Symmetry and crystal structure of montregianite, $Na_4K_2Y_2Si_{16}O_{38} \cdot 10H_2O$, a double-sheet silicate with zeolitic properties

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Abstract

Montregianite, $Na_4K_2Y_2Si_{16}O_{38} \cdot 10H_2O$ from Mont St. Hilaire, originally reported to be orthorhombic, is actually monoclinic (pseudo-orthorhombic) with unit-cell dimensions $a = 9.512(2)$, $b = 23.956(4)$, $c = 9.617(2)$ Å, $\beta = 93.85(1)°$; space group $P2_1/n$, $Z = 2$. The crystal structure has been determined by direct methods followed by least-squares refinement to an R factor of 0.059 for 4877 reflections measured on an automatic single-crystal X-ray diffractometer.

The crystal structure consists of two different types of layers alternating along the [010] direction: (a) a double silicate sheet, where the single silicate sheet is of the apophyllite type with four- and eight-membered rings, and (b) an open octahedral sheet composed of $[YO_6]$ and three distinct $[NaO_4(H_2O)_2]$ octahedra. The composite layers are parallel to the (010) plane, which is a plane of perfect cleavage, reminiscent of micas. The K atom in tenfold coordination and the six water molecules (three in partially occupied sites) are located within large channels formed by the planar eight-membered silicate rings. Thermal dehydration of montregianite begins above 25° and is completed at 400°C, a behavior similar to that of fibrous zeolites (mesolite and scolecite).

Introduction

Montregianite, a hydrous sodium potassium yttrium silicate from Mont St. Hilaire, Québec, Canada, was first described by Chao (1978). At Mont St. Hilaire, it occurs in miarolitic cavities and thermally metamorphosed inclusions and rheomorphic breccias in nepheline syenite. The associated minerals are calcite, pectolite, microcline, albite, aegirine, and arfvedsonite and minor amounts of phlogopite, fluorite, quartz, ekanite, sepiolite, ashcroftine, harmotome, apophyllite, molybdenite, and pyrite. Chao (1978) reported the chemical composition of montregianite, its optical and crystallographic properties, and the thermal dehydration behavior. He considered the symmetry of montregianite to be orthorhombic and classified it with the macdonaldite, delhayelite, and rhodesite group of minerals from the similarities of their chemical compositions and unit-cell dimensions. All these minerals are characterized by double silicate sheets, where the single sheet is of the apophyllite type with four- and eight-membered rings. From differential thermal and thermogravimetric analyses, three distinct stages of dehydration were found starting immediately above room temperature and essentially completed at 400°C. This be-

havior is very similar to that of macdonaldite and the fibrous zeolites mesolite and scolecite (Alfors et al., 1965). We have undertaken a detailed crystal-chemical study of montregianite to clarify the structural basis of its zeolitic behavior. We have found the true symmetry of montregianite to be monoclinic. Nevertheless, we have confirmed its structural similarity with macdonaldite, $BaCa_4H_2Si_{16}O_{38} \cdot (8 + xH_2O)$ (Cannillo et al., 1968) delhayelite, $Ca_4(Na_3Ca)K_7(Si_{14}Al_2)O_{38}Cl_2F_4$ (Cannillo et al., 1969), and rhodesite, $Ca_4Na_2K_2Si_{16}O_{38} \cdot 12H_2O$ (Hesse, 1979) as postulated by Chao (1978).

Symmetry

From Weissenberg and precession photographs, the symmetry of montregianite was considered to be orthorhombic with unit-cell dimensions $a = 14.014(4)$, $b = 23.910(5)$ and $c = 13.096(2)$ Å and space group $Bmab$ or $B2ab$ (Chao, 1978). Initially we assumed the orthorhombic symmetry, but changed the setting to $Cmca$ (or $C2ca$) to conform to the standard setting given in *The International Tables for X-ray Crystallography* (vol. 1, 1969). Wilson statistics of reflection intensities indicated a centrosymmetric space group. However, the determination

TABLE 1.	Montregianite, $Na_4K_2Y_2Si_{16}O_{38}\cdot10H_2O$: Crystal data

Mont St. Hilaire, Quebec, Canada		
Monoclinic (pseudo-orthorhombic): 2/m		
Colorless, transparent, thin prismatic crystals		
Space group	$P2_1/n$	$C112_1/a$
a (Å)	9.512(2)	13.973(2)
b (Å)	23.956(4)	13.064(2)
c (Å)	9.617(2)	23.956(4)
α (°)	90	90
β (°)	93.85(1)	90
γ (°)	90	90.62(1)
V(Å³)	2186.5(6)	4372.8(10)
Z	2	4
d_m (g/cm³)	2.42	2.42
d_c (g/cm³)	2.41	2.41
μ(MoKα) (cm⁻¹)	35.45	35.45

and refinement of the crystal structure in the space group *Cmca* revealed anomalously large standard deviations in bond lengths (see below), which led us to suspect that the true symmetry might be monoclinic and a subgroup of

Cmca. Subsequently, accurate unit-cell dimensions were determined on an automatic four-circle X-ray diffractometer, which showed that the gamma angle is in fact 90.62(1)° and the space group is $C112_1/a$ (Table 1). The monoclinic symmetry was further confirmed by the inequivalence of a number of intensities (hkl) and $(h\bar{k}\bar{l})$ reflections. The unit-cell dimensions in the standard monoclinic setting $P2_1/n$ (second setting) were obtained from the setting $C112_1/a$ by the transformation:

$$\begin{bmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{bmatrix}\begin{bmatrix} a_C \\ b_C \\ c_C \end{bmatrix} = \begin{bmatrix} a_P \\ b_P \\ c_P \end{bmatrix}$$

The unit-cell dimensions are listed in Table 1. We note here that such cases of pseudosymmetry may be more common in silicate minerals than is commonly believed. For example, bikitaite, $LiAlSi_2O_6\cdot H_2O$, which was reported to be monoclinic (Kocman et al., 1974), is in fact triclinic (pseudomonoclinic) (Ståhl et al., 1984).

