

Two independent refinements of the structure of paracelsian, $\text{BaAl}_2\text{Si}_2\text{O}_8$

G. CHIARI

*Dipartimento di Scienze della Terra
Van San Massimo 22, Torino, 10123, Italy*

G. GAZZONI

*III Sezione Centro Nazionale di Cristallografia del C. N.R.
c/o Dipartimento di Scienze della Terra
Via San Massimo 22, Torino, 10123, Italy*

J. R. CRAIG, G. V. GIBBS, AND S. J. LOUISNATHAN

*Department of Geological Sciences
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061*

Abstract

Two independent refinements of natural paracelsian, $\text{BaAl}_2\text{Si}_2\text{O}_8$, using different crystals from Benallt mine, Carnarvonshire, England, yielded comparable R values ($R = 3.47\%$, $R_w = 2.95\%$ and $R = 3.5\%$, $R_w = 4.3\%$). Unit cell parameters and atomic coordinates are significantly different in the two refinements, but the Ba polyhedra distances and the OTO and TOT angles are very similar. Although the grand mean TO values are equal, the tetrahedra show systematic variations which are ascribed to differences in the degree of Al-Si disorder.

Introduction

The crystal structure of paracelsian, the relatively rare barium feldspar, $\text{BaAl}_2\text{Si}_2\text{O}_8$, was first investigated by Smith (1953). His refinement, using two-dimensional Fourier maps, showed that paracelsian is monoclinic (S.G. $P2_1/a$) with a strong orthorhombic pseudo-symmetry (S.G. $Pnam$). Subsequently, by using Smith's intensity data and assuming analogy with hurlbutite, $\text{CaBe}_2\text{P}_2\text{O}_8$, Bakakin and Belov (1961) attempted to differentiate the Al-Si populations of the tetrahedral T-sites and were able to reduce the R value of Smith by 5%.

The present paper reports the results of two independent refinements carried out at the Dipartimento di Scienze della Terra di Torino (Chiari and Gazzoni noted below as CG) and at the Virginia Polytechnic Institute and State University (Craig, Gibbs, and Louisnathan noted below as CGL). Both studies employed natural paracelsian as this mineral has not been synthesized in the $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$ system (Lin and Foster, 1968; Calleri and Gazzoni, 1977 and references therein). These two refinements offer a unique opportunity to examine the degree to which different, but compositionally identical, crystals from one locality vary in crystal structure.

Experimental details

Both refinements were carried out using crystals of paracelsian from the Benallt Mine, Carnarvonshire, U.K., kindly provided by

the British Museum (no. 1969, 193) to CG and by the U.S. National Museum of Natural History to CGL.

The crystal used by CG was ground to a rough sphere, 0.025 mm in diameter; the crystal used by CGL was nearly equant, with a diameter of about 0.08 mm. Qualitative electron probe analysis of the first sample revealed the presence of no elements other than those necessary for the formula. Quantitative analysis of the second crystal yielded a composition of $\text{Ba}_{0.96}\text{Na}_{0.02}\text{K}_{0.04}\text{Al}_{1.96}\text{Si}_{2.04}\text{O}_8$.

CG refined unit cell parameters on the basis of 25 reflections automatically centered on a Nicolet R3 diffractometer using graphite monochromatized $\text{MoK}\alpha$ radiation in the range of 13 to 67° and $\text{MoK}\alpha$ radiation from 67 to 83° 2θ . CGL refined unit cell parameters on the basis of 28 reflections automatically centered on a Picker four-circle X-ray goniostat using Nb-filtered $\text{MoK}\alpha$ radiation (0.71069 Å) in the range of 30-65° 2θ . Lorentz polarization corrections were applied in both refinements, and CG employed empirical absorption coefficients of 1.00 to 1.13 based upon the ψ scan method of North, Phillips, and Mathews (1968). For the refinement CG used 4480 reflections with $I > 1.96 \delta_0$ of a total of 4902 reflections measured on the basis of monoclinic symmetry. CGL measured more than 1450 non-equivalent reflections, assuming orthorhombic symmetry, of which 1277 had magnitudes more than six times one standard deviation and were used for the refinement.

