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ROEBLING MEDAL PAPER

Toward theoretical mineralogy: A bond-topological approach

FRANK C. HAWTHORNE[1,*]

[1]Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

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. (H_2O) 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

INTRODUCTION

Minerals are the stuff of the Earth; without them, there would be no Earth or any other rocky planet. As geologists sensu lato (i.e., scientists who study the Earth), we are all interested in the properties of minerals and how minerals behave in Earth processes—how they respond to changing temperature, pressure, etc., how they interact with each other, and especially how they interact with both natural and anthropogenic fluids. Moreover, minerals are our principal source of economic materials and a major constituent of soils, and their chemical compositions and surface properties are key in this regard. Thus, mineralogy has focused on describing minerals and characterizing their chemical compositions and physical properties, providing this information for use in petrology, geochemistry, geophysics, soil science, etc. However, from the perspective of Mineralogy as a science, we also wish to understand why minerals have the chemical compositions, atomic arrangements, and physical and surface properties that they do. Such understanding requires a theoretical framework within which we can consider the constitution and behavior of minerals, and it is such a framework that I will consider here.

ESTABLISHED THEORETICAL METHODS

What kind of methods do we have to understand and interpret mineralogical information? We use crystal chemistry to systematize mineral properties, classical thermodynamics to analyze processes involving minerals, and computational mineralogy to understand mineral properties and to calculate properties of minerals, the stabilities of which are beyond the range of current experimental methods. Using thermodynamics, we can make calculations for mineral reactions while not knowing much about where the atoms are and what the atoms are doing. There is now an enormous amount of information on atomic arrangements in minerals, and we would prefer to have an atomic-scale understanding of the factors controlling atomic arrangements, chemical

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* E-mail: frank_hawthorne@umanitoba.ca

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compositions, mineral stability, and chemical reactions. We have gained significant understanding of minerals, mineral stability, and mineral reactions though crystal chemistry, thermodynamics, and computational mineralogy. However, these methods have tended to dictate the questions that we ask about minerals—we ask questions to which these methods can give us answers. There are many other questions of scientific interest, which resist our current theoretical approaches. Such questions tend to be ignored as they are seen as intractable, or even irrelevant to current issues in petrology, geochemistry, geophysics, etc. Let us consider some of these questions: (1) why do minerals have the chemical formulas that they do; (2) why do they have their specific structural arrangements; (3) why are minerals stable over specific ranges of pH, Eh, temperature, pressure, and activities of their various constituents; and (4) what are the relations between crystal structure and both enthalpy and Gibbs free energy of formation? Many of these questions are fundamental to our understanding of minerals and their behavior, and yet have tended to be ignored in the past because they are not susceptible to established theoretical techniques in physics and chemistry.

We conventionally represent a crystal structure as a space group plus a set of unit-cell dimensions plus a list of atom coordinates (and displacement parameters), and we use these parameters together with techniques in computational mineralogy to calculate various properties of the crystal. This general approach is extremely successful in understanding the physical properties of materials, and it is successful for a reason. The underlying theories deal with electron sharing between atoms fairly rigorously, and many physical properties of crystals are dependent on the details of electron sharing between atoms. However, what the underlying theory does not do is explain the origin of translational (and quasi-crystal) symmetry in crystals. Moreover, crystal-structure arrangements can be surprisingly insensitive to major variations in electron delocalization and corresponding variations in physical properties. For example, the NaCl structure is adopted both by the insulator LiF, with a band gap of 13.6 eV, and the semiconductor PbS, with a band gap of 0.37 eV. Here, structure type is quite insensitive to bond type (although other semiconductors with small band gaps do adopt the sphalerite and wurtzite arrangements).

What is also interesting is that our perceptions of crystal structure are very insensitive to the structural parameters used for such calculations. We cannot generally appreciate the salient features of a crystal structure from its space group, unit-cell dimensions and atom coordinates; we need a picture of that structure to recognize these features. This has been obvious since the dawn of crystal-structure determination, and crystal structures have been classified and interpreted according to the details of their atom connectivity as expressed visually (e.g., Barlow 1883, 1898; Bragg 1930; Belov 1961; Moore 1970, 1974; Burns 1999, 2005; Krivovichev 2004, 2008, 2009; Krivovichev et al. 1998; Hawthorne 1985, 1986, 1990, 2014; Grice et al. 1999; Hawthorne and Huminicki 2002; Huminicki and Hawthorne 2002). This suggests (at least to me) that if we wish to understand why crystal structures have the atom arrangements that they do, we should not seek this understanding via calculations that involve the sharing of electrons between atoms/ions; we need to understand the commonalities and differences in atom connectivity in crystal structures (cf. Bowen 1928).