TABLE 2.	Montregianite, $Na_4K_2Y_2Si_{16}O_{38}\cdot10H_2O$: Positional parameters and equivalent isotropic temperature factors for non-H atoms

Atom	K^*	x	y	z	$U_{eq}{}^{**}$
K(1)	0.62	0.0685(8)	0.2488(3)	0.5702(9)	0.042(2)
K(2)	0.38	0.541(1)	0.2478(5)	0.047(1)	0.036(2)
Na(1)	0.95	0.3713(3)	0.4991(1)	0.6312(3)	0.0180(7)
Na(2A)	0.47	0.50000	0.50000	0.00000	0.017(1)
Na(2B)	0.45	0.00000	0.50000	0.50000	0.018(1)
Y(Ce)	0.60 (0.40)	−0.25645(4)	0.49845(2)	0.74445(4)	0.00432(9)
Si(1)	1.0	−0.2661(2)	0.18159(6)	0.7344(2)	0.0072(4)
Si(2A)	1.0	−0.4972(2)	0.38752(7)	0.2288(2)	0.0073(4)
Si(2B)	1.0	0.2275(2)	0.38831(7)	−0.4931(2)	0.0078(4)
Si(3)	1.0	−0.4548(2)	0.38870(7)	0.5524(2)	0.0077(4)
Si(4)	1.0	−0.2553(2)	0.31464(7)	0.7465(2)	0.0067(4)
Si(5A)	1.0	0.2269(2)	0.11133(7)	−0.4953(2)	0.0081(4)
Si(5B)	1.0	0.4979(2)	0.11160(7)	0.2246(2)	0.0082(4)
Si(6)	1.0	−0.4521(2)	0.10614(7)	0.5519(2)	0.0083(4)
O(1)	1.0	−0.2588(5)	0.2481(2)	0.7358(5)	0.015(1)
O(2A)	1.0	−0.6183(4)	0.3414(2)	0.1882(5)	0.015(1)
O(2B)	1.0	0.2029(5)	0.3384(2)	−0.6097(5)	0.020(1)
O(3)	1.0	−0.3907(5)	0.1646(2)	0.6230(5)	0.019(1)
O(4A)	1.0	0.1264(4)	0.1277(2)	−0.3711(4)	0.012(1)
O(4B)	1.0	−0.3769(4)	0.1272(2)	0.1274(5)	0.012(1)
O(5A)	1.0	−0.4349(5)	0.3718(2)	0.3891(5)	0.017(1)
O(5B)	1.0	0.3827(4)	0.3798(2)	−0.4176(5)	0.021(1)
O(6A)	1.0	0.4517(4)	0.4501(2)	0.2176(5)	0.015(1)
O(6B)	1.0	0.2110(5)	0.4491(2)	0.4465(5)	0.017(1)
O(7)	1.0	−0.4038(5)	0.4494(2)	0.5892(5)	0.015(1)
O(8)	1.0	−0.3758(5)	0.3390(2)	0.6428(5)	0.020(1)
O(9A)	1.0	−0.2757(5)	0.3320(2)	0.9063(5)	0.019(1)
O(9B)	1.0	0.8934(5)	0.3343(2)	−0.2989(6)	0.024(1)
O(10A)	1.0	−0.4379(5)	0.1155(3)	0.3852(5)	0.027(2)
O(10B)	1.0	0.3843(4)	0.1067(2)	−0.4185(5)	0.018(1)
O(11A)	1.0	0.6829(5)	0.4428(2)	−0.0799(5)	0.015(1)
O(11B)	1.0	−0.0778(5)	0.4450(2)	0.6889(5)	0.019(1)
O(12)	1.0	−0.3704(5)	0.0540(2)	0.6113(6)	0.027(2)
O(13)W(1)	1.0	0.8428(7)	0.4480(4)	0.3443(9)	0.059(3)
O(14)W(2)	1.0	0.3238(8)	0.4521(4)	0.8570(7)	0.051(2)
O(15)W(3)	0.95	0.622(1)	0.2492(4)	0.359(1)	0.059(3)
O(16)W(4)	0.46	0.891(1)	0.187(1)	0.356(2)	0.105(8)
O(17)W(5)	0.35	0.382(2)	0.182(1)	0.865(2)	0.08(1)
O(18)W(6)	0.37	0.633(3)	0.750(1)	−0.610(3)	0.09(1)

Note: Standard deviations of the last digit are in parentheses.
* K = occupancy.
** U_{eq} = ⅓ trace of orthogonalized U tensor.

TABLE 3. Montregianite, $Na_4K_2Y_2Si_{16}O_{38}\cdot10H_2O$: Anisotropic thermal parameters for non-H atoms