The structure refinements

The CGL refinement was initiated using Smith's (1953) atomic coordinates; whereas, the CG refinement was car-

Table 1. Crystal data. $\text{BaAl}_2\text{Si}_2\text{O}_8$, $M = 375.5$, monoclinic, space group $P2_1/a$, $F_{(000)} = 696$, $D_c = 3.33 \text{ Mg m}^{-3}$, $Z = 4$, $\mu_{(\text{MoK}\alpha)} = 58.8 \text{ mm}^{-3}$

	Cell Parameters		
	Smith (1953)	CG	CLG
a	9.076(5) Å	9.072(2) Å	9.065(3) Å
b	9.583(5)	9.588(2)	9.568(1)
c	8.578(5)	8.577(2)	8.578(5)
β	$\sim 90^\circ$	90.21(2)°	90.01(4)°
V	746.1(8) Å ³	746.0(4) Å ³	744.0(6) Å ³

ried out from scratch using the direct method program SOLV of the SHELXTL package (Nicolet, 1981). CG located the positions of the Ba and two T-atom sites on the E-map and used difference Fourier maps to define the remaining atom sites. They assigned the distribution of Al and Si in the T-sites on the basis of average TO distances. CG, after four least squares cycles with unit weights and isotropic temperature factors, obtained an initial R value of 4.6%; the introduction of anisotropic temperature factors reduced the R value to 3.6%. Application of empirical extinction corrections with the SHELXTL program (Larson, 1967), a weighting scheme of $w = 1/\delta_{F_o}^2$ (where δ_{F_o} is the e.s.d.), and the omission of the three strongest reflections (201, 201, 205), which were clearly affected by extinction, resulted in final R values of $R = 3.47\%$, $R_w = 2.95\%$, and a goodness of fit of 4.16. CG computed atomic scattering factors, including anomalous dispersion corrections using the analytical expression of Cromer and Weber (1974). All scattering factors were calculated assuming neutral atoms.

CGL's initial refinement using unweighted data and isotropic temperature factors converged after six cycles to yield an R of 0.183. Three further least squares iterations, carried out using a weighting scheme, anisotropic temper-

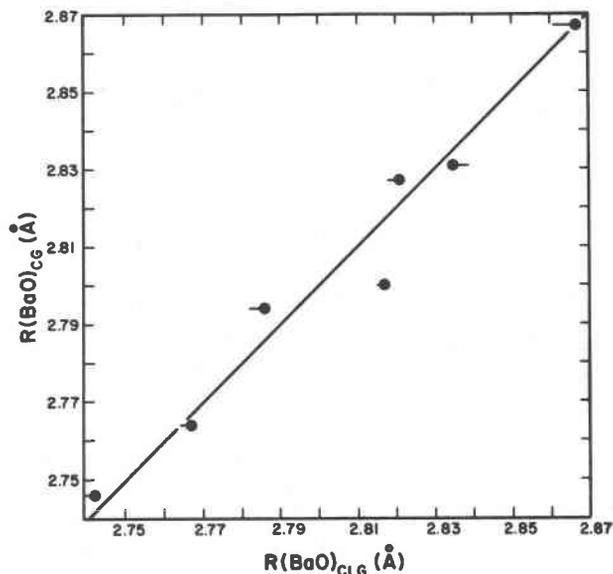


Fig. 1. BaO distances obtained by CG plotted against the corresponding values obtained by CGL. Dots refer to CGL values calculated using CG cell parameters. Ends of tails refer to CGL values calculated using their cell. All values agree with 3 e.s.d.

ature factors, and anomalous dispersion corrections for the scattering functions of Ba, Al, and Si (Cromer and Weber, 1974), yielded final R factors of $R = 0.035$ and $R_w = 0.043$. The weighting scheme was:

$$w = \{1 + [(F_{\text{obs}} - \text{PA.FT})/\text{FT.xx}]^2\}^{-1}$$

where PA, FT, and xx were variables which were adjusted until $\langle w\Delta^2 \rangle$ was constant over the equally populated

Table 2. Atomic coordinates, equivalent isotropic temperature factors for the two refinements of the paracelsian structure