MINERAL CHEMISTRY AND STRUCTURE

Consider the hydrated magnesium-sulfate compounds, $Mg(SO_4)(H_2O)_n$ where n = 0–7, 11: synthetic $Mg(SO_4)$, kieserite, sanderite, synthetic $Mg(SO_4)(H_2O)_3$, starkeyite, $Mg(SO_4)(H_2O)_4$, cranswickite, $Mg(SO_4)(H_2O)_4$, pentahydrite, hexahydrite, epsomite and meridianiite, $Mg(SO_4)(H_2O)_{11}$. The $Mg(SO_4)$ part of the chemical formulas is fixed by the electroneutrality principle, but other factors control the degree of hydration of each mineral. With increasing (H_2O) content, there is a gradual depolymerization of the $(Mg\Phi_6)$ and (SO_4) polyhedra (Φ = O, H_2O) as the valence-sum rule (Brown 2002a) prevents linkage of these polyhedra through (H_2O) ligands (Hawthorne 1992; Hawthorne and Sokolova 2012). We know that (H_2O) tends to depolymerize the structures of minerals (and synthetic inorganic solids). However, we have little idea of (1) how such depolymerization is quantitatively related to increasing (H_2O) content, and (2) what is the effect of interstitial cations on the bond topologies of the resulting structures.

Consider structurally and chemically complicated minerals such as botryogen, $Mg_2(H_2O)_{12}[Fe^{3+}_2(SO_4)_4(OH)_2](H_2O)_2$, or metavoltine, $K_2Na_6Fe^{2+}(H_2O)_6[Fe^{3+}_3O(SO_4)_6(H_2O)_3]_2(H_2O)_6$. Their chemical formulas are constrained by the requirement of electroneutrality, but what dictates the other details of their chemical formulas? Why does botryogen have Mg_2 as its interstitial cation, and not Ca_2 or Na_4? Why does botryogen have 14 (H_2O) groups in its formula? Why does not it have (for example) 8 (H_2O) groups? Why does botryogen contain any (H_2O) groups at all and what are the roles of these (H_2O) groups in the structure? How do these aspects of chemistry and structure relate to the stability of botryogen as a function of Eh and pH?

Such questions as these commonly cannot be addressed by our established methods of theoretical investigation, and for those that can, we often must be satisfied with explanations at the macroscopic scale. Here I will examine: (1) how we can address such questions for oxygen-bearing minerals from a theoretical perspective, and (2) what are the advantages of trying to incorporate process (e.g., crystallization, dissolution) into these considerations. The ideas given here are based on bond topology, the arrangement of chemical bonds in space. I also emphasize that these ideas are currently under development, and urge others (particularly students) to develop new modifications and applications of this approach (and other approaches) to answering the very basic questions raised here.

GRAPH THEORY

A graph is a mathematical structure that is used to examine pairwise relations between discrete objects. A chemical bond defines the pairwise relation between bonded atoms; similarly, linkage between structural fragments (e.g., coordination polyhedra) also defines such a pairwise relation. Thus a graph seems a natural representation of a bonded array of atoms, with the advantage that we may use graph theory to examine the properties of such bonded arrays.

A graph is defined as a nonempty set of elements, V(G), called vertices, and a nonempty set of unordered pairs of these vertices, E(G), called edges (Wilson 1979). We may label the vertices, we may color the vertices, we may assign a direction to the edges, and we may assign weights to the edges, resulting in a weighted labeled polychromatic digraph, shown pictorially in Figure 1a. The square molecule shown in Figure 1b corresponds to the graph of Figure 1a as there is a one-to-one mapping of the atoms of the molecule (Fig. 1b) onto the vertex set of the graph (Fig. 1a) and of the chemical bonds of the molecule (Fig. 1b) onto the edge set of the graph (Fig. 1a). We may represent this graph as a matrix (Fig. 2) in which each column and row of the matrix is associated with a specific (colored labeled) vertex and the corresponding matrix entries denote whether (positive) or not (zero) two vertices are adjacent (that is, joined by an edge). If the matrix elements are the weight functions of the edge set, then this matrix is called the adjacency matrix, which is thus a numerical representation of the graph. The number of edges involving a vertex is known as the degree of that vertex. In a digraph, the indegree of a vertex is the number of edges incident at that vertex, and the outdegree of a vertex is the number of edges exident at that vertex.