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K(1)	0.0558(36)	0.0257(21)	0.0458(33)	0.0045(19)	0.0148(23)	0.0074(21)
K(2)	0.0387(41)	0.0316(32)	0.0380(40)	−0.0062(27)	0.0122(30)	−0.0104(27)
Na(1)	0.0167(12)	0.0219(14)	0.0158(12)	−0.0046(11)	0.0036(10)	−0.0019(11)
Na(2)	0.0111(17)	0.0257(22)	0.0186(19)	0.0032(18)	0.0083(15)	0.0038(17)
Na(3)	0.0109(16)	0.0224(21)	0.0193(18)	0.0007(17)	0.0066(14)	0.0004(16)
Y(1)	0.0022(2)	0.0053(2)	0.0057(2)	−0.0002(1)	0.0017(1)	−0.0001(1)
Si(1)	0.0051(6)	0.0083(7)	0.0083(7)	0.0000(5)	0.0019(5)	0.0006(5)
Si(2A)	0.0035(6)	0.0108(7)	0.0082(7)	0.0000(5)	0.0035(5)	−0.0005(5)
Si(2B)	0.0037(6)	0.0118(7)	0.0084(7)	−0.0007(5)	0.0045(5)	−0.0003(5)
Si(3)	0.0030(6)	0.0120(7)	0.0082(7)	−0.0009(5)	0.0008(5)	0.0006(5)
Si(4)	0.0044(6)	0.0092(6)	0.0067(6)	−0.0008(5)	0.0009(5)	−0.0001(5)
Si(5A)	0.0044(6)	0.0125(7)	0.0077(7)	−0.0003(5)	0.0032(5)	−0.0009(5)
Si(5B)	0.0047(6)	0.0125(7)	0.0078(7)	0.0005(5)	0.0034(5)	−0.0007(5)
Si(6)	0.0046(6)	0.0133(7)	0.0070(6)	0.0003(6)	0.0009(5)	−0.0001(5)
O(1)	0.0165(20)	0.0084(18)	0.0207(21)	−0.0015(18)	0.0000(16)	−0.0036(17)
O(2A)	0.0075(18)	0.0204(23)	0.0186(21)	−0.0050(17)	0.0061(16)	−0.0060(16)
O(2B)	0.0262(24)	0.0219(25)	0.0144(21)	−0.0071(19)	0.0093(18)	−0.0063(19)
O(3)	0.0108(20)	0.0200(24)	0.0247(24)	−0.0063(19)	−0.0075(18)	0.0001(17)
O(4A)	0.0072(18)	0.0185(21)	0.0112(19)	−0.0030(16)	0.0084(15)	−0.0009(15)
O(4B)	0.0098(18)	0.0162(21)	0.0118(19)	−0.0008(16)	0.0054(15)	−0.0036(16)
O(5A)	0.0215(22)	0.0222(23)	0.0068(19)	−0.0021(17)	0.0021(17)	0.0062(18)
O(5B)	0.0039(18)	0.0362(28)	0.0219(24)	0.0083(20)	0.0015(17)	−0.0019(18)
O(6A)	0.0097(19)	0.0161(22)	0.0203(22)	0.0016(18)	0.0029(16)	0.0034(16)
O(6B)	0.0175(22)	0.0166(22)	0.0190(22)	0.0054(18)	0.0067(18)	0.0038(18)
O(7)	0.0151(21)	0.0150(21)	0.0161(21)	−0.0038(17)	0.0015(17)	−0.0014(17)
O(8)	0.0224(24)	0.0179(23)	0.0189(22)	0.0017(18)	−0.0089(19)	0.0053(19)
O(9A)	0.0296(25)	0.0182(23)	0.0108(20)	−0.0037(18)	0.0107(18)	−0.0009(19)
O(9B)	0.0090(19)	0.0274(27)	0.0376(29)	−0.0050(23)	0.0130(19)	−0.0095(19)
O(10A)	0.0202(24)	0.0511(35)	0.0092(20)	−0.0004(21)	0.0008(18)	−0.0109(23)
O(10B)	0.0038(17)	0.0320(27)	0.0177(21)	0.0001(19)	0.0041(15)	−0.0004(17)
O(11A)	0.0125(20)	0.0225(24)	0.0119(20)	0.0091(17)	0.0080(16)	0.0039(17)
O(11B)	0.0165(21)	0.0197(23)	0.0235(24)	0.0061(19)	0.0134(18)	0.0127(19)
O(12)	0.0223(24)	0.0149(24)	0.0421(31)	0.0060(22)	−0.0083(22)	0.0053(19)
O(13)W(1)	0.0260(33)	0.0914(59)	0.0583(44)	−0.0468(42)	0.0008(30)	0.0061(35)
O(14)W(2)	0.0532(42)	0.0704(50)	0.0293(34)	−0.0026(33)	0.0064(30)	−0.0342(37)
O(15)W(3)	0.0715(58)	0.0374(44)	0.0671(55)	−0.0029(42)	−0.0020(45)	0.0034(42)
O(16)W(4)	0.0337(62)	0.2355(232)	0.0435(80)	−0.0613(111)	−0.0199(59)	0.0493(96)
O(17)W(5)	0.0273(111)	0.1617(243)	0.0395(121)	−0.0390(138)	−0.0030(94)	0.0155(129)
O(18)W(6)	0.1136(215)	0.0273(108)	0.1160(199)	−0.0050(127)	−0.0549(166)	−0.0003(126)

Note: Standard deviations of the last digit are in parentheses.

DETERMINATION AND REFINEMENT OF THE CRYSTAL STRUCTURE

Initially, a data set of 2209 reflections was collected based on orthorhombic symmetry from a small cleavage fragment on an automatic single-crystal X-ray diffractometer at the Nicolet XRD Corporation in Madison, Wisconsin, using monochromatized $MoK\alpha$ radiation. The data were corrected for Lorentz, polarization, and absorption factors. Intensity statistics indicated *Cmca* as the possible space group. The crystal structure was determined by direct methods using the SHELX system of programs and refined by the method of least squares using anisotropic temperature factors to an *R* factor of 0.066. Although the refinement had reached convergence, the standard deviations of Si–O bond lengths ranged from ±0.007 to ±0.013 Å, which were larger in some cases than the standard deviations of Na–O bond lengths (±0.007 Å). These anomalous results led us to suspect that the true symmetry might be monoclinic, which in fact turned out to be the case. The X-ray intensity data were recollected from a cube-shaped cleavage fragment (0.34 × 0.32 × 0.34 mm) on a Syntex P1̄ X-ray single-crystal diffractometer at Seattle using $MoK\alpha$ radiation, monochromatized by reflection from a graphite "single" crystal. The minimum scan rate was 2°/min. All intensities within one hemisphere of reciprocal space in the monoclinic $C112_1/a$ setting were collected within a 2θ limit of 65°. A total of 13 724 reflections were measured, which were re-indexed to conform to the standard setting $P2_1/n$. They were averaged to yield 5669 inequivalent reflections out of which 792 were less than $3\sigma(F_o)$, where $\sigma(F_o)$ is the standard deviation of F_o as determined from the counting statistics. The intensities were corrected for Lorentz, polarization, and absorption factors. The atomic positional parameters from the pseudo-orthorhombic structure, transformed to conform to the $P2_1/n$ space-group symmetry, were used as input parameters. The atomic scattering factors for K, Na, Y (Ce), Si, and O were taken from the *International Tables* (vol. 2, 1974) and were corrected for anomalous dispersion. The observed structure factors (F_o values) were weighted by $1/\sigma_{(F_o)}$. The XTAL program (Stewart et al., 1985) was used for the final full-matrix least-squares refinement. The atomic position of K turned out to be split with variable

TABLE 4. Montregianite, $Na_4K_2Y_2Si_{16}O_{38}\cdot10H_2O$: Interatomic distances (Å) and angles (°)

K polyhedron

K1–O(2A)	3.069(9)	K2–O(2A)	3.077(13)	
–O(2B)	3.084(9)	O(2B)	3.034(13)	
–O(4A)	2.998(9)	O(4A)	3.176(12)	
–O(4B)	3.059(9)	O(4B)	3.076(12)	
–O(9A)	2.955(9)	O(9A)	3.044(13)	
–O(9B)	2.978(10)	O(9B)	2.886(13)	
–O(15)(W(3))	2.761(12)	O(15)(W3)	3.017(15)	
–O(16)(W(4))	2.956(20)	O(16)(W4)	2.726(23)	
–O(17)(W(5))	3.049(27)	O(17)(W5)	2.732(28)	
–O(18)(W(6))	2.866(31)	O(18)(W6)	3.144(32)	
	2.978*		2.991*	