	CG				CLG				Δ^* (Å)
	x	y	z	$U_{\text{equiv}}(\text{Å}^2)$	x	y	z	$U_{\text{equiv}}(\text{Å}^2)$	
Ba	.89778(2)	.41169(1)	.25051(2)	.008	.89785(5)	.41174(4)	.25107(5)	.008	.0049(5)
Si(1)(o)	.06737(7)	.19879(7)	.93951(8)	.005	.0688(2)	.1994(2)	.9411(2)	.004	.020(2)
Al(1)(m)	.06389(8)	.19453(8)	.57128(8)	.005	.0642(3)	.1939(2)	.5726(3)	.005	.013(3)
Al(2)(o)	.22539(8)	.92092(8)	.93134(8)	.005	.2242(3)	.9214(2)	.9302(3)	.005	.015(3)
Si(2)(m)	.23099(7)	.91692(7)	.56341(8)	.006	.2307(2)	.9167(2)	.5625(2)	.005	.008(2)
O(1)(o)	.1953(2)	.0886(2)	.9985(2)	.010	.1948(7)	.9898(5)	.9991(7)	.008	.013(6)
O(2)(o)	.1285(2)	.3604(2)	.9569(2)	.008	.1272(7)	.3605(5)	.9556(7)	.010	.016(6)
O(2)(m)	.1313(2)	.3632(2)	.5450(2)	.008	.1315(6)	.3642(5)	.5445(7)	.008	.011(5)
O(3)(o)	.9273(2)	.1850(2)	.0575(2)	.010	.9298(6)	.1848(5)	.0595(6)	.008	.028(6)
O(3)(m)	.9117(2)	.1852(2)	.4494(2)	.010	.9091(6)	.1844(5)	.4495(7)	.005	.025(6)
O(4)	.0192(2)	.1666(2)	.7632(2)	.013	.0188(7)	.1657(5)	.7642(7)	.012	.013(6)
O(5)	.2936(2)	.9107(2)	.7422(2)	.011	.2916(7)	.9108(5)	.7390(6)	.009	.033(6)

Δ^* in the last column is the distance in Å between corresponding atoms in the two refinements calculated using the cell parameters of CG.

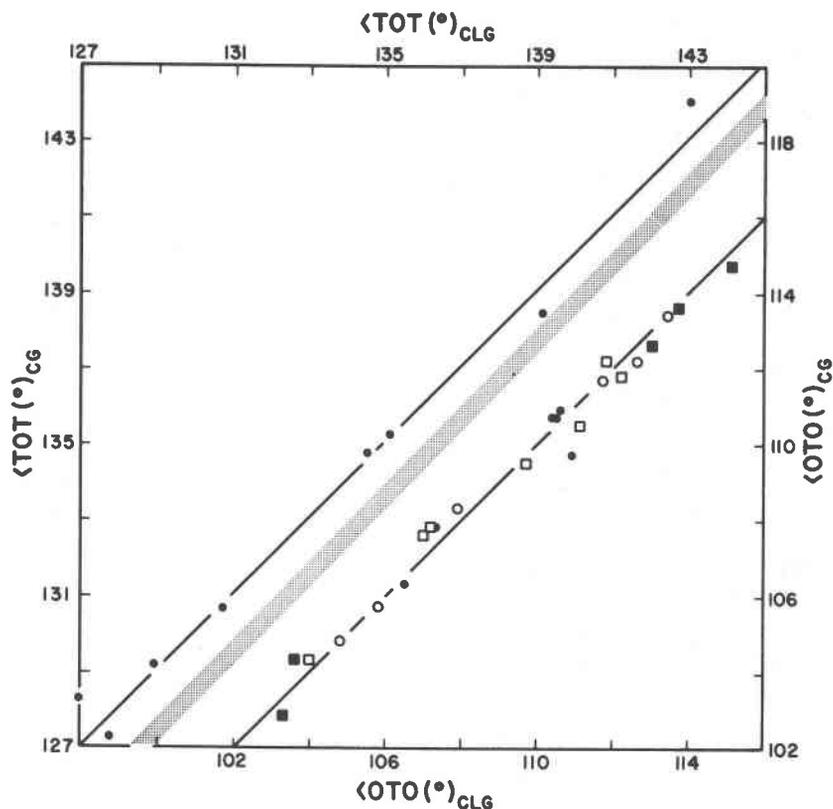


Fig. 2. TOT angles (upper left) and OTO angles (lower right) obtained by CG are plotted against corresponding values obtained by CG1. For the OTO angles, full circles refer to the Si(1)(o), open circles to Si(2)(m), full squares to Al(2)(o) and open squares to Al(2)(m) tetrahedra.

groups of increasing $|F_{\text{obs}}|$; the final values of PA, FT, and α were 1.31, 28.9, and 2.82, respectively. Because the β angle is so close to 90° , it was not possible to distinguish between hkl and $hk0$ reflections; changing the sign of the third index did not alter the R values, positional parameters, or temperature factors. The 15 most intense reflections were left out of the data set in the final refinement because it appeared evident that these were affected by secondary extinction.

