

## High-Pressure Silicate Pyrochlores, $\text{Sc}_2\text{Si}_2\text{O}_7$ and $\text{In}_2\text{Si}_2\text{O}_7$

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The silicate compounds  $\text{Sc}_2\text{Si}_2\text{O}_7$  and  $\text{In}_2\text{Si}_2\text{O}_7$  have been converted from thortveitite type to pyrochlore type at  $1000^\circ\text{C}$ , 120 kbar, with resulting cell constants of 9.287(3) and 9.413(3) Å, respectively. Invariant reflection intensities in the X-ray powder diffraction patterns allowed precise absorption corrections to be made, and refinement of thermal parameters and of the single structural parameter  $x$  gave values of 0.4313(21) and 0.4272(15), respectively. The corresponding six-coordinate Si-O distances were 1.761(7) and 1.800(5) Å, and the average eight-coordinate distances for Sc-O<sub>8</sub> and In-O<sub>8</sub> were 2.267 and 2.275 Å. Values of structure-refined bond lengths for compounds containing six-coordinate silicon are surveyed, and overall weighted average octahedral distances of 1.782(14) Å for Si-O and 2.520(18) Å for O-O are derived. Pyrochlore phases were not produced from rare-earth disilicate or monosilicate phases subjected to the same reaction conditions as the Sc and In compounds.

### 1. Introduction

The high density of the deeper mantle of the earth requires that the silicate minerals of which it is primarily composed must contain silicon in six-coordinate form (1-3). A knowledge of such dense silicates is thus of great importance to an understanding of the mantle.

Numerous "model" compounds, isotopic with those believed to compose the mantle, have been investigated (3-5), and a number of examples of high-pressure silicates containing six-coordinate silicon have now been found. These include stishovite (6), the rutile form of  $\text{SiO}_2$ , the hollandite forms of the feldspar compositions  $\text{KAlSi}_3\text{O}_8$  (7),  $\text{Ba}_x\text{Al}_{2x}\text{Si}_{4-2x}\text{O}_8$  and  $\text{Sr}_x\text{Al}_{2x}\text{Si}_{4-2x}\text{O}_8$ ,  $x \approx 0.75$  (8), and the perovskite form of  $\text{CaSiO}_3$  (9). In the high-pressure garnet forms of (Mg, Fe) $\text{SiO}_3$  (10), aluminous enstatites (11), and  $\text{MnSiO}_3$  (12), silicon is distributed between tetrahedral and

octahedral sites. Recently, ilmenite (13) and perovskite (14, 15) forms of  $\text{MgSiO}_3$  have also been produced.

The only compounds formed at zero pressure so far known to contain silicon octahedrally bonded to oxygen are the polymorphs of  $\text{Si}_2\text{P}_2\text{O}_7$  (16-18), the hydroxide mineral thaumasite,  $\text{Ca}_3[\text{Si}(\text{OH})_6](\text{SO}_4)(\text{CO}_3) \cdot 12\text{H}_2\text{O}$  (19, 20), and the coordination compound pyridinium-tris(*o*-phenylenedioxy)-silicate (21). In these compounds the atoms bonded to the O atoms attached to Si are of relatively high electronegativity.

In the present work we describe the synthesis and structural refinement of dense, high-pressure pyrochlore forms of thortveitite,  $\text{Sc}_2\text{Si}_2\text{O}_7$ , and of  $\text{In}_2\text{Si}_2\text{O}_7$ , and discuss some implications of their crystal chemistry for the behavior of Sc, In, and Si in high-pressure oxide structures and in the mantle of the earth. A comparison of the Si-O<sub>6</sub> octedral para-

meters for those structures which have been refined so far is also presented.

A preliminary report on the occurrence of the pyrochlore silicates has been made elsewhere (22).

## 2. Experimental

Synthetic thortveitite (23),  $\text{Sc}_2\text{Si}_2\text{O}_7$ , and  $\text{In}_2\text{Si}_2\text{O}_7$  of thortveitite form were prepared by reaction at  $1500^\circ\text{C}$  of finely ground 1:2 molar mixture of  $\text{Sc}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  with precipitated silica. Three cycles of grinding followed by heating for 20-hr periods were found to give single phases with the thortveitite structure. Approximately 10 mg of each material was reacted for 5 min at 100 kbar and  $1000^\circ\text{C}$  in an opposed anvil apparatus (24) and cooled to

room temperature before the release of pressure.