Y octahedron

Y–O(6A)	2.295(5)	O(7)–O(6A)**	3.081(7)	84.2(2)
–O(6B)	2.276(5)	O(7)–O(11A)**	3.207(7)	89.8(2)
–O(7)	2.300(5)	O(7)–O(11B)**	3.216(7)	90.3(2)
–O(11A)	2.245(5)	O(7)–O(6B)**	3.090(7)	85.0(2)
–O(11B)	2.235(5)	O(6A)–O(6B)**	3.283(7)	91.8(2)
–O(12)	2.217(5)	O(6B)–O(11B)**	3.085(7)	86.3(2)
	2.261*	O(11B)–O(11A)**	3.289(7)	94.5(2)
		O(11A)–O(6A)**	3.121(7)	86.9(2)
		O(12)–O(6A)**	3.194(7)	90.1(2)
		O(12)–O(6B)**	3.233(7)	92.0(2)
		O(12)–O(11B)**	3.287(7)	95.2(2)
		O(12)–O(11A)**	3.240(7)	93.1(2)
			3.194*	89.9*
		O(6A)–O(11B)**	—	174.4(2)
		O(6B)–O(11A)**	—	174.7(2)
		O(7)–O(12)**	—	173.5(2)

Na(1) octahedron

Na(1)–O(6A)	2.473(5)	O(6A)–O(14)	3.566(10)	83.1(2)
–O(6B)	2.557(6)	O(6A)–O(13)	3.870(11)	103.9(2)
–O(7)	2.523(6)	O(6A)–O(7)	3.081(7)	76.1(2)
–O(7′)	2.469(6)	O(6A)–O(7′)	3.710(11)	97.3(2)
–O(13)(W(1))	2.442(8)	O(7′)–O(14)	3.735(10)	97.6(2)
–O(14)(W(2))	2.495(8)	O(14)–O(13)	3.399(11)	87.0(3)
[–O(5B)	2.900(6)]	O(13)–O(7)	3.434(9)	88.7(2)
		O(7)–O(7′)	3.427(7)	86.7(2)
	2.493†	O(6B)–O(14)	3.984(11)	104.1(2)
	2.551‡	O(6B)–O(13)	3.233(10)	80.5(2)
		O(6B)–O(7)	3.090(7)	98.8(2)
		O(6B)–O(7′)	3.092(9)	75.9(2)
			3.468*	89.97*
		O(6A)–O(6B)		171.9(2)
		O(7)–O(14)		175.7(2)

Na(2A) octahedron

Na(2A)–O(6A)	2.461(5) (× 2)	O(6A)–O(11A)	3.121(7)	80.0(2)
–O(11A)	2.393(5) (× 2)	O(6A)–O(11A′)	3.719(7)	100.0(2)
–O(14)(W(2))	2.394(5) (× 2)	O(6A)–O(14)	3.565(9)	94.5(2)
	2.416*	O(6A)–O(14′)	3.295(9)	85.5(2)
		O(11A)–O(14)	3.472(9)	93.0(2)
		O(11A)–O(14′)	3.294(9)	87.0(2)
			3.411*	90.0*

Na(2B) octahedron

Na(2B)–O(6B)	2.450(5) (× 2)	O(6B)–O(11B)	3.085(7)	79.2(2)
–O(11B)	2.389(5) (× 2)	O(6B)–O(11B′)	3.729(7)	100.8(2)
–O(13)(W(1))	2.395(5) (× 2)	O(6B)–O(13)	3.609(10)	96.3(2)
	2.411*	O(6B)–O(13′)	3.233(10)	83.7(2)
		O(11B)–O(13)	3.447(10)	92.2(2)
		O(11B)–O(13′)	3.316(9)	87.8(2)
			3.403*	90.0*

Si(1) tetrahedron

Si–O(1)	1.594(5)	O(1)–O(2A)	2.589(7)	107.7(3)
–O(2A)	1.612(5)	O(1)–O(2B)	2.581(7)	107.6(3)
–O(2B)	1.605(5)	O(1)–O(3)	2.564(7)	106.9(3)
–O(3)	1.598(5)	O(2A)–O(2B)	2.664(7)	111.8(3)
	1.602*	O(2A)–O(3)	2.655(7)	111.6(3)
		O(2B)–O(3)	2.640(7)	111.0(3)
			2.616*	109.4*