The handshaking lemma

The sum of the degrees of all the vertices of a graph is equal to twice the total number of its edges.

Each edge in a graph contributes two degrees to the sum of the degrees of all the vertices of a graph, and hence this sum must be even. This relation is known as the handshaking lemma (Wilson 1979) for obvious reasons: each edge involves two vertices, just as a handshake involves two hands, and hence the sum of the degrees of all vertices in a graph is even, as is the number of hands shaken, independent of the number of vertices in the graph or the number of people shaking hands. The handshaking lemma is extremely powerful in dealing with problems involving coordination number and connectivity in structures, particularly where the vertex set is partitioned into two subsets, as is the case where there are significant differences in electronegativity of the constituent atoms in a structure, and atoms of the same set do not bond to one another. For example, in AB compounds, the coordination numbers of A and B must be equal (e.g., [6] in NaCl and [8] in CsCl), whereas in AB_2 compounds, the coordination number of A must be twice that of B (e.g., [6] and [3] in TiO_2 and [8] and [4] in CaF_2).

Graphs with multiple edges

The definition of a graph given above is that of a simple graph; that is, a graph where there cannot be more than one edge connecting two vertices. We may define a general graph (or more simply, a graph) as a nonempty set of elements, V(G), called vertices, and a nonempty family of unordered pairs of these vertices, E(G), called edges. A family is a collection of elements, some of which may occur several times in that collection. The existence of family (rather than a set) in the definition of a general graph allows multiple edges between a pair of vertices, and this gives us much greater flexibility in applying graph theory to crystal structures than would otherwise be the case.

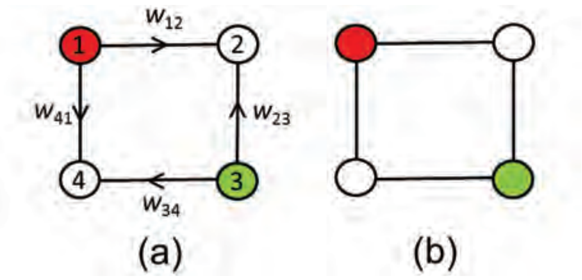
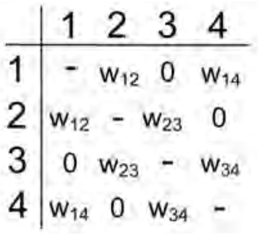


FIGURE 1. (**a**) A weighted polychromatic digraph with the colored vertex set {1, 2, 3, 4} and the directed weighted edge set {12, 32, 34, 14}; (**b**) a simple idealized square molecule consisting of four atoms labeled 1–4; different chemical types of atoms are indicated by different colors.

Graphical representation of linkage between polyhedra

Above, we were using simple graphs to represent the linkage of individual atoms by chemical bonds. However, complicated crystal structures are widely considered as (and represented by) arrangements of linked coordination polyhedra. We may assign different coordination polyhedra to different vertices of a (general) graph, and the capability of having multiple edges allows us to efficiently denote the details of linkage between different coordination polyhedra (Hawthorne 1983). Polyhedra may be represented by colored vertices of a labeled graph in which different colors represent different coordination and labels denote chemically and crystallographically distinct polyhedra. Linkage is indicated by an edge or edges between vertices, and the number of edges between two vertices denotes the number of atoms common to both polyhedra (Fig. 3, M = octahedrally coordinated cation; T = tetrahedrally coordinated cation; φ = unspecified ligand); round parentheses and curly parentheses denote a polyhedron or a group, e.g., (SO_4), (H_2O); square parentheses denote linked polyhedra, e.g., $[M(TO_4)_2\varphi_4]$. For two vertices, no edge denotes disconnected polyhedra (Fig. 3a), one



	1	2	3	4
1	-	w_{12}	0	w_{14}
2	w_{12}	-	w_{23}	0
3	0	w_{23}	-	w_{34}
4	w_{14}	0	w_{34}	-

FIGURE 2. The adjacency matrix corresponding to the graph in Figure 1a.