The X-ray diffraction pattern of the products was recorded in a Debye-Scherrer camera of 114-mm diameter, using nickel-filtered  $\text{CuK}\alpha$  radiation. Line spacings were measured with a traveling microscope, and back-angle measurements were used to apply film shrinkage corrections. Lattice parameters for the cubic cells were obtained by extrapolation to  $\theta = 90^\circ$  of the plot of lattice parameter vs  $\frac{1}{2}[(\cos^2\theta/\sin\theta) + (\cos^2\theta/\theta)]$  (25).

X-ray reflection intensities were obtained from a series of three films placed one behind the other in the Debye-Scherrer camera and simultaneously exposed. Intensities were determined by measuring the areas of peaks obtained from scans of these films with a precision microphotometer.

TABLE I  
PYROCHLORE-TYPE  $\text{Sc}_2\text{Si}_2\text{O}_7$  X-RAY POWDER DATA<sup>a</sup> FOR  $\text{CuK}\alpha$  WHERE  $\lambda = 1.5418 \text{ \AA}$

<i>h k l</i>	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	$I_{\text{calc}}^b$	$I_{\text{obs}}^c$
2 2 2	2.680	2.681	102.33	100.00
4 0 0	2.321	2.322	9.14	9.81
3 3 1	2.130	2.131	23.43	24.40
4 2 2	1.8979	1.8957	2.57	3.04
5 1 1 } 3 3 3 }	1.7887 —	1.7873 } 1.7873 }	8.18	8.71
4 4 0	1.6418	1.6417	49.52	50.23
5 3 1	1.5706	1.5698	1.61	1.48
6 2 0	1.4702	1.4684	1.76	2.12
6 2 2	1.3999	1.4001	29.70	29.83
4 4 4	1.3405	1.3405	5.87	5.79
7 1 1 } 5 5 1 }	1.3009 —	1.3004 } 1.3004 }	0.77	1.39
7 3 1 } 5 5 3 }	1.2090 —	1.2091 } 1.2091 }	0.62	1.41
8 0 0	1.1609	1.1609	5.49	6.84
7 3 3	1.1347	1.1346	2.33	1.55
6 6 0 } 8 2 2 }	1.0946 —	1.0945 } 1.0945 }	2.32	1.58
6 6 2	1.0654	1.0653	11.04	10.88
8 4 0	1.0382	1.0383	8.29	7.88
8 4 4	0.9478	0.9479	8.81	8.64

<sup>a</sup>  $a_0 = 9.287(3) \text{ \AA}$ .

<sup>b</sup> Using a weight  $1/(I_{\text{obs}} + I_{\text{wt}})$  with  $I_{\text{wt}} = 3.0$ .

<sup>c</sup> Corrected for absorption coefficient  $\mu_r = 1.96$ .

### Absolute Correction of X-Ray Absorption in Pyrochlores

For pyrochlores, the intensities of reflections (222), (622), and (662) are derived only from metal atoms and are invariant with respect to the oxygen coordinate  $x$ . Thus, for a given set of metal atoms the calculated ratios between these reflection intensities can be compared with the observed ratios to give precise values of the correction factor versus  $\sin^2\theta$ . Such plots, usually calculated from  $\mu r$  values, are linear for  $\sin^2\theta$  values of less than 0.825 (25).

The correction factors thus obtained corresponded to  $\mu r \approx 1.96$  for  $\text{Sc}_2\text{Si}_2\text{O}_7$  and  $\approx 1.98$

for  $\text{In}_2\text{Si}_2\text{O}_7$ , for which a very small polycrystalline solid fragment,  $\sim 300 \mu\text{m}$  long, was used for intensity collection. These corrections were consistent with the diameter of the specimens and the mass absorption coefficients of their constituents.

### 3. Results

The powder patterns of the high-pressure forms of  $\text{Sc}_2\text{Si}_2\text{O}_7$  and  $\text{In}_2\text{Si}_2\text{O}_7$  could readily be indexed on the basis of cubic cells with  $a_0 = 9.287 \pm 0.003 \text{ \AA}$  and  $a_0 = 9.413 \pm 0.003 \text{ \AA}$ , respectively (see Tables I and II).