TABLE 4.—*Continued*

		Si(2) tetrahedron		
Si(2A)–O(2A)	1.633(5)	O(2A)–O(4A)	2.565(6)	104.4(2)
–O(4A)	1.613(5)	O(2A)–O(5A)	2.616(6)	105.9(3)
–O(5B)	1.644(5)	O(2A)–O(6A)	2.701(7)	114.4(2)
–O(6B)	1.579(5)	O(4A)–O(5A)	2.582(6)	104.9(2)
	1.617*	O(4A)–O(6A)	2.684(6)	114.4(3)
		O(5A)–O(6A)	2.670(7)	111.8(3)
			2.636*	109.3*
		Si(2B) tetrahedron		
Si(2B)–O(2B)	1.637(5)	O(2B)–O(4B)	2.567(7)	104.1(3)
–O(4B)	1.617(5)	O(2B)–O(5B)	2.624(7)	107.1(3)
–O(5B)	1.625(5)	O(2B)–O(6B)	2.704(7)	115.0(3)
–O(6B)	1.569(5)	O(4B)–O(5B)	2.566(6)	104.7(3)
	1.612*	O(4B)–O(6B)	2.686(7)	114.9(3)
		O(5B)–O(6B)	2.621(7)	110.8(3)
			2.628*	109.4*
		Si(3) tetrahedron		
Si(3)–O(5A)	1.629(5)	O(5A)–O(5B)	2.633(7)	108.2(3)
–O(5B)	1.621(5)	O(5A)–O(7)	2.664(7)	112.8(3)
–O(7)	1.568(5)	O(5A)–O(8)	2.566(7)	104.0(3)
–O(8)	1.627(5)	O(5B)–O(7)	2.643(7)	111.9(3)
	1.611*	O(5B)–O(8)	2.549(7)	103.4(3)
		O(7)–O(8)	2.705(7)	115.7(3)
			2.627*	109.3*
		Si(4) tetrahedron		
Si(4)–O(1)	1.598(5)	O(1)–O(8)	2.581(7)	108.5(3)
–O(8)	1.582(5)	O(1)–O(9A)	2.594(7)	108.4(3)
–O(9A)	1.600(5)	O(1)–O(9B)	2.567(7)	107.1(3)
–O(9B)	1.592(5)	O(8)–O(9A)	2.629(7)	111.4(3)
	1.593*	O(8)–O(9B)	2.613(7)	110.8(3)
		O(9A)–O(9B)	2.623(7)	110.5(3)
			2.601*	109.4*
		Si(5A) tetrahedron		
Si(5A)–O(4A)	1.624(5)	O(4A)–O(9A)	2.564(7)	103.1(3)
–O(9A)	1.649(5)	O(4A)–O(10B)	2.600(6)	105.6(3)
–O(10B)	1.640(4)	O(4A)–O(11A)	2.691(7)	114.8(3)
–O(11A)	1.570(5)	O(9A)–O(10B)	2.639(7)	106.7(3)
	1.621*	O(9A)–O(11A)	2.691(7)	113.4(3)
		O(10B)–O(11A)	2.667(6)	112.4(3)
			2.642*	109.3*
		Si(5B) tetrahedron		
Si(5B)–O(4B)	1.611(5)	O(4B)–O(9B)	2.536(7)	102.3(3)
–O(9B)	1.645(6)	O(4B)–O(10A)	2.575(7)	106.1(3)
–O(10A)	1.611(5)	O(4B)–O(11B)	2.687(7)	115.6(3)
–O(11B)	1.565(5)	O(9B)–O(10A)	2.601(7)	106.0(3)
	1.608*	O(9B)–O(11B)	2.668(8)	112.4(3)
		O(10A)–O(11B)	2.656(7)	113.5(3)
			2.621*	109.3*
		Si(6) tetrahedron		
Si(6)–O(3)	1.647(5)	O(3)–O(10A)	2.564(7)	103.6(3)
–O(10A)	1.616(5)	O(3)–O(10B)	2.578(7)	104.3(3)
–O(10B)	1.617(5)	O(3)–O(12)	2.660(7)	111.9(3)
–O(12)	1.562(5)	O(10A)–O(10B)	2.623(7)	108.5(3)
	1.611*	O(10A)–O(12)	2.652(8)	113.1(3)
		O(10B)–O(12)	2.674(7)	114.5(3)
			2.625*	109.3*

		Si–O–Si angles	
Si(1)–O(1)–Si(4)	176.5(3)	Si(2A)–O(5A)–Si(3)	140.2(3)
Si(1)–O(2A)–Si(2A)	142.6(3)	Si(2B)–O(5B)–Si(3)	140.6(3)
Si(1)–O(2B)–Si(2B)	144.8(4)	Si(3)–O(8)–Si(4)	153.7(4)
Si(1)–O(3)–Si(6)	136.2(3)	Si(4)–O(9A)–Si(5A)	139.0(3)
Si(2A)–O(4A)–Si(5A)	150.7(2)	Si(4)–O(9B)–Si(5B)	138.4(3)
Si(2B)–O(4B)–Si(5B)	151.3(3)	Si(5B)–O(10A)–Si(6)	150.5(4)
		Si(5A)–O(10B)–Si(6)	143.4(3)

Note: Standard deviations of the last digit are in parentheses.
  * Mean.
** For the corresponding angle, read O7–Y–O6A, etc.
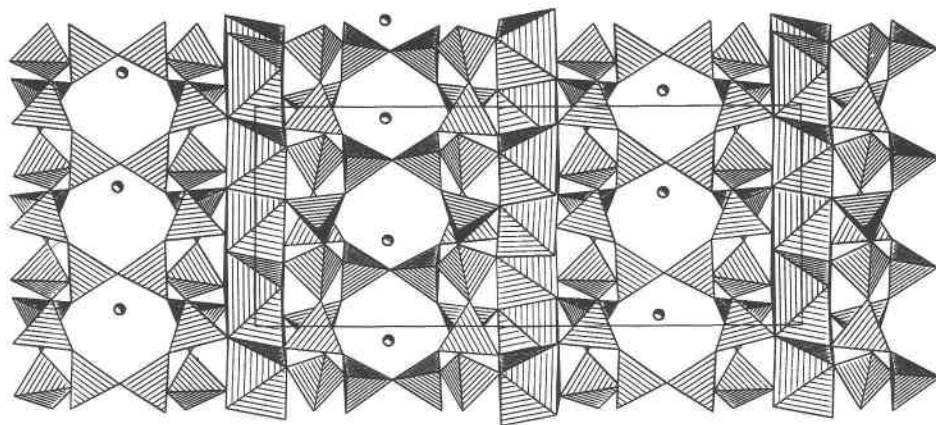 † Mean of six.
  ‡ Mean of seven.

Fig. 1.   A view of the crystal structure of montregianite down the **a** axis. Note the alternating octahedral sheet and double silicate sheet along the **b** axis. The positions of the K atoms are shown by dotted spheres.

occupancies, and the site occupancy at the Y atom position was found to be greater than one, which was compensated for by assigning 0.40 Ce atoms at this position. At the final stages, the site occupancies of water molecules were refined along with anisotropic temperature factors for all atoms. H atom positions were searched for in the final difference Fourier synthesis, but none were found, presumably owing to partial site occupancies and high thermal vibrations of the water molecules.

The final R factor for 4877 observed structure factors is 0.059 ($R_w = 0.061$). The final atomic positional and equivalent isotropic thermal parameters are listed in Table 2 and anisotropic temperature factors in Table 3. Table 4 lists bond lengths and angles. Table 5[1] lists the observed and calculated structure factors. The average standard deviations of Si–O, Y–O, and Na–O bond lengths are ±0.005, ±0.005 and ±0.006 Å, respectively, whereas those of K–O bond lengths are ±0.011 and ±0.021 Å, respectively, involving oxygen atoms and water molecules.

Atom nomenclature

The atoms denoted by A and B are related by a pseudo–mirror plane parallel to (101). If it were a true mirror plane, the symmetry of montregianite would be orthorhombic, space group *Cmca*.