Comparison of the two refinements

Cell dimensions. The refinement by CG yielded cell dimensions that were within one standard deviation of those reported by Smith (1955); whereas, the values obtained by CGL on a different crystal were somewhat smaller (Table 1).

Atomic coordinates. Table 2, which lists atomic coordinates and the equivalent isotropic U (defined as one-third of the trace of the orthogonalized U_{ij} tensor; Hamilton, 1959), reveals that there are small, but real, differences between the atom positions as determined by the two refinements. The slightly larger e.s.d.'s of the CGL refinement result from the differences in the numbers of observations (4484 for CG and 1277 for CGL).

Thermal parameters. The thermal parameters, U , of the two refinements are in good agreement (Table 2) in spite of CG having used much higher $\sin \theta/\lambda$ values. The largest difference between the two refinements was for the O(3)(m) atom, for which there are the largest differences in the Si-O and Al-O distances as well.

Distances and angles. The bond distances and angles determined in the two studies of different paracelsian crystals are shown in Table 2. The Ba-O distances of the two refinements have been plotted against one another in Figure 1 to test for the presence of systematic errors. In Figure 1, dots refer to CGL values calculated using CG cell parameters, whereas the ends of the tails correspond to CGL values calculated using CGL cell parameters. The plot reveals that the differences between the two refinements are essentially random. The average Ba-O distances, assuming seven-fold coordination for Ba, are statistically identical (2.804 and 2.803 Å). The shift in the position of the heavy Ba atom in the two structures is thus apparently controlled by the rearrangement of the oxygen atoms in the coordination polyhedron. The resulting configuration corresponds to the minimal potential energy.

The OTO and TOT angles determined in the two refinements are very similar, as shown in Figure 2. Although the

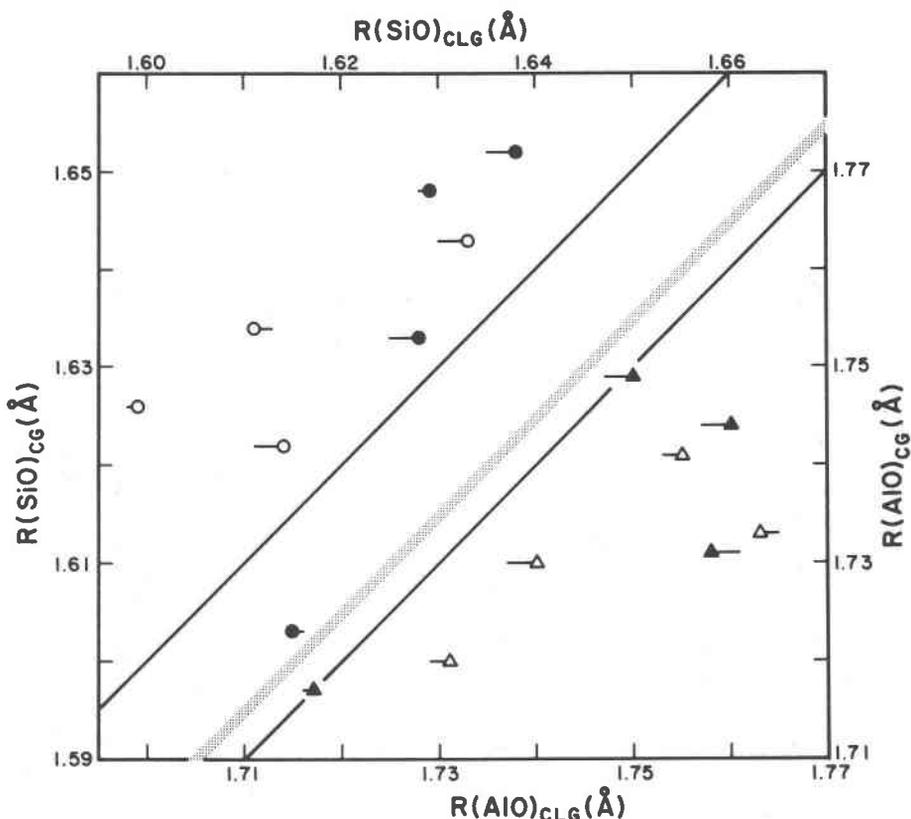


Fig. 3. SiO distances (upper left) and AlO distances (lower right) obtained by CG plotted against corresponding values obtained by CG1. All the SiO points but one are above the 45° line, while the AlO points are systematically below the 45° line. This can be explained with a larger degree of disorder in the CG sample.

