NOTE

Variation of Mean Si–O Bond Lengths in Silicon–Oxygen Octahedra

WERNER H. BAUR

Department of Geological Sciences, University of Illinois, Chicago, Illinois 60680

The mean bond length Si–O in silicon–oxygen octahedra is a function of the mean coordination number of the oxygen atoms (CN) in the octahedron: $(Si–O)_{mean} = 1.729 + 0.013CN$. The radius of Si in six coordination against oxygen is 0.407 Å.

Recently Reid *et al.* (*1*) have reported on the synthesis of high-pressure pyrochlore-type $Sc_2^{[8]}Si_2^{[6]}O_7^{[4]}$ and $In_2^{[8]}Si_2^{[6]}O_7^{[4]}$ (the superscripts refer to the coordination numbers of the atoms). This adds two more compounds to the short list of substances containing six-coordinated silicon. Since octahedrally coordinated silicon must occur in the lower mantle of the earth the dimensions of the SiO_6 group are of interest for the discussion of the crystal chemistry of mantle minerals. Therefore Reid *et al.* tabulated these dimensions for those structures containing $Si^{[6]}$ and known to them. Their Table V contains data on seven crystallographically independent SiO_6 octahedra in seven different compounds. The weighted mean of the Si–O distance is reported by them to be 1.782(14) Å.

However, the number of crystallographically independent SiO_6 octahedra can be almost doubled by including the six SiO_6 octahedra observed in the cubic polymorph of SiP_2O_7 (*2*). The weighted mean of the average Si–O distances in the 13 octahedra is then 1.771 Å (Table I). In going from the smaller to the larger data sample the range of the values increases from 0.04 Å (1.761 to 1.800 Å) to 0.07 Å (1.730 to 1.800 Å). This larger scatter

is due most likely to the dependence of the octahedral Si–O distance on the coordination number of the oxygen atoms. In Table I the mean coordination numbers of the oxygen atoms in a given octahedron are listed together with calculated Si–O values obtained from the equation

$$(Si–O)_{mean} = 1.729 + 0.013CN, \qquad (1)$$

which is based on regression calculations involving the 13 observed Si–O distances. The magnitude of the slope of this equation is very close to the value of the slope (0.012) which can be obtained from the radii of oxygen with different coordination numbers listed by Shannon and Prewitt (*8*). The calculated values agree reasonably well with the observed values (considering the standard deviations of the observations) in all cases save one. The mean Si–O bond length in tris(*o*-phenylenedioxy)-siliconate is observed as 0.025 Å longer than it is calculated and it is also the most precisely determined of the values in Table I. The length of this Si–O bond might be due to the fact that the oxygen atoms are not only bonding to Si but also forming strong, covalent, partial double bonds with carbon (mean length of C–O 1.357 Å).

TABLE I

OBSERVED AND CALCULATED MEAN DISTANCES Si[6]–O

Substance	$(Si-O)_{obs}$ (Å)	CN of O[a]	$(Si-O)_{calc}$ (Å)	Δ[b] (Å)	Reference
Cubic SiP_2O_7	1.750(12)[c]	2	1.755	−0.005	(2)
Cubic SiP_2O_7	1.750(12)	2	1.755	−0.005	(2)
Cubic SiP_2O_7	1.755(12)	2	1.755	0	(2)
Cubic SiP_2O_7	1.758(12)	2	1.755	0.003	(2)
Cubic SiP_2O_7	1.755(12)	2	1.755	0	(2)
Cubic SiP_2O_7	1.730(11)	2	1.755	−0.025	(2)
SiP_2O_7 AIII	1.763(7)	2	1.755	0.008	(3)
SiP_2O_7 AIV	1.798(31)	2	1.755	0.043	(4)
$(C_5H_5NH)_2[(C_6H_4O_2)_3Si]$	1.784(3)	2.33	1.759	0.025	(5)
Stishovite	1.775(7)	3	1.768	0.007	(6)
$Sc_2Si_2O_7$	1.761(7)	4	1.781	−0.020	(1)
$In_2Si_2O_7$	1.800(5)	4	1.781	0.019	(1)
Thaumasite	1.783(7)	4	1.781	0.002	(7)
Weighted grand mean	1.771(13)				

[a] Mean coordination number of all oxygen atoms in SiO_6 octahedron.

[b] Difference $(Si-O)_{obs} - (Si-O)_{calc}$.

[c] Standard deviations calculated by taking the square root of the sum of the variances of the individual bond lengths divided by 5. They are in units of the least significant digits of the value.

Using Eq. (1) it can be estimated that the Si–O bond length in perovskite-type $MgSiO_3$ (9) should be 1.790(7) Å, since the average coordination number of oxygen in this compound is 4.67 (10). This estimate is identical with the prediction made by Reid et al. (1) based on the bond length vs molar volume relationship for the perovskite type.

Based on Eq. (1) the radius of silicon in six coordination against oxygen is 0.407 Å. This is slightly larger than the radius of 0.400 Å reported previously (8, 11). The reason for the difference may be due to the fact that the bond lengths used in deriving the earlier radius were taken from SiF_6 groups and from SiO_6 groups.

Acknowledgment

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