To confirm the structures of these phases,

TABLE II  
PYROCHLORE-TYPE  $\text{In}_2\text{Si}_2\text{O}_7$  X-RAY POWDER DATA<sup>a</sup> FOR  $\text{CuK}\alpha$ , WHERE  $\lambda = 1.5418 \text{ \AA}$

$h k l$	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	$I_{\text{calc}}^b$	$I_{\text{obs}}^a$
1 1 1	5.4281	5.4346	375.3	374.0
3 1 1	2.8366	2.8381	200.0	201.6
2 2 2	2.7167	2.7173	1014.6	1000.0
4 0 0	2.3530	2.3533	235.3	239.1
3 3 1	2.1575	2.1595	297.5	305.8
5 1 1	1.8113	1.8115	124.5	117.6
3 3 3	—	1.8115		
4 4 0	1.6628	1.6640	446.0	449.7
5 3 1	1.5901	1.5911	98.7	89.1
5 3 3	1.4341	1.4355	18.7	21.1
6 2 2	1.4186	1.4191	349.2	357.9
4 4 4	1.3588	1.3587	78.3	79.4
7 3 1	1.2249	1.2255	38.4	45.0
5 5 3	—	1.2255		
8 0 0	1.1768	1.1766	56.7	58.2
7 3 3	1.1500	1.1500	34.3	37.7
7 5 1	1.0871	1.0869	32.8	28.3
5 5 5	—	1.0869		
6 6 2	1.0797	1.0797	136.8	139.7
8 4 0	1.0529	1.0524	110.9	104.7
9 1 1	1.0333	1.0332	40.8	29.2
7 5 3	—	1.0332		
8 4 4	0.9607	0.9607	113.2	113.2
9 5 1	0.9102	0.9100	27.7	21.1
7 7 3	—	0.9100		
10 2 2	0.9059	0.9058	144.0	151.1
6 6 6	—	0.9058		

<sup>a</sup>  $a_0 = 9.413(3) \text{ \AA}$ .

<sup>b</sup> Using a weight  $1/(I_{\text{obs}} + I_{\text{wt}})$  with  $I_{\text{wt}} = 150$ .

<sup>c</sup> Corrected for absorption coefficient  $\mu r = 1.98$ .

and to determine the Si-O<sub>6</sub> octahedral parameters, intensity calculations were initiated using pyrochlore fractional coordinates (26, 27) with Sc or In at the centric origin of Fd3m:

16 Sc in 16(c): 0, 0, 0, etc.

16 Si in 16(d):  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ , etc.

8 O(1) in 8(a):  $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ , etc.

48 O(2) in 48(f):  $x, \frac{1}{8}, \frac{1}{8}$ , etc.

Neutral atom scattering curves for Sc, Si, and O were taken from International Tables (28).

Refinement was performed directly on the observed intensities, using the program described by Rossell and Scott (29) in which the function minimized is  $f(I) = \sum_i w_i [I_i(\text{obs}) - I_i(\text{calc})]^2$  and the residual is  $R = \frac{1}{2} (f(I) / \sum_i w_i [I_i(\text{obs})]^2)^{\frac{1}{2}}$ .

This is effectively equal (29) to a weighted residual based on  $F$ , denoted  $R''$  by Hamilton (30). Weights were of the form  $w = 1/(I_{\text{obs}} + I_0)$  and were statistically appropriate to counting intensities (31). For the present film data  $I_0$  was taken as five times the smallest intensity measured. This approximates a theoretical weight of  $1/(\text{Variance})$ , which would give both weak and strong reflections an equal contribution to the refinement, but would also take into account the uncertainty in the measurement of the weak reflections against the noise level of the microdensitometer traces taken from the Debye-Scherrer films.

TABLE III

REFINED CRYSTALLOGRAPHIC PARAMETERS FOR PYROCHLORE SILICATES

	Sc <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	In <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>
$a_0$ (Å)	9.287 (3) <sup>a</sup>	9.413 (3)
Number of reflections	18	21
$R_I$	0.031	0.015
$x$	0.4313 (21)	0.4272 (15)
$B(\text{Sc or In})$ (Å <sup>2</sup> )	0.37 (31)	0.80 (8)
$B(\text{Si})$	1.28 (49)	0.09 (22)
$B(\text{O1})$	0.88 (136)	0.47 (100)
$B(\text{O2})$	1.67 (41)	0.62 (50)
Si-O (Å)	1.761 (7)	1.800 (5)

<sup>a</sup> Errors in parentheses refer to the e.s.d. in the last digit of the value.