grand mean TO distances for the four tetrahedra are identical (1.683 Å) for the two refinements, the average TO values, $\langle TO \rangle$, for each pair of individual tetrahedra are not. CG found $\langle SiO \rangle$ values (1.634, 1.631) which are significantly larger than those found by CGL (1.626, 1.613). Conversely, the CG $\langle AlO \rangle$ values (1.735, 1.731) are significantly smaller than those found by CGL (1.745, 1.746). The same observation holds for individual bonds, except for Si(2)(m)-O(3)(m), as shown in Figure 3. The O...O distances follow the same trend (Table 3c) without exception.

The most likely explanation for these systematic differences is a larger degree of Al-Si disorder in the crystal studied by CG than in the crystal studied by CGL. This suggestion is supported by the smaller cell dimensions reported for the CGL crystal. The Al occupancies of the various tetrahedra, calculated on the basis of $\langle TO \rangle_{tet}$ according to the equation:

$$Al/(Al + Si) = -10.281 + 6.412\langle TO \rangle$$

(from Gibbs, pers. comm.) are reported in Table 2a. The Al contents for both structures add up to 2.03 in good agree-

ment with the expected value of 2.00 which corresponds to a 1:1 Al-Si ratio.

Pseudo-symmetry. The monoclinic unit cell of paracelsian has a strong orthorhombic pseudo-symmetry. If the cell were orthorhombic, the tetrahedra identified by the suffix (o) and (m) would be symmetry related; the tetrahedra would display complete Al-Si disorder. Accordingly, the differences in the coordinates between the pseudo-symmetric atoms is a measure of the deviation from the orthorhombic symmetry. Table 5 lists the distances in Å for pairs of atoms after applying pseudo-symmetry operations on the z-coordinate calculated using the CG cell parameters. The "splits," which are systematically larger for the CGL than for the CG structure, are indicative of the greater degree of Al-Si order in the CGL sample.

Conclusions. Two independent crystal structure refinements on compositionally equivalent paracelsian crystals from the same locality reveal differences in unit cell dimensions, bond distances, and bond angles. These differences are interpreted as the result of differing degrees of Al-Si disorder, suggesting that the two specimens either formed or re-equilibrated under different sets of *P-T* conditions.