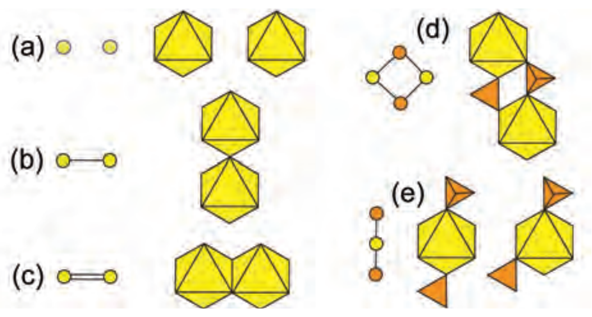


FIGURE 3. Graphical representation of polyhedron clusters; octahedra are shown in yellow, tetrahedra are shown in orange. Each cluster of polyhedra is represented by a graph in which the yellow vertices represent octahedra, the orange vertices represent tetrahedra, and the edges represent the number of vertices common to pairs of polyhedra: (**a**) $(M\varphi_6)_2$; (**b**) $[M_2\varphi_{11}]$; (**c**) $[M_2\varphi_{10}]$; (**d**) $[M_2(TO_4)_2\varphi_8]$; (**e**) graphical isomers of $[M(TO_4)_2\varphi_4]$.

edge denotes corner-sharing between two polyhedra (Fig. 3b), and two edges denote edge-sharing between two polyhedra (Fig. 3c). Figure 3d shows the cluster $[M_2(T\varphi_4)_2\varphi_8]$ and its graphical representation. In a graphical representation, geometrical information is lost. This is illustrated in Figure 3e, which shows two different possible arrangements of the corner-linked cluster $[M(T\varphi_4)_2\varphi_4]$. Both these clusters are described by the same graph; such clusters are called geometrical isomers (Hawthorne 1983). It is very useful to represent the fundamental building block (FBB) of a mineral in this graphical fashion as the hierarchical aspects of the classification are immediately grasped from the arrangement of the constituent graphs. This type of graphical representation is used quite commonly to consider the bond topology of complex structures (e.g., Hawthorne 1983, 1994; Hawthorne et al. 2000a; Krivovichev 2008, 2009; Burns 1995, 1999, 2005; Burns et al. 1995).

BOND-VALENCE THEORY

Bond topology, bond-valence theory, and bond-valence curves

Eighty-five years ago, Pauling (1929) introduced his “rules for ionic structures” (discussed in detail by Hawthorne 2007a). These rules were extremely useful in helping to solve crystal structures in the early days of structural crystallography. While some of the rules were given justification via somewhat vague ionic arguments (Burdett and McLarnan 1984), they are actually collective observations of the structural arrangements available at that time. Hence they need no “theoretical justification” and their long-term utility in comparing structural arrangements should not be surprising. For many years, Pauling’s rules were identified with “ionic materials,” despite the fact that Pauling (1929) discussed bond angles and Pauling (1960) states that quite covalent materials may obey rules similar to those applicable to ionic crystals. Moreover, Bragg (1930) interpreted Pauling’s second rule in terms of only nearest-neighbor forces, this being the first covalent interpretation of Pauling’s second rule (see Hawthorne 2007b for details).

In the late 1960s, it became apparent from the large amount of crystal-structure data (made available by the development of automated X-ray diffractometers) that there are relations between the lengths of chemical bonds (for specific pairs of atoms) and the strengths of those bonds, and many schemes were put forward to relate these variables in a quantitative manner. Pauling (1929) introduced the term bond strength to represent the strength of a bond between a cation and an anion as measured by the cation valence divided by the cation coordination number. It became apparent in the 1970s that a new term was needed for the strength of a bond, where this strength is a function of bond length, to distinguish it from the Pauling bond-strength, and the term bond valence was introduced. Bond valence is defined as the strength of a chemical bond where, for any pair of bonded atoms, that strength is inversely proportional to the distance between those atoms. Brown and Shannon (1973) introduced their widely used bond-valence parameters; these have been (and are continually being) refined (e.g., Brown 2002a, 2009, 2013) and are now almost universally used to check the validity of refined crystal structures.