Isotropic temperature factors for each atom were refined together with the single variable in the O(2) coordinates ( $x, \frac{1}{8}, \frac{1}{8}$ ). Although reasonable values of thermal parameters were obtained (Table III) their standard deviations were large. However, their inclusion in the refinement provides a more realistic estimate of uncertainty in  $x$  than refinement of  $x$  alone.

Observed intensities corrected for absorption, together with calculated intensities and observed and calculated  $d$  spacings are given for Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> in Table I and In<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> in Table II. Refinement parameters are given in Table III, and bond lengths for the two compounds are given in Table IV.

#### *Effect of High Pressure on Rare-Earth Disilicates*

A number of disilicates (32), including Lu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, were prepared by methods similar to those described for Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, and subjected to similar conditions of temperature and pressure. No pyrochlore phases were produced, although Lu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> transformed, as has been reported by Bocquillon *et al.* (33), from thortveitite type to the considerably denser triclinic  $\alpha$ -form (34) isotopic with yttrialite (35).

#### *Effect of High Pressures on M<sub>2</sub>SiO<sub>5</sub> Silicates*

Several silicates of M<sub>2</sub>SiO<sub>5</sub> type, including Sc<sub>2</sub>SiO<sub>5</sub>, Y<sub>2</sub>SiO<sub>5</sub>, and Nd<sub>2</sub>SiO<sub>5</sub>, were subjected to pressures of 120 kbar at 1000°C. However, no indication of disproportionation to dense new phases was obtained.

## 4. Discussion

### *The Pyrochlore Structure Type*

The structure of pyrochlore, A<sub>2</sub>B<sub>2</sub>O<sub>7</sub>, can be considered (26, 36, 37) to derive from that of fluorite, with the cubic fluorite axis doubled to allow A and B atoms to alternate in the fluorite metal atom sites, and with one-eighth of the oxygen atoms missing. The structure is thus characterized by a set of A-O<sub>8</sub> polyhedra formed from distorted cubes corner-joined through O(1) atoms to form a network which is interpenetrated by a network of symmetrically distorted corner-joined B-O<sub>6</sub> octahedra

TABLE IV  
BOND LENGTHS<sup>a</sup> AND ANGLES IN Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> AND In<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>  
PYROCHLORES (Å)

	Sc <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	In <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>
6 × Si–O (2)	1.761 (7)	1.800 (5)
2 × (Sc or In)–O (1)	2.0107 (6)	2.0380 (6)
6 × (Sc or In)–O (2)	2.352 (14)	2.356 (10)
Mean (Sc or In)–O <sub>8</sub> distance	2.267 (13)	2.277 (9)
O(2) <sub>5</sub> –O(2) <sub>6</sub> <sup>b</sup>	2.437 (7)	2.454 (5)
O(2) <sub>4</sub> –O(2) <sub>5</sub> <sup>b</sup>	2.544 (30)	2.633 (19)
O(1)–O(2) <sub>1</sub> <sup>c</sup>	2.845 (20)	2.845 (13)
O(1)–O(2) <sub>2</sub> <sup>c</sup>	3.325 (3)	3.364 (2)
O(2) <sub>4</sub> –Si–O(2) <sub>5</sub>	92.5 (7)	94.0 (6)
O(2) <sub>5</sub> –Si–O(2) <sub>6</sub>	87.5 (7)	86.0 (6)

<sup>a</sup> Oxygen numbering after Ref. (22).

<sup>b</sup> Si–O<sub>6</sub> octahedra.

<sup>c</sup> Sc–O<sub>8</sub> or In–O<sub>8</sub> polyhedron.

in which all B–O bonds are of equal length. Each O(1) is at the center of a regular tetrahedron of A atoms, and the O(2) atoms are also four-coordinated, with two bonds to A atoms and two to B atoms.