Table 3. Bond distances (Å) and angles (°) for paracelsian

(a) Tetrahedral interatomic distances										
	C.G.		C.L.G.		C.G.		C.L.G.		C.L.G.	
Si(1)(o) - O(1)(o)	1.648(2)		1.628(6)		Al(2)(o) - O(1)(o)	1.730(2)		1.737(5)		
- O(2)(o)	1.652(2)		1.635(5)		- O(2)(o)	1.733(2)		1.765(7)		
- O(3)(o)	1.633(2)		1.625(6)		- O(3)(o)	1.721(2)		1.729(6)		
- O(4)	1.603(2)		1.616(6)		- O(5)	1.741(2)		1.753(6)		
Mean	1.634		1.626		Mean	1.731		1.746		
Al occupancy*	0.196		0.145		Al occupancy*	0.813		0.916		
Al(1)(m) - O(1)(m)	1.749(2)		1.747(6)		Si(2)(m) - O(1)(m)	1.622(2)		1.611(5)		
- O(2)(m)	1.744(2)		1.757(5)		- O(2)(m)	1.643(2)		1.630(6)		
- O(3)(m)	1.731(2)		1.761(6)		- O(3)(m)	1.626(2)		1.598(6)		
- O(4)	1.718(2)		1.716(7)		- O(5)	1.634(2)		1.613(6)		
Mean	1.735		1.745		Mean	1.631		1.613		
Al occupancy*	0.844		0.908		Al occupancy*	0.177		0.062		
Grand mean	1.683		1.683		Sum of Al occupancy	2.03		2.03		
(b) Bond angles (°) at tetrahedral sites. All e.s.d. = 0.1(°) for C.G. and 0.3(°) for C.L.G.										
	01-02	01-03	01-04	01-05	02-03	02-04	02-05	03-04	03-05	Mean
Si(1)(o)	109.7 110.9	107.9 107.3	110.8 110.8		106.4 106.5	110.9 110.5		111.0 110.6		109.5** 109.4
Al(1)(m)	109.6 109.8	107.7 107.1	111.9 112.3		104.4 104.1	110.6 111.1		112.3 112.0		109.4 109.4
Al(2)(o)	104.4 103.6	113.7 113.8		114.8 115.2	112.7 113.2		102.9 103.5		107.9 107.2	109.4 109.4
Si(2)(m)	105.8 105.9	111.8 111.6		113.5 113.5	112.3 112.7		104.9 104.8		108.4 108.1	109.5 109.4
(c) Oxygen-oxygen distances within tetrahedra (Å)										
Si(1)(o)	2.699(3) 2.688(7)	2.652(3) 2.620(8)	2.767(3) 2.671(1)		2.630(3) 2.612(8)	2.680(3) 2.671(8)		2.667(3) 2.665(8)		2.668** 2.655
Al(1)(m)	2.854(3) 2.867(6)	2.809(3) 2.822(8)	2.872(3) 2.875(9)		2.746(3) 2.773(7)	2.847(3) 2.864(8)		2.865(3) 2.882(8)		2.832 2.847
Al(2)(o)	2.736(3) 2.751(8)	2.889(3) 2.904(7)		2.924(3) 2.946(8)	2.875(3) 2.917(8)		2.717(3) 2.763(8)		2.799(3) 2.802(8)	2.823 2.847
Si(2)(m)	2.605(3) 2.586(7)	2.689(3) 2.655(7)		2.723(3) 2.697(8)	2.716(3) 2.686(8)		2.598(3) 2.569(8)		2.644(3) 2.599(8)	2.662 2.632

*Al occupancy calculated according to the equation: $Al/Al+Si = -10.281 + 6.412 <T0>$.

**The first line of each entry refers to C.G. refinement; the second line to C.L.G. refinement.

Table 4. TOT angles (°)

	C.G.	C.L.G.
Si(1)(o) - O(1)(o) - Al(2)(o)	127.3(1)	126.9(4)
Si(2)(m) - O(1)(m) - Al(1)(m)	130.7(1)	130.8(4)
Si(1)(o) - O(2)(o) - Al(2)(o)	128.3(1)	126.9(3)
Si(2)(m) - O(2)(m) - Al(1)(m)	129.2(1)	129.1(3)
Si(1)(o) - O(3)(o) - Al(2)(o)	135.3(1)	135.1(3)
Si(2)(m) - O(3)(m) - Al(1)(m)	134.8(1)	137.7(4)
Si(1)(o) - O(4) - Al(1)(m)	144.1(1)	143.2(4)
Si(2)(m) - O(5) - Al(2)(o)	138.5(1)	139.2(4)
Mean	133.5	133.2

Table 5. BaO distances (within 3.5 Å)

	C.G.	C.L.G.
Ba - O(1)(o)	2.831(2)	2.839(6)
- O(1)(m)	2.868(2)	2.861(6)
- O(2)(o)	2.827(2)	2.818(5)
- O(2)(m)	2.794(2)	2.782(5)
- O(3)(o)	2.746(2)	2.739(5)
- O(3)(m)	2.764(2)	2.764(5)
- O(5)	2.800(2)	2.816(6)
Mean	2.804	2.803
Ba - O(2)(o)	3.317(2)	3.315(6)
- O(2)(m)	3.323(2)	3.321(6)

Table 6. Distances (Å) between pseudo-symmetry related atoms for the two structures, calculated with CG cell parameters, after applying the pseudo-symmetry operations to the z parameter.

	CG	CLG
Si(1)(o) - Al(1)(m)	0.106(1)	0.136(3)
Si(2)(m) - Al(2)(o)	0.078(1)	0.097(3)
O(1)(o) - O(1)(m)	0.156(3)	0.169(6)
O(2)(o) - O(2)(m)	0.040(3)	0.053(8)
O(3)(o) - O(3)(m)	0.157(3)	0.206(8)

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