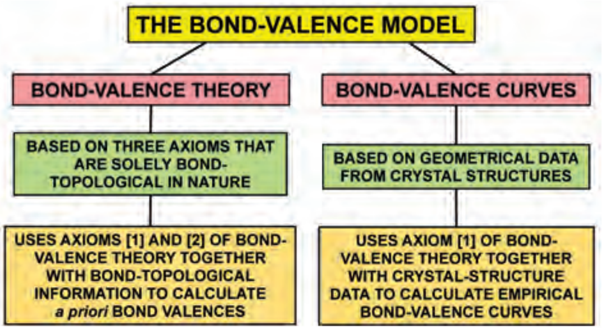


FIGURE 4. The two components of the bond-valence model: Bond-valence theory (left) and bond-valence curves (right).

The bond-valence model: Background

I am interested primarily in oxide and oxysalt minerals, which have significant differences between the electronegativities of the bonded atoms; I will refer to these atoms as cations and anions, with no implication as to the character of their chemical bonding. Let us define a crystal, liquid, or molecule as a network that consists of atoms connected by heteronuclear chemical bonds. Cations and anions alternate along any bond path through this network, and the network must conform to the law of electroneutrality: the total valence of the cations is equal to the total valence of the anions. Bond valence is defined as the strength of a chemical bond between any two ions.

There has been extensive work relating the form and numerical parameters of bond-valence curves to different models of chemical bonding (e.g., Burdett and Hawthorne 1993; Preiser et al. 1999; Gibbs et al. 2014), and it has become apparent that this approach is quite general in that it applies equally well to structures with predominantly ionic bonds and with predominantly covalent bonds. Brown (1981, 2002a, 2002b, 2009, 2013) has systematically developed this approach into a comprehensive model, the Bond-Valence Model that addresses many aspects of chemical bonding in inorganic crystals. The bond-valence model actually consists of two distinct parts, Bond-Valence Theory and empirical bond-valence curves (Fig. 4). Most scientists have tended to ignore bond-valence theory and focus solely on using empirical bond-valence curves for: (1) validating the stereochemical details resulting from crystal-structure refinement, and (2) various crystal-chemical purposes. It does not seem to be generally realized that bond-valence theory is formally independent of the analytical bond-valence curves used extensively in crystallography and crystal chemistry.

Bond-valence theory

Bond-valence theory is based on three principal axioms (Fig. 5): (1) the valence-sum rule; (2) the loop rule; and (3) the valence-matching principle.

The valence-sum rule. The sum of the bond valences at each atom is equal to the magnitude of the atomic valence.

For any field, Gauss’ law relates the flux of the field intensity through a closed surface to the total net charge enclosed within that surface. The valence-sum rule is thus a corollary of Gauss’s theorem applied to the electrostatic potential field, and the fluxes linking atoms in this model correlate very strongly with the bond valences assigned in the bond-valence method (Preiser et al. 1999). Topological properties of the various fields associated with an array of atoms are discussed by Brown (2002b). Long-range Coulombic interactions are inductively transmitted through a crystal by the operation of Gauss' law on the Coulomb field at each atom in the crystal (Preiser et al. 1999).

The loop rule. The sum of the directed bond valences around any closed path (loop) of bonds in the structure is equal to zero.

The valence-matching principle. The Lewis acid strength of a cation may be defined as its characteristic (bond) valence, which is equal to its atomic (formal) valence/mean coordination-number (Brown 1981).

The Lewis-base strength of an anion can be defined as the characteristic valence of the bonds formed by the anion. If two ions form a bond, the magnitude of the strength of the bond from the cation to the anion is controlled by the Lewis-acid strength of that cation, and the magnitude of the strength of the bond from the anion to the cation is controlled by the Lewis-base strength of that anion. However, the bond from the cation to the anion is the same bond as that from the anion to the cation, and hence the magnitudes of the Lewis acid strength and the Lewis base strengths of the constituent ions must be approximately the same for that bond to form (Fig. 6). This argument leads to a particular criterion for chemical bonding, the valence-matching principle (Brown 2002a, 2009):

Stable structures will form where the Lewis-acid strength of the cation closely matches the Lewis-base strength of the anion.

As a chemical bond involves both a cation and an anion, the electron-attracting capacity of the cation must match the electron-donating capacity of the anion for a chemical bond to form.

