The Bond Topology of Structural Units in Oxysalt Minerals

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For any structure, the structural unit may be defined as the strongly bonded part of the structure. Structural units are linked together by interstitial species that are involved in much weaker bonding. This scheme gives a *binary representation* of even the most complex structure, and the interaction between the structural unit and the interstitial species can be simply but quantitatively evaluated using the Lewis basicity of the structural unit, the Lewis acidity of the interstitial complex, and the principle of correspondence of Lewis acidity-basicity. The structural unit plays a major role in all aspects of structural mineralogy, and it is of interest to explore the factors that affect its Lewis basicity. There are two aspects of the structural unit that are important in this regard: (1) its bond topology (polyhedral connectivity), and (2) the nature of its constituent cations and anions. We may write the Lewis basicity of a structural unit as the effective charge on the structural unit divided by the number of bonds required by the structural unit. Changes in stoichiometry, chemical composition and polyhedral connectivity thus affect the Lewis basicity of the structural unit. Of major interest in this regard are the specific changes in these variables that cause the Lewis basicity of the structural unit to change in a particular direction (*i.e.,* increase or decrease). If a relative decrease in the charge on the structural unit is greater than the corresponding relative decrease in the number of bonds required by the structural unit (for a specific change in stoichiometry, chemical composition and polyhedral connectivity), then the Lewis basicity of the structural unit decreases; similarly, if a proportional decrease in the denominator exceeds that of the numerator, the Lewis basicity of the structural unit increases.

The factors that affect the Lewis basicity (or acidity) of the structural unit are examined for structural units of the general formula $[^{[6]}M_k (^{[4]}T\varphi_4)_m \varphi_n]^{x-}$ where k, m and n take any integer values and φ are unspecified mono- or zero-valent anions (usually OH or H_2O). Increasing numbers of mono- or zero-valent anions (n) lead to an increase in the CDA (Charge Deficiency per anion) and hence in the Lewis basicity of the structural unit. Increasing values of k (relative to m) also lead to increase in the CDA (Charge Deficiency per anion) and hence in the Lewis basicity of the structural unit. Examination of minerals of general stoichiometry $X_l[M_k(T\varphi_4)_m\varphi_n]\varphi_p$ (where X and φ are any interstitial cation and anion species, respectively, and k, l, m, n and p take any values) shows that minerals with a 1:1 M:T ratio are the most abundant. As the M:T ratio departs from 1:1, in both directions, the number of minerals decreases strongly, and the number of minerals becomes quite small outside the range 4:1 ≥ M:T ≥ 1:4 (except for 0:1 and 1:0, for which large numbers of minerals exist). Thus the majority of minerals have structural units of fairly simple stoichiometry. Although the distribution is not a normal distribution, the most common stoichiometry is M:T = 1:1, and the number of minerals decreases rapidly as the structural unit departs from this ratio. This is a result of the fact that arrangements of strongly bonded atoms for which $M \gg T$ and $M \ll T$ have Lewis basicities greater than the minimum values possible for a structural unit (~ 0.30 *vu*).