

## Bonded interactions in silica polymorphs, silicates, and siloxane molecules

G.V. GIBBS,<sup>1,\*</sup> A.F. WALLACE,<sup>1</sup> D.F. COX,<sup>2</sup> R.T. DOWNS,<sup>3</sup> N.L. ROSS,<sup>1</sup> AND K.M. ROSSO<sup>4</sup>

<sup>1</sup>Department of Geosciences, Virginia Tech, Blacksburg, Virginia 24061, U.S.A.

<sup>2</sup>Department of Chemical Engineering, Virginia Tech, Blacksburg, Virginia 24061, U.S.A.

<sup>3</sup>Department of Geosciences, University of Arizona, Tucson, Arizona 85721, U.S.A.

<sup>4</sup>Chemical and Materials Science Division, and the W.R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99352, U.S.A.

### ABSTRACT

Experimental model electron density distributions obtained for the silica polymorphs coesite and stishovite are comparable with electron density distributions calculated for various silicates and siloxane molecules. The Si-O bond lengths and Si-O-Si angles calculated with first-principles density functional theory methods as a function of pressure are also comparable with the bond lengths and angles observed for coesite and quartz within the experimental error. The similarity of the topological properties of the Si-O bonded interactions and the experimental and the geometry-optimized structures for the silica polymorphs provide a basis for understanding the properties and crystal chemistry of silica. The agreement supports the argument that the bulk of the structural and physical properties of the silica polymorphs are intrinsic properties of molecular-like coordination polyhedra such that the silica polymorphs can be pictured as “supermolecules” of silica bound by virtually the same forces that bind the Si and O atoms in simple siloxane molecules. The topology of the electron density distribution is consistent with the assertion that the Si-O bonded interaction arises from the net electrostatic attraction exerted on the nuclei by the electron density accumulated between the Si and O atoms. The correlation between the Si-O bond length and Si-O-Si angle is ascribed to the progressive local concentration of the electron density in the nonbonded lone pair region of the O atom rather than to a bonded interaction that involves the *d*-orbitals on Si.

The accumulation of deformation electron density,  $\Delta\rho(\mathbf{r})$ , in the bonded and nonbonded regions of the Si-O bond, the close proximity of the bond critical point,  $\mathbf{r}_c$ , of the bond with the nodal surface of the Laplacian and the negative value of the total energy density are taken as evidence that the bond has a nontrivial component of shared character. For M-O bonded interactions for first and second row metal atoms bonded to O,  $\nabla^2\rho(\mathbf{r}_c)$  is positive and increases linearly as  $\rho(\mathbf{r}_c)$  and  $G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$  both increase and as the value of  $H(\mathbf{r}_c)$  decreases; the greater the shared character of the interaction, the larger the values of both  $\nabla^2\rho(\mathbf{r}_c)$  and  $G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$ . In addition, a mapping of  $\nabla^2\rho(\mathbf{r})$  serves to highlight those Lewis base domains that are susceptible to electrophilic attack by H, like the O atoms in coesite involved in bent Si-O-Si angles; the narrower the angle, the greater the affinity for H. On the basis of the net charges conferred on the Si and O atoms and the bonded radii of the two atoms, the Si-O bond for stishovite, with six-coordinated Si and three-coordinated O, is indicated to be more ionic in character than that in quartz with four-coordinated Si and two-coordinated O. Unlike the conclusion reached for ionic and crystal radii, it is the bonded radius of the O atom that increases with the increasing coordination number of Si, not the radius of the Si atom. The modeling of the electron density distributions for quartz, coesite, and beryl as a function of pressure suggests that the shared character of the bonded interactions in these minerals increases slightly with increasing pressure. The insight provided by the calculations and the modeling of the electron density distributions and the structures of the silica polymorphs bodes well for future Earth materials studies that are expected to improve and clarify our understanding of the connection between properties and structure within the framework of quantum mechanical observables, to find new and improved uses for the materials and to enhance our understanding of crystal chemistry and chemical reactions of materials in their natural environment at the atomic level.

**Keywords:** Bonded interactions, electron density distributions, silica, coesite, quartz, stishovite, cristobalite, siloxane