The above definition of Lewis basicity is often not very useful, as variations in bond valence around anions are much greater than variations in bond valence around cations, and any characteristic bond valence that is assigned has too large a dispersion to be useful. For example, in dravite (Hawthorne et al. 1993), Na is [9]-coordinated and the O atoms to which it is bonded receive on average 0.11 v.u. from each Na-O bond. In CrO_3 (Stephens and Cruickshank 1970), which consists of pyroxene-like chains of $^{[4]}CrO_3$, one O is bonded only to Cr^{6+} and receives 2.00 v.u. from the Cr-O bond. With this amount of variation in bond valence, 0.11–2.00 v.u., it is not useful to define a Lewis-base strength for O^{2-}. Consider a complex oxyanion such as $(SO_4)^{2-}$ (Fig. 7): The central S^{6+} cation provides 1.5 v.u. to each coordinating O atom and these need an additional 0.5 v.u. from other neighboring cations. If the coordination number of O^{2-} is [n], then the average valence of the bonds to O^{2-} (exclusive of the S-O bond) is 0.5/(n – 1) v.u.; where n = 2, 3, 4, or 5, the mean bond valences to O^{2-} are 0.50, 0.25, 0.17, or 0.11 v.u., respectively. The average bond valence received by the $(SO_4)^{2-}$ group is the same as the average bond valence received by each individual O^{2-} anion, and allows us to define a Lewis basicity for the oxyanion group. For the $(SO_4)^{2-}$ oxyanion, the possible average bond valences are quite tightly constrained (0.50–0.11 v.u.) and we may calculate a useful Lewis basicity. Tables 1 and 2 list Lewis acidities and Lewis basicities for geochemically common cations and oxyanions.

The valence-matching principle is the most important and powerful idea in bond-valence theory (Hawthorne 2012): it allows us not just to interpret known structures or compounds; we can test the stability of possible compounds (in terms of whether they can exist or not), which moves us from a posteriore to a priori analysis. I will consider three simple examples (taken from Hawthorne 1994) to illustrate this principle.

Consider the composition Na_2SO_4. The Lewis basicity of the (SO_4) group is 0.17 v.u. (Table 2) and the Lewis acidity of Na is 0.17 v.u. (Table 1). The Lewis basicity of the anion matches the Lewis acidity of the cation, the valence-matching principle is satisfied, and thenardite, Na_2SO_4, is stable.

Consider the composition Na_4SiO_4. The Lewis basicity of the (SiO_4) group is 0.33 v.u. (Table 2) and the Lewis acidity of Na

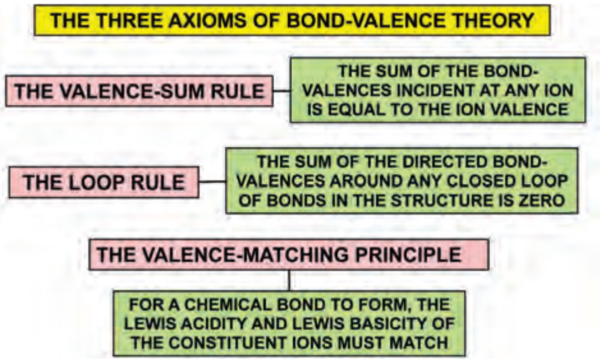


FIGURE 5. The three axioms of bond-valence theory.

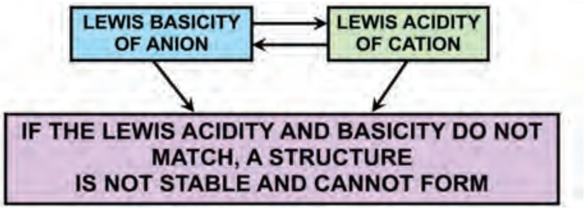


FIGURE 6. The valence-matching principle.

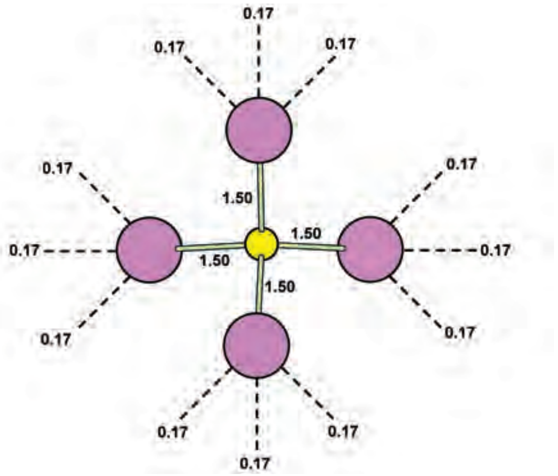


FIGURE 7. The bond-valence structure of the $(SO_4)^{2-}$ oxyanion in thenardite, with the individual bond valences shown in valence units (after Hawthorne 1994).

