Molecular Structure: Chemical Reactivity and Biological Activity

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53. A general structural hierarchy for oxy-salt minerals

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ABSTRACT

Recently, it has been proposed that structures may be ordered or classified according to the polymerization of those coordination polyhedra with higher bond-valences (Hawthorne, 1983). Here I consider oxysalt minerals with triangular, tetrahedral and octahedral coordination of small highly-charged (2+) cations. Structures are described and ordered according to their basic heteropolyhedral cluster, or fundamental building block, and the way in which this cluster polymerizes to form the structure module, a complex anionic polyhedral array whose excess charge is balanced by the presence of large low-valence cations. These descriptions are particularly useful for loosely packed and highly hydrated minerals, the structures of which often resist adequate description in terms of such traditional concepts as close-packing.

1. INTRODUCTION

As increasing amounts of crystal structure information have become available, structural correlations among quite large chemical groups of minerals have been set up: silicates

(Bragg, 1927; Liebau, 1985), aluminofluorides (Pabst, 1954), phosphates (Moore, 1982). These schemes focus on the polymerization of a specific complex anionic group, and are essentially geometrical in nature. The next step in the development of general structural systematics of minerals is to broaden the class of minerals considered to include all oxysalt minerals.

2. GENERAL APPROACH

The principal thrust of this work is not to produce a structural classification of minerals, but to develop a method of description of a structure that incorporates both graphical and chemical information. That this is feasible is suggested by simple molecular orbital theory, which indicates that there is considerable chemical information inherent in the graphical aspects (often called 'topology') of bond connectivity. In dealing with the structural complexity of hydroxy-hydrated oxysalts, it is advantageous to deal with ideas that are simple and intuitive, and what I will use to approach this problem is Pauling's (1960) second rule, together with its generalizations that Brown (1981) has systematized into the coherent framework of bond-valence theory. In this regard, it should be noted that this approach is not based on an ionic model; use of the terms 'cation' and 'anion' indicates merely that some atoms are more electropositive than others, and carries no connotation as to chemical bonding.

Formal bond-strength may be defined as cation charge divided by cation coordination number, and Pauling's second rule states that the sum of the bond-strengths around an anion is approximately equal to the magnitude of the anion valence. There is a very useful way in which we can think about this law with regard to the satisfaction of bond-strength requirements around each atom in a structure. For the cations, by definition the bond-strength requirements are satisfied by the formation of anion coordination polyhedra around them. Thus, we can think of the structure as an array of complex anions, which polymerize in order to satisfy their anionic bond-strength requirements. The most important polymerizations are those involving the coordination polyhedra of higher bond-strengths, as these contribute most to the satisfaction of the anion bond-strength requirements.

If the major imperative of a structure is the satisfaction of its cation and anion bond-strength requirements, the most important features of the structure are the type of cation coordination polyhedra, and the way in which the higher bond-strength polyhedra polymerize. This suggests the following hypothesis: structures may be profitably described and ordered according to the polymerization of those coordination polyhedra with higher bond-valences (Hawthorne, 1983).

In order to exploit the chemical content of the graphical aspects of structure, the following definitions are useful. The most strongly bonded cluster of coordination polyhedra in a structure is the fundamental building block of that structure. This is repeated (often polymerized) by the translational symmetry operators to form the module of the structure, an anionic polyhedral array whose excess charge is balanced by the presence of large low-valence cations.

3. MAJOR CATEGORIES OF STRUCTURES

Structures may be ordered into classes according to the dimensionality of their structure modules: (i) isolated polyhedra; (ii) finite clusters; (iii) infinite chains; (iv) infinite sheets; (v) infinite frameworks. From a graphical viewpoint, classes (i) and (ii) could be combined; however, paragenesis suggests that it will be more convenient to have them separate.

4. STRUCTURAL TRENDS IN OXYSALTS

The idea of fundamental building blocks and structure modules can be used in conjunction with the structure-based scale of Lewis acid and base strengths developed by Brown (1981) to provide considerable insight into structure type as a function of chemical composition. The Lewis acid strength of a cation is the average valence of a bond formed by that cation. The Lewis base strength of an anion is the average valence of a bond formed by that anion. Simple anions often show a great range of bond-valences, but this is generally greatly reduced for complex anions (Hawthorne, 1985).

The hypothesis introduced above considers the polymerization of the most tightly-bonded oxyanions in a structure. Increasing polymerization will decrease the resultant Lewis base strength, suggesting that the degree of polymerization in such structures should be related to the average Lewis base strength of their component oxyanions; that this is the case has been shown by Hawthorne (1985, 1986).

5. LARGE CATION CHEMISTRY IN OXYSALTS

The structure module may be considered as a very complex oxyanion, and a Lewis basicity may be calculated for it. The valence-matching principle (Brown, 1981) states that the most stable structures will form when the Lewis acid strength of the cation most closely matches the Lewis base strength of the anion. This indicates that the Lewis base strength of the structure module should match the Lewis acidity of the extra-module cation(s). Hawthorne (1985, 1986) has shown this to be the case for a large and diverse group of oxysalt minerals. Thus the characteristics of the structure module exert a strong control over the chemical identity of the extra-module cations.

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