The existence fields for pyrochlores A<sub>2</sub><sup>4+</sup>B<sub>2</sub><sup>3+</sup>O<sub>7</sub>, where A = Sc, In, Y, Tl and the rare earths, and B = Ge, Ti, Ru, Pt, Ir, Te, Sn, Zr, and Pb, have been plotted by Shannon and Sleight (37), who showed that for germanate pyrochlores pressure extended the stability field to ionic radii ratios  $r_A/r_B$  of approximately 1.8 ( $r_{Gd^{3+}}/r_{Ge^{4+}}$ ) (39). In the present work the formation of In<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> extends this value to 1.98 ( $r_{In^{3+}}/r_{Si^{4+}}$ ). Lu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> ( $r_{Lu^{3+}}/r_{Si^{4+}}$ ) = 2.12, did not form a pyrochlore at 120 kbar, and calculations for probable cell volume and x values for such a phase indicate an Si–O bond length of 1.83 Å or greater.

Formation of the phase even at higher pressures does not seem probable, and in the silicate mineralogy of the deeper mantle, Sc and In will probably not follow that of the rare earths. Perovskite structures such as (R.E.) AlO<sub>3</sub> and ScAlO<sub>3</sub> (40) may of course provide an alternative accommodation for the small amounts of Sc, In, and rare earths in mantle compositions.

It is interesting to note that pyrochlore type In<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, with a volume per unit formula of

104.25 Å<sup>3</sup>, is 5% more dense than an equivalent mixture of the high-pressure forms of the constituent oxides, corundum type In<sub>2</sub>O<sub>3</sub> (41), and rutile type SiO<sub>2</sub> (6), which have a corresponding volume of 109.59 Å<sup>3</sup>, and considerably more dense than C-rare earth plus rutile mixtures. The scandium and indium silicate pyrochlores can therefore be expected to be stable to extremely high pressures.

#### Scandium and Indium Coordination

The eight-coordinate distorted cube of oxygen atoms surrounding Sc or In in the pyrochlore structure gives rise to average Sc–O<sub>8</sub> and In–O<sub>8</sub> bond lengths of 2.267(13) and 2.275(9) Å, somewhat greater, for Sc–O<sub>8</sub>, than the average of 2.212 Å in HScC<sub>7</sub>H<sub>5</sub>O<sub>2</sub> (42, 43), 2.232 Å in Sc<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O (44), 2.23 Å in ScPO<sub>4</sub> (45), or 2.25 Å in ScAlO<sub>3</sub> (40). However, the standard deviations in the present values are relatively low, and as the local coordination in the pyrochlore structure is simple and symmetric, the values must be regarded as correctly characterizing Sc and In in these structures.

#### Six-Coordinate Silicon

Octahedral Si–O parameters for those structures which have been refined so far are shown in Table V. Earlier, unrefined values for stishovite (6, 46) were omitted. The

TABLE V  
STRUCTURE-REFINED BOND LENGTHS IN SILICON-OXYGEN OCTAHEDRA

Compound	SiO <sub>2</sub>	SiP <sub>2</sub> O <sub>7</sub> (A IV)	SiP <sub>2</sub> O <sub>7</sub> (A III)	Sc <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	In <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	Thaumasite -[Si(OH) <sub>6</sub> ]-	(C <sub>2</sub> H <sub>5</sub> NH) <sub>2</sub> [(C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> ) <sub>3</sub> Si]
Refinement	Bauer and Khan (47)	Liebau and Hesse (18)	Bissert and Liebau (17)	This work	This work	Edge and Taylor (20)	Flynn and Boer (21)
Method	Powder	Single crystal	Single crystal	Powder	Powder	Single crystal	Single crystal
Reflections	29	265 (2D)	810 (3D)	18	21	1163 (3D)	1321 (3D)
Number of coordinates	2	30	30	1	1	30 <sup>a</sup>	55 <sup>a</sup>
Number of temperature factors	4 <sup>b</sup>	20	10	4	4	13	60 <sup>b</sup>
R Factor	0.047	0.087	0.070	0.031	0.015	0.094	0.058
Si-O distances (Å)	1.75(5) × 4 1.810(8) × 2	1.76(1), 1.77(2) 1.80(3), 1.81(3) 1.82(2), 1.84(1)	1.732(12), <sup>c</sup> 1.746(12) 1.765(12), 1.766(12) 1.774(12), 1.793(12)	1.761(7) × 6	1.800(5) × 6	1.731(7) × 3 1.835(7) × 3	1.765(3) × 2 1.775(3) × 2 1.813(3) × 2
Average Si-O octahedral distance, (Å) <sup>d,e</sup>	1.775(7)	1.800(24)	1.763(14)	1.761(7)	1.800(5)	1.783(8)	1.784(4)
O-O distances in Si-O <sub>6</sub> octahedra, (Å)	2.291 × 2 2.522 × 8 2.6649 × 2	2.45, 2.48 2.50, 2.50 2.51, 2.53 2.56, 2.57 2.59, 2.59 2.61, 2.63	2.454, 2.461 2.467, 2.469 2.485, 2.495 2.496, 2.497 2.498, 2.510 2.525, 2.559	2.437 × 6 2.544 × 6	2.454 × 6 2.633 × 6	2.432 × 3 2.451 × 3 2.594 × 3 2.597 × 3	2.482, 2.494 × 2 2.501 × 2 2.508 × 2 2.428 × 2 2.589 × 2 2.605
Average O-O distance, (Å) <sup>f</sup>	2.507	2.54 <sub>3</sub>	2.493	2.491	2.544	2.519	2.527
Ratio of average O-O and Si-O distances (1.4142 for ideal octahedron) <sup>g</sup>	1.412 <sub>4</sub>	1.413	1.414 <sub>1</sub>	1.414 <sub>5</sub>	1.414 <sub>5</sub>	1.412 <sub>5</sub>	1.416 <sub>6</sub>