DESCRIPTION OF THE CRYSTAL STRUCTURE

The crystal structure of montregianite consists of two types of alternating layers normal to the **b** axis with a 23-Å repeat: (1) an open octahedral sheet consisting of Y and three crystallographically distinct Na atoms and (2) a tetrahedral double silicate sheet, where the single silicate sheet is of the apophyllite type with four- and eight-membered rings (Fig. 1). K atoms and water molecules occur in large channels defined by the planar eight-membered rings. The perfect (010) cleavage breaks through the Na–O and Y–O bonds and is reminiscent of the cleavage in micas.

Octahedral sheet

The open octahedral sheet parallel to (010) is formed by [YO_6] and three different types of [NaO_4(H_2O)_2] oc-
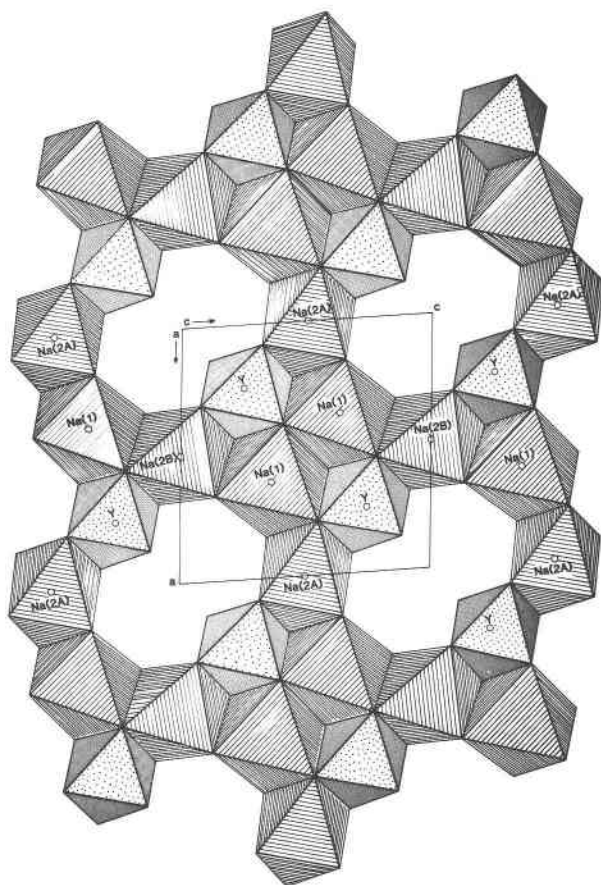

Fig. 2.   An open mixed octahedral layer parallel to the (010) plane consisting of Y and three different Na octahedra.

[1] To obtain a copy of Table 5, order Document AM-87-330 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.
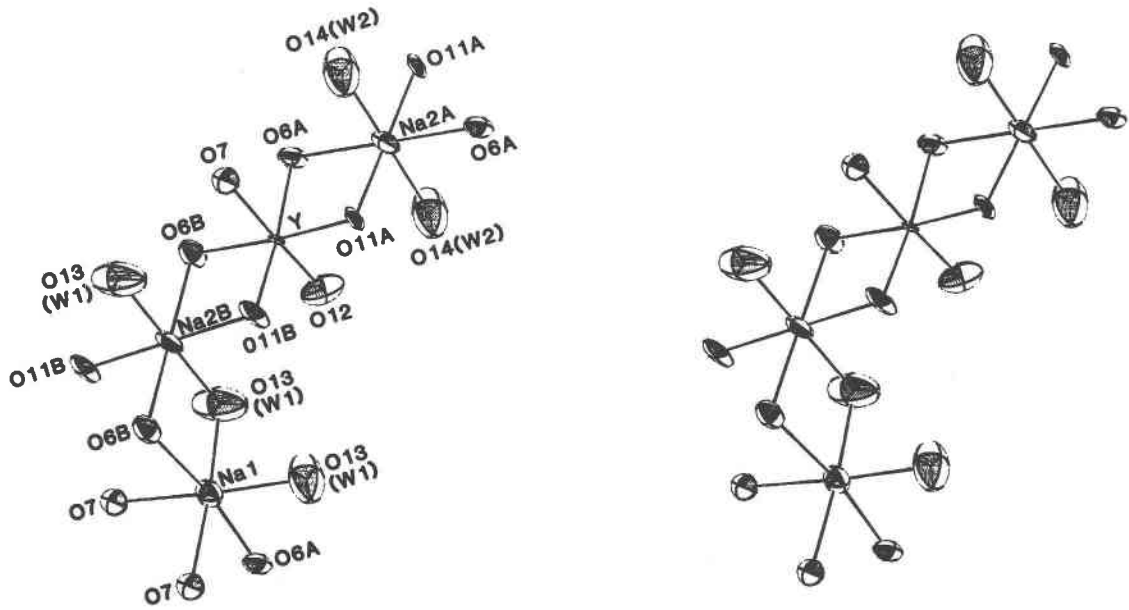
Fig. 3. Stereoscopic view of a fragment of the mixed octahedral layer showing the details of Y and Na coordinations and the atomic thermal-vibration ellipsoids.

tahedra sharing edges, such that mixed octahedral rings are formed, whose centers coincide with the corners of the base of the unit cell in the (010) plane (Fig. 2). The eight-membered octahedral rings with two Y and six Na octahedra are elliptical in shape, the long axis of the ellipse being parallel to [101].

The details of the Y and Na coordination are shown in Figure 3. The $[YO_6]$ octahedron is fairly regular with an average Y–O bond length of 2.261 (±0.030) Å and an average deviation of $\pm2.92°$ from the ideal octahedral O–Y–O angle of 90°. The $[Na(1)O_4(H_2O)_2]$ octahedron with an average Na–O bond length 2.493 (±0.032) Å is slightly larger than the $[Na(2A)O_4(H_2O)_2]$ and the $[Na(2B)O_4(H_2O)_2]$ octahedra [avg. Na–O bond lengths 2.416 (±0.030) Å and 2.411 (±0.026) Å, respectively]. In addition, Na(1) forms a weak seventh bond with O(5B) at 2.900 Å. The small amount of Ca reported in the chemical analysis (Chao, 1978) may be located at the Na(1) position. The Na(2A) and Na(2B) octahedra, both with point symmetry $\bar{1}$, are related by the pseudo–mirror plane parallel to (101) and are very similar in configuration.

