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The relationship between Si-O distances and Si-O-Si bond angles in the silica polymorphs

A DETAILED study of bond distances and angles in framework silicates (Brown, Gibbs, and Ribbe, 1969) has shown that individual T -O distances ($T = \text{Si, Al}$) decrease with increasing T -O- T angle. They found that the slope of the regression line for the relationship above was steeper for the silica polymorphs than those calculated for the other framework silicates.

The present paper re-examines the relationship above after the T -O bond lengths have been corrected for the anisotropic thermal motion of their oxygens. Unfortunately anisotropic temperature factors were not available for keatite and α -cristobalite so that they could not be included. The maximum root-mean-square thermal motions of the oxygen atoms in coesite and α -quartz at room temperature are similar, 0.118 to 0.154 Å, and so the corrections are similar and small. The maximum root-mean-square thermal motion of the oxygen atoms in β -quartz at 600 °C and high tridymite at 220 °C are much greater, 0.285 and approximately 0.40 Å respectively, and cause significant shortening of the Si-O bond lengths. The correction for the thermal motion of the oxygen atoms was obtained by an approximation after Cruickshank (1956): $y = s^2/2r$ where y is the apparent shortening, r the observed bond length, and s^2 the mean squared amplitude of oscillation of the oxygen atom relative to the silicon atom (in the present work this is taken to be the maximum root-mean-square thermal motion of the oxygen atom). After correcting for thermal motion a straight line was fitted

to the data (see references) by the method of least squares giving one-third weight to the three sets of data for α -quartz, and including two Si-O distances for each Si-O-Si angle. It is now found that the regression line for the silica polymorphs, fig. 1, is less steep than those calculated for other framework silicates by Brown *et al.* (1969). The slope of the regression of Si-O on Si-O-Si in fig. 1 is -0.00029 with an estimated

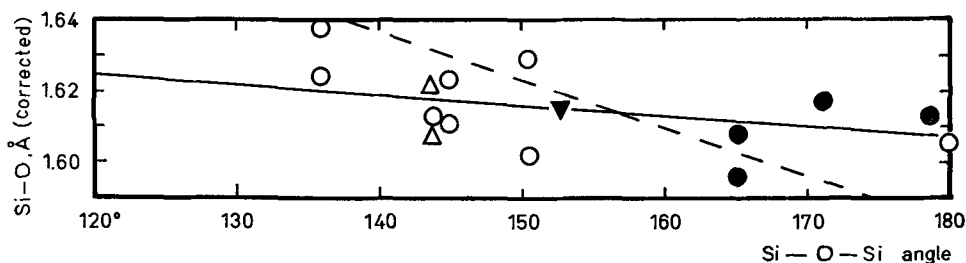


FIG. 1. The relationship between Si-O distances, after correction for thermal motion of the oxygens, and Si-O-Si angles in the silica polymorphs. The symbols used are: ○ coesite (1), ● high-tridymite (4), △ α -quartz (6, 8, 9) and ▼ β -quartz, 600 °C (7). The figures in brackets indicate the references from which the data were obtained. The full line gives the regression of Si-O on Si-O-Si and the dashed line the regression of Si-O-Si on Si-O. Only the former is comparable with the data of Brown *et al.* (1969).

standard deviation of 0.00013 . The probability of the slope being zero is a little less than 5 %. This regression coefficient and estimated standard deviation should be compared with the original values for the silica polymorphs (Brown *et al.*, 1969) of -0.0014 and 0.0003 respectively. The main factor effecting the change in the slope of the regression line for the silica polymorphs was the correction for thermal motion to the Si-O bonds in high tridymite. The scatter about the regression line in fig. 1 is high; in fact the regression of the Si-O distances on the Si-O-Si angles only accounts for about 20 % of the variance of the Si-O distances. The observation of different Si-O distances in the same structure, for example α -quartz, for identical Si-O-Si angles suggests that an unidentified structural factor may have a more significant effect on individual bond lengths in the tetrahedra. Because of the similarity in the slopes of the regression lines for the silica polymorphs and the framework silicates and the great degree of scatter about the regression lines, these results indicate that there are no grounds for suggesting that the relationship between T-O distances and T-O-T angles is affected by the degree of substitution of Al for Si or the presence of interframework cations. In fact, because of the degree of scatter, the prediction of Si-O distances from Si-O-Si angles alone does not appear possible.

The possibility of the size of the Si-O-Si angle influencing the size of associated Si-O distances is important in the structure of vitreous silica. There is evidence for excellent short range order in the structure of vitreous silica with silicon surrounded tetrahedrally by oxygens, but poor long range order due to random variation in the Si-O-Si angle (Mozzi and Warren, 1969). Such random variation, probably from 120 to 180°, could give rise to an amount of variation in the individual Si-O distances

that may well account for the variation in the Si-O distance about the mean value 1.62 Å observed by Mozzi and Warren (1969).

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Variations in optical properties of muscovite due to 70 KEV proton irradiation

THE effect of high energy, 70 KEV, protons with a total fluence of 8.3×10^{16} protons per cm^2 on mica crystals was investigated as part of an initial study of solar wind bombardment of minerals.

The optical properties of the mica before irradiation were: α 1.565, β 1.603, γ 1.609, $2V$ $42^\circ 36'$. After irradiation α was 1.559, β 1.589, γ 1.599, and $2V$ $56^\circ 4'$. Since it was suspected that part of the observed differences in optical properties may have been due to mainly thermal effects related to proton bombardment (Nash, 1967), non-irradiated mica was heated to 450°C . The optical properties of heated non-irradiated mica were similar to the original mica.

The drastic change in optical properties would indicate a significant change in the refractivity related to either a decrease in the polarizability or a dimensional change of the mica lattice.

Initial X-ray topography by means of a Lang camera before and after irradiation