	2.671 (6)
M3—O1 ^{vii}	2.0730 (10)	AM ['] —O5 ^{xii}	2.809 (4)
M3—O1 ^{viii}	2.0730 (10)	A2—O7 ^{xi}	2.463 (4)

M4A—O4 ^{ix}	2.3450 (12)	A2—O5 ^{viii}	2.53 (2)
M4A—O4 ⁱⁱⁱ	2.3450 (12)	A2—O5 ^{xi}	2.53 (2)
M4A—O2 ⁱⁱ	2.3930 (13)	A1—O6 ^{xiv}	2.53 (3)
M4A—O2	2.3930 (13)	A1—O5 ^{xi}	2.55 (3)
M4A—O6 ⁱⁱⁱ	2.6283 (12)	A1—O7 ^{xi}	2.644 (17)
M4A—O6 ^{ix}	2.6283 (12)	A1—O5 ^{viii}	2.70 (3)
M4A—O5 ⁱⁱⁱ	3.0160 (12)		
O3 ⁱ —M1—O3	81.68 (6)	O1 ^{vi} —M2—O1	76.60 (5)
O3 ⁱ —M1—O2	175.50 (5)	O3 ⁱ —M3—O3 ^v	180.00 (6)
O3—M1—O2	94.98 (4)	O3 ⁱ —M3—O1	84.47 (4)
O3 ⁱ —M1—O2 ⁱⁱ	94.98 (4)	O3 ^v —M3—O1	95.53 (4)
O3—M1—O2 ⁱⁱ	175.50 (5)	O3 ⁱ —M3—O1 ^{vi}	95.53 (4)
O2—M1—O2 ⁱⁱ	88.50 (6)	O3 ^v —M3—O1 ^{vi}	84.47 (4)
O3 ⁱ —M1—O1	83.68 (5)	O1—M3—O1 ^{vi}	84.81 (5)
O3—M1—O1	96.35 (5)	O3 ⁱ —M3—O1 ^{vii}	95.53 (4)
O2—M1—O1	93.72 (4)	O3 ^v —M3—O1 ^{vii}	84.47 (4)
O2 ⁱⁱ —M1—O1	86.24 (4)	O1—M3—O1 ^{vii}	180.00 (6)
O3 ⁱ —M1—O1 ⁱⁱ	96.35 (5)	O1 ^{vi} —M3—O1 ^{vii}	95.19 (5)
O3—M1—O1 ⁱⁱ	83.68 (5)	O3 ⁱ —M3—O1 ^{viii}	84.47 (4)
O2—M1—O1 ⁱⁱ	86.24 (4)	O3 ^v —M3—O1 ^{viii}	95.53 (4)
O2 ⁱⁱ —M1—O1 ⁱⁱ	93.72 (4)	O1—M3—O1 ^{viii}	95.19 (5)
O1—M1—O1 ⁱⁱ	179.95 (6)	O1 ^{vi} —M3—O1 ^{viii}	180.00 (3)
O4 ⁱⁱⁱ —M2—O4 ^{iv}	101.65 (7)	O1 ^{vii} —M3—O1 ^{viii}	84.81 (5)
O4 ⁱⁱⁱ —M2—O2 ^v	92.64 (4)	O1—Si1—O6	111.41 (5)
O4 ^{iv} —M2—O2 ^v	97.47 (4)	O1—Si1—O5	112.64 (5)
O4 ⁱⁱⁱ —M2—O2 ⁱⁱ	97.47 (4)	O6—Si1—O5	111.04 (6)
O4 ^{iv} —M2—O2 ⁱⁱ	92.64 (4)	O1—Si1—O7	110.92 (6)
O2 ^v —M2—O2 ⁱⁱ	163.97 (6)	O6—Si1—O7	106.35 (7)
O4 ⁱⁱⁱ —M2—O1 ^{vi}	166.32 (4)	O5—Si1—O7	104.05 (7)
O4 ^{iv} —M2—O1 ^{vi}	91.14 (4)	O4—Si2—O2	117.68 (6)
O2 ^v —M2—O1 ^{vi}	80.77 (4)	O4—Si2—O5 ^x	110.52 (6)
O2 ⁱⁱ —M2—O1 ^{vi}	86.65 (4)	O2—Si2—O5 ^x	108.75 (6)
O4 ⁱⁱⁱ —M2—O1	91.14 (4)	O4—Si2—O6	106.26 (6)
O4 ^{iv} —M2—O1	166.32 (4)	O2—Si2—O6	108.33 (6)
O2 ^v —M2—O1	86.65 (4)	O5 ^x —Si2—O6	104.45 (6)
O2 ⁱⁱ —M2—O1	80.77 (4)		

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x, y, -z+1$; (iii) $-x+1/2, -y+1/2, -z+1$; (iv) $x-1/2, -y+1/2, z-1$; (v) $x, y, z-1$; (vi) $-x, y, -z$; (vii) $-x, -y, -z$; (viii) $x, -y, z$; (ix) $x-1/2, -y+1/2, z$; (x) $x, y, z+1$; (xi) $-x+1, -y, -z$; (xii) $-x+1, y, -z$; (xiii) $-x+1, y, -z+1$; (xiv) $-x+1, -y, -z+1$.

Fig. 1