Double silicate sheet

The double silicate sheet consists of two polymerized single silicate sheets of the apophyllite type with four- and eight-membered rings (Fig. 4). The single silicate sheet consists of single chains of corner-sharing tetrahedral four-membered silicate rings parallel to [101]; adjacent chains by sharing tetrahedral corners give rise to the silicate sheet with eight-membered rings. Within each silicate chain, there are two types of alternating four-membered rings formed by (1) Si(4)–Si(5A)–Si(6)–Si(5B) and (2) Si(1)–Si(2B)–Si(3)–Si(2A) (Fig. 4). Two silicate tetrahedra [Si(1)
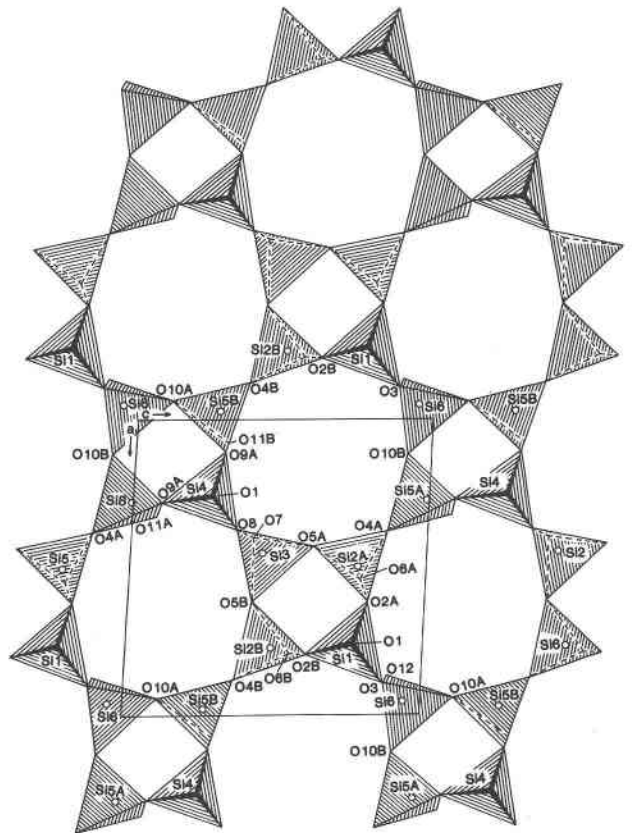

Fig. 4. An apophyllite-type single silicate sheet of montregianite parallel to the (010) plane consisting of four- and eight-membered rings. Two such single silicate sheets related by n-glide share the apical oxygen atom O(1) between Si(1)- and Si(4)-tetrahedra to form the double silicate sheet.
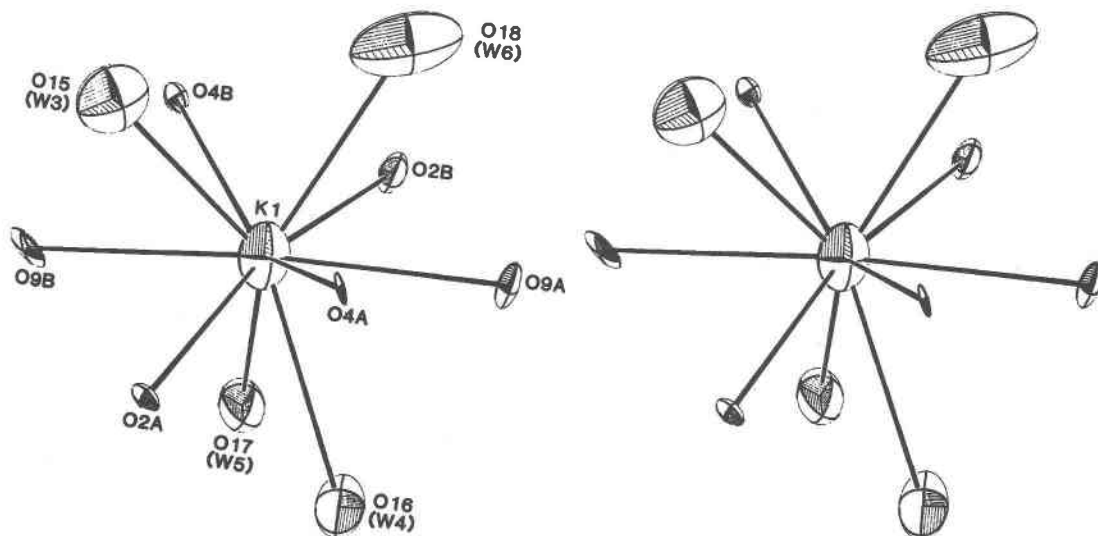
Fig. 5.   Stereoscopic view of the coordination polyhedron around the K(1) atom and the atomic thermal-vibration ellipsoids.

and Si(4)], one each within the two four-membered rings belonging to a single sheet, have upward-pointing [O(1)] apices that are shared with the apices of the two downward-pointing corresponding tetrahedra [Si(4) and Si(1), respectively] in the second silicate sheet, which is related to the first sheet by the *n*-glide parallel to (010). The Si–O–Si angle at the shared apical oxygen is very close to 180° [Si(1)–O(1)–Si(4): 176.5°]. Polymerization of two single silicate sheets in this manner creates additional collapsed boat-shaped eight-, ten-, and twelve-membered rings. The *n*-glide operation creating the second sheet superposes it almost exactly on the first one parallel to (010), such that the largest channel opening is provided by the nearly planar open eight-membered rings in the single sheet, the channel direction being parallel to [010].

Potassium atom

The K atom occurs in a split position [K(1) and K(2)] with a separation of 0.34 Å and site occupancies of 0.62 and 0.38 within these large channels. The tenfold [$KO_6(H_2O)_4$] coordination (Fig. 5) is quite irregular with an average K–O bond length of 2.978 Å at K(1) and 2.991 Å at K(2). The K polyhedron is similar to the Ba polyhedron in macdonaldite and can be described by an irregular hexagon formed by the six oxygen ligands, where two water molecules occur above and two below the hexagonal plane and form a tetrahedral arrangement around K. Compared to the other atoms in the double silicate and octahedral layers, the anisotropic thermal vibration of the K atom is very pronounced, as are those of the ligand water molecules, particularly W(6) with a site occupancy of 0.37.