Bond angles in Si-O <sub>6</sub> octahedra	81.4 × 2 90 × 8 98.6 × 2	85.7 to 93.2 <sup>f</sup>	88.1 to 92.0 <sup>f</sup>	87.5 × 6 92.5 × 6	86.0 × 6 94.0 × 6	83.8 × 3 89.3 × 3 93.3 × 3 93.5 × 3	86.4, 88.0 × 2 89.6 × 4 89.8 × 2 92.7 × 2, 94.4 175.4 × 2 179.1
	180 × 3	177.4, 178.5 179.4	173.4, 177.4 178.2	180 × 3	180 × 3	176.3 × 3	

<sup>a</sup> Excluding H atoms.

<sup>b</sup> Anisotropic, excluding cross terms.

<sup>c</sup> Averaged standard deviations (17).

<sup>d</sup> Standard deviations derived from individual bond length variances by  $\sigma_{av} = (\sigma_i^2/(n-1))^{1/2}$ .

<sup>e</sup> Weighted combined mean for Si-O equals 1.782(14) Å; that for O-O equals 2.520(18) Å; the ratio of mean Si-O to mean O-O distances equals 1.4142(16) Ref. (46).

thaumasite parameters derive from a more complete refinement (20) of this structure than that available to Liebau in his earlier review of six-coordinate silicon (46). Values for high pressure KAlSi<sub>3</sub>O<sub>8</sub> (7) in which the octahedral site is occupied by ( $\frac{1}{4}$ Al +  $\frac{3}{4}$ Si), and for which refinement has not been performed, were also omitted.

Average Si-O<sub>6</sub> distances for the variety of compounds given in Table V show a relatively small range of  $\pm 0.02$  Å, with an overall mean, weighted inversely as the standard deviations of the individual averages, of  $1.782 \pm 0.014$  Å. The overall mean of the octahedral edge O-O distances, similarly weighted, is 2.520 Å, and the ratio of the mean of O-O to the mean of Si-O distances is 1.4142 (16), essentially identical with that for an ideal octahedron, 1.4142. Such a correspondence is of course necessary if the concept of an average octahedral bond length or average ionic radius is to have meaning.

The central value of 1.78 Å derived for octahedral Si-O distances, and the observed standard deviation and ranges,  $\pm 0.014$  and  $\pm 0.020$  Å, respectively, appear to be reliable parameters for describing the dimensions of the Si-O<sub>6</sub> octahedron both in ordinary pressure phases and in those produced at high pressures or expected in the earth's mantle. Indeed, the recently synthesized perovskite form of MgSiO<sub>3</sub>, which is expected to comprise a substantial portion of the deeper mantle (3, 14, 40), has a cell volume (48) which, when fitted to the precise bond length molar volume relationships which have been found to apply to the perovskite structure type (40), gives an average Si-O<sub>6</sub> distance of  $1.79 \pm 0.01$  Å.

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