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Insights into the crystal chemistry of Earth materials rendered by electron density distributions: Pauling's rules revisited

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Abstract

Experimental and calculated electron density distributions determined for oxide and silicate crystals and siloxane molecules provide a new basis for addressing the classic foundation of the crystal chemistry of silicates, including atomic/ionic radii, the radius ratio rule and the nexus between the Pauling's bond strength, resonance bond number, and bond length. The distributions indicate that the charge density of a bonded oxygen atom is highly distorted with its bonded radius decreasing systematically from 1.50 Å when bonded to highly electropositive atoms like sodium to ~0.65 Å when bonded to highly electronegative atoms like nitrogen. Rather than a single radius, the atom has as many bonded radii as it has bonded interactions. Bonded radii determined for the metal atoms match the Shannon effective ionic radii for the more electropositive atoms, but they depart and decrease systematically as the electronegativity of the M atoms increases. Pauling's first rule is considered to be irrelevant given the asphericity and the range of the bonded radii displayed by the O atom.

A power law regression expression is formulated between the average M-O bond lengths, $\langle R(M\text{-}O)\rangle$, and the average value of the electron density, $\langle \rho(\mathbf{r}_c)\rangle = r[1.41/\langle R(M\text{-}O)\rangle]^{4.76}$, at the bond critical point, $\mathbf{r}_c$, between pairs of bonded M-O atoms. The expression applies to a host of crystals and molecules comprising M-atoms for all rows, r, of the periodic table. The $\langle \rho(\mathbf{r}_c)\rangle$ values correlate with bond strength and resonance bond strength for the M-O bonded interactions on a one-to-one basis, demonstrating that the Pauling bond strength is a direct measure of the electron density involved in a bonded interaction and the accumulation of the electron density between the bonded pair. The widespread applications of the Brown-Shannon bond valence model in the Earth sciences and material science owes much of its success to the direct connection that exists between bond strength and the quantum mechanical observable, the electron density distribution. Compelling evidence is presented that supports the argument that the Si-O bonded interactions within siloxane molecules and silicate crystals are fundamentally the same, and that the local Si-O bonded interactions comprising molecules are, at the very core, equivalent to the Si-O bonded interactions observed in silicate crystals. Bond paths between the O atoms comprising shared polyhedral edges are consistent with Pauling's third rule, the shorter the O-O shared edges, the greater the accumulation of the electron density between the O atoms, the greater the stabilization of the shared edges.

Keywords: Pauling, electron density distribution, bonded radii, bond strength