WATER MOLECULES

Of the six independent water molecules, two [W(1) and W(2)] are part of the octahedral layer with full site occupancies (Fig. 3). Of the other four, W(3) is nearly fully

occupied (0.95), whereas site occupancies of the rest [W(4), W(5), W(6)] range between 0.35 and 0.46. The latter three water molecules are bonded to one K atom each and are not H-bonded, presumably corresponding to the essentially free O–H stretching frequency of 3610 cm^{-1} in the infrared spectrum (see Chao, 1978). They show pronounced anisotropic thermal vibration and presumably leave the structure at the beginning of the second stage of dehydration (80–200°C) (see Chao, 1978, for the dehydration curve), whereas disordered zeolitic water molecules adsorbed within the channels leave the structure during the first stage (25–80°C). The water molecule W(3)—which is bonded to K at an average distance of 2.89 Å and is probably H-bonded to W(4) and W(5) at distances of 2.984 and 2.987 Å, respectively, in a bifurcated bond—probably leaves the structure next. This possible H bond is weak and may correspond to the observed O–H stretching frequency of 3510 cm^{-1}. Next to leave the structure are the water molecules W(1) and W(2), corresponding to the sharp peak at 240°C in the dehydration curve. Both water molecules are bonded to two Na atoms each. In addition, one H atom in each water molecule may be H-bonded to oxygen atoms O(10A) and O(10B), which occur at distances of 2.874 and 3.019 Å from W(1) and W(2), respectively. These H bonds may correspond to the O–H stretching frequency of 3460 cm^{-1}. As reported by Chao (1978), dehydration is essentially complete at 400°C, but rehydration occurs on cooling within 2 h following heating to 650°C. This behavior—which is very similar to that found in macdonaldite and the fibrous zeolites mesolite and scolecite (Alfors et al., 1965)—and the structural details establish the zeolitic nature of montregianite.

RELATED STRUCTURES

This structure determination confirms the observation made by Chao (1978) that montregianite belongs to the

same family of orthorhombic or pseudo-orthorhombic alkali silicate minerals macdonaldite (Cannillo et al., 1968), delhayelite (Cannillo et al., 1969), and rhodesite (Hesse, 1979). Although all four minerals are characterized by the same type of double silicate sheets, important differences exist with respect to the constitution of the octahedral layers and the channel constituents. In macdonaldite and rhodesite, the octahedral layer consists of H-bonded chains of edge-sharing Ca octahedra, whereas in delhayelite, the octahedral layer is a solid wall consisting of Ca and Na octahedra. K atoms and water molecules are located in the channels defined by the eight-membered silicate rings in rhodesite as in montregianite, whereas Ba takes the place of K in macdonaldite. In the anhydrous mineral delhayelite, the channel constituents are K and Cl atoms.

In view of the similarities of the chemical compositions and crystal structures of montregianite, $K_2Na_4Y_2Si_{16}O_{38}\cdot 10H_2O$, and rhodesite, $K_2Ca_4Na_2Si_{16}O_{38}\cdot 12H_2O$ (Gard and Taylor, 1957; Mountain, 1957; Sheppard and Gude, 1969), it is very likely that these two structures are related by the substitution $(Na_4Y_2) \rightarrow (Ca_4Na_2)$ and are closely comparable. The reported unit-cell dimensions of rhodesite [$a = 23.416(2)$, $b = 6.555(1)$ and $c = 7.050(1)$ Å (Hesse, 1979)] are most likely in error and the true b and c dimensions are double those reported. Hesse (1979) reported the chemical composition of rhodesite as $H_2K_2Ca_4Si_{16}O_{38}\cdot 10H_2O$, which lacks Na as an essential constituent. This mineral should be re-examined to establish its correct chemical composition, symmetry, and the unit-cell dimensions. If, indeed, b and c are double those reported previously, the crystal structure needs reinvestigation.

DISCUSSION

Si-O bond lengths and Si-O-Si angles

Within the double silicate sheet consisting of eight crystallographically distinct silicate tetrahedra, Si(1) and Si(4) are unique where all four Si–O bonds are bridging (avg. Si–O 1.598 Å); within each of the other six tetrahedra, three Si–O bonds are bridging and one is nonbridging (avg. Si–O 1.613 Å). The Si(1) and Si(4) tetrahedra are not only smaller but are also more regular with respect to bond lengths and angles than the other six tetrahedra (Table 3). This difference in the average Si–O bond lengths in the two types of silicate groups has also been observed in macdonaldite (Cannillo et al., 1968) and appears to be statistically significant. One reason for the short average Si–O bond lengths within the Si(1) and Si(4) tetrahedra may be the unusually large Si–O–Si angle of 176.5° mentioned earlier, since quantum mechanical calculations have shown that shorter Si–O bond lengths are associated with larger Si–O–Si angles (Tossell and Gibbs, 1977). Within the latter group of six tetrahedra, the average bridging and nonbridging Si–O bond lengths are 1.628 and 1.569 Å, respectively. The shortest nonbridging bond length (1.562 Å) involves the most charge-deficient oxy-

gen [O(12)], which is bonded to a Y atom in addition to the Si atom. The oxygen atoms involved in other nonbridging Si–O bonds are also somewhat charge-deficient and are bonded to one Y and two Na atoms, in addition to one Si. The O–Si–O angles within these six tetrahedra range between 102° and 116°, whereas those within the Si(1) and Si(4) tetrahedra range between 107° and 112°. The distribution of the Si–O–Si angles [except Si(1)–O(1)–Si(4)] shows two maxima at 151.6° and 140.7° with average Si–O bond lengths 1.613 and 1.625 Å, respectively.

Planarity of the four- and eight-membered tetrahedral rings within the single silicate sheet

Within the single silicate sheet, there are two different four-membered rings (Fig. 4): (1) Si(1)–O(2B)–Si(2B)–O(5B)–Si(3)–O(5A)–Si(2A)–O(2A) and (2) Si(4)–O(9B)–Si(5A)–O(10B)–Si(6)–O(10A)–Si(5B)–O(9A). The maximum and minimum deviations of the ring oxygens from the least-squares planes passed through the four Si atoms only are 0.46 and 0.18 Å for ring (1) and 0.48 and 0.09 Å for ring (2), respectively, the acute angle between the two rings being 3.2°.

The eight-membered ring consisting of (3) Si(2A)–O(5A)–(Si(3)–O(8)–Si(4)–O(9A)–Si(5B)–O(4B)–Si(2B)–O(2B)–Si(1)–O(3)–Si(6)–O(10B)–Si(5A)–O(4A) is much more irregular; the maximum and minimum deviations of the ring oxygens from the least-squares plane passed through the eight Si atoms only are 1.23 and 0.14 Å. The acute angles between (1) and (3) and between (2) and (3) are 28.5° and 31.7°, respectively.

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