Bond topology and structural arrangements in inorganic crystals

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Atomic arrangements may be investigated using graph theory and topology, where the focus is on the connectivity of structural arrangements rather than on interatomic distances and angles. Polyhedra may be represented by colored vertices of a labeled graph in which different colors represent different coordinations and labels denote chemically and crystallographically distinct polyhedra. Linkage is indicated by edges between vertices, and the number of edges between two vertices denotes the number of atoms common to both polyhedra. The graph may be completely represented by its adjacency matrix, and we may represent the N independent matrix elements by the ordered set *{a,b,c,...,N}*. The collection of all permutations of the vertex labellings that preserve isomorphism is the automorphism group *F(G)* of the graph. *F(G)* is a subgroup of the symmetric group S_n, and the complementary disjoint subgroup of S defines all distinct graphs whose vertex sets correspond to the (unordered) set *{a,b,c,...,N}*. It is more convenient in practice to work with the corresponding matrix-element symmetries that form a permutation group, denoted P. Graphical isomers can be enumerated using Polya's theorem, by substitution of permitted matrix elements as weight functions into the cycle index of the permutation group P, and can be derived as nonequivalent derangements of the integer set *{a,b,c,...,N}*. Geometrical isomers can be enumerated for a specific graphical isomer by successively applying Polya's theorem to the distribution of shared elements over the total element set of each polyhedron in turn. Thus all arrangements of a specific set of coordination polyhedra can be derived in this fashion.

Many crystal structures contain similar modular elements that (1) allow them to be associated into broad groups, and (2) allow prediction of new but related structures. This type of behavior can be quantified in a very concise manner by incorporating aspects of the bond topologies and chemical compositions of these structures into a general formula by writing the local topological details of each cation and anion, along with their chemical identity, as a general expression called a **structure-generating function**. Here, I describe this procedure for polysomatic T–O–T (pyroxene, amphibole, pyribole and mica) and H–O–H (rinkite-group TS-block minerals, astrophyllite, mica) supergroup structures which consist of alternating layers of tetrahedra (T sheets), octahedra (O sheets) or both (H sheets). We may write tetrahedrally coordinated cations and their associated anions as $\{T_{2n}\Theta_m\}$. For $\{T_{2n}\Theta_m\}$ to be a chain or ribbon, m = 5n + N, where N is an integer. Within the $\{T_{2n}\Theta_{(5n+N)}\}$ unit, we may recognize three types of anion vertices: (1) bridging anions, Θ^{br}, that are bonded to two T cations; (2) apical anions, Θ^{ap}, that are involved in linkage to other cations out of the plane of the bridging anions; and (3) linking anions, Θ^l, that link to non-T cations in the plane of the bridging anions. We may incorporate the connectivity of the cations in our algebraic representation of the chain as follows: $\{T_{2n}\Theta^{br}{}_a\Theta^{ap}{}_b\Theta^l{}_c\}$ where a + b + c = 5n + N. The apical anions of the T- or H-sheets provide some anions of the layer of octahedra. We may use the handshaking di-lemma of graph theory to examine the interaction between the two types of layers, and write a structure-generating function, $S_{(N;n)}$, that gives both the stoichiometry and aspects of the bond topology of the structures. We may follow the same procedure for the H–O–H structures. As the structure-generating functions are algebraic expressions, we may combine them into a general structure-generating function for both groups of structures:

$$S_{(N;n)} = X_i[M_{(3n+2N-3)}\Psi_{2(n+N-2)}D_{2(N-1)}\Phi^{ap}{}_{2(N-1)}\{T_{2n}\Theta^{br}{}_{(3n-N)}\Theta^{ap}{}_{2n}\Theta^l{}_{2N}\}2\Phi^t{}_{0-2(N-1)}]$$

Different values of N and n generate different chemical compositions and structural arrangements. Moreover, using more than one value of n generates mixed-module structures, e.g.

$$S_{(1;2+3)} = X_i[M_{13}\Psi_6\{T_{10}\Theta^{br}{}_{13}\Theta^{ap}{}_{10}\Theta^l{}_4\}_2] = Mg_4[Mg_{13}(OH)_6\{Si_{10}O^{br}{}_{13}O^{ap}{}_{10}O^l{}_4\}_2] = \text{chesterite}$$

$$S_{(2;1+4)} = X_i[M_{17}\Psi_{10}(D_4\Phi_4\{T_2\Theta^{br}\Theta^{ap}{}_2\Theta^l{}_4\}_2\{T_8\Theta^{br}{}_{10}\Theta^{ap}{}_8\Theta^l{}_4\}_2)\Phi^t{}_{0-4}]$$
$$= KNa(H_2O)_3[(Fe^{2+}{}_5Fe^{3+}{}_4Mn_6Ca\square)(OH)_{10}(Nb_4O_4\{Si_2O_7\}\{Si_8O_{22}\}_2)O_2] = \text{veblenite}.$$

Any structure-building algorithm can form the basis for a structure-generating function, and such algorithms can be combined algebraically to form more general functions.