

ROEBLING MEDAL PAPER

Toward theoretical mineralogy: A bond-topological approach

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ABSTRACT

The patterns of linkage of chemical bonds in space contain significant energetic information that may be used as the basis of a theoretical approach to the structure and chemical composition of minerals. This approach combines aspects of graph theory, bond-valence theory, and the moments approach to the electronic-energy density-of-states to interpret topological aspects of crystal structures, and allows consideration of many issues of crystal structure, mineral composition, and mineral behavior that are not addressed by established theoretical methods. The chemical composition of a mineral is controlled by the weak interaction between the structural unit and the interstitial complex. The principle of correspondence of Lewis acidity-basicity asserts that stable structures will form when the Lewis-base strength of the structural unit closely matches the Lewis-acid strength of the interstitial complex. This principle allows analysis of the factors that control the chemical compositions and aspects of the structural arrangements of minerals, and provides a mechanism to understand the relations between structure, the speciation of its constituents in aqueous solution, and its mechanism of crystallization. (H₂O) groups in the structural unit limit the polymerization of the structural unit in one or more directions, controlling the polymerization of the structural unit. This is a major cause of structural diversity in oxygen-based minerals, and accounts for the systematic distribution in mineral species from the core to the surface of the Earth.

The moments approach to the electronic-energy density-of-states provides a bond-topological interpretation of the energetics of a structure. When comparing structures, the most important structural differences involve the first few disparate moments of the electronic-energy density-of-states. We may classify chemical reactions according to the lowest-order moment of the electronic-energy density-of-states that is conserved, which allows us to identify the principal structural changes that drive chemical change: (1) coordination number for discontinuous reactions, and (2) short-range order for continuous reactions. This relation between the bond topology of a structure and its enthalpy of formation from constituent oxides is indicated by a correlation between change in anion-coordination number and reduced enthalpy of formation for the reactions ${}^{[6]}Mg_m{}^{[4]}Si_nO_{(m+2n)} = mMgO + nSiO_2$.

Keywords: Bond topology, graph theory, bond-valence theory, electronic-energy density-of-states, polyhedron linkage, chemical composition, structural unit, interstitial complex