TABLE 1. Lewis acid strengths (v.u.) for cations

Li	0.21	Sc	0.49	Cu^{2+}	0.45
Be	0.50	Ti^{3+}	0.50	Zn	0.35
B	0.87	Ti^{4+}	0.67	Ga	0.65
C	1.35	V^{3+}	0.50	Ge	0.89
N^{5+}	1.67	V^{5+}	1.20	As^{5+}	1.13
Na	0.16	Cr^{3+}	0.50	Se^{6+}	1.50
Mg	0.33	Cr^{6+}	1.50	Rb	0.12
Al	0.57	Mn^{2+}	0.34	Sr	0.23
Si	1.00	Mn^{3+}	0.52	Sn^{4+}	0.68
P	1.25	Mn^{4+}	0.67	Sb^{5+}	0.83
S	1.50	Fe^{2+}	0.34	Te^{6+}	1.00
Cl^{7+}	1.75	Fe^{3+}	0.50	Cs	0.11
K	0.13	Co^{2+}	0.35	Ba	0.20
Ca	0.27	Ni^{2+}	0.34	Pb^{2+}	0.20

Note: Values taken from Brown (2002), except V^{5+} (Schindler et al. 2000) and Pb^{2+}, which was estimated from several oxysalt mineral structures.

TABLE 2. Lewis basicities (v.u.) for selected oxyanions

$(BO_3)^{3B}$	0.33	$(CO_3)^{2B}$	0.22
$(SiO_4)^{4B}$	0.33	$(NO_3)^{3B}$	0.11
$(AlO_4)^{3B}$	0.42	$(VO_4)^{3B}$	0.25
$(PO_4)^{3B}$	0.25	$(SO_4)^{2B}$	0.17
$(AsO_4)^{3B}$	0.25	$(CrO_4)^{2B}$	0.17

is 0.17 v.u. The Lewis basicity of the anion does not match the Lewis acidity of the cation, the valence-matching principle is not satisfied, and Na_4SiO_4 is not a mineral (or stable structure).

Consider the composition $Na[AlSiO_4]$. The Lewis basicity of the $[AlSiO_4]$ group is 0.13 v.u. and the Lewis acidity of Na is 0.17 v.u. The Lewis basicity of the anion matches (approximately) the Lewis acidity of the cation, the valence-matching principle is satisfied, and nepheline, $Na\,AlSiO_4$ is a stable structure. Moreover, nepheline shows incommensurate behavior (e.g., Angel et al. 2008), perhaps reflecting the slight mismatch between the Lewis basicity and acidity of its constituents.

These arguments illustrate the power of the valence-matching principle. We may consider the possible stability of specific chemical compositions of interest. It is important to recognize that this is a priori analysis; we need no crystal-structure information to evaluate the potential stability (i.e., existence) of any chemical formula. Moreover, this is a "back-of-the-envelope" calculation that is not obscured by numerical complexity.

A priori bond valences. The valence-sum rule and the loop rule provide a series of simultaneous equations (sometimes called network equations) relating bond valences to the constraints of the valence-sum rule and the loop rule. We may designate these bond valences as a priori bond valences as they need no geometrical information (i.e., experimental bond lengths) to be calculated: they are derived from the bond topology of the structural arrangement and the charges of the ions at the vertices of the graph of this arrangement.

Bond-valence curves

For any pair of bonded atoms, bond valence is inversely proportional to the length of the bond: large bond valences are associated with short bonds, and small bond valences are associated with long bonds. To obtain numerical values for the bond valences, each bond is assigned a bond valence such that the valence-sum rule is satisfied (Brown 2002a): The sum of the bond valences at each atom is equal to the magnitude of the atomic valence. Thus bond valences are scaled to the formal valences of the cations and anions involved in the chemical bonds. If this is done for a relatively large number of structures, one may derive numerical parameters, bond-valence parameters (or bond-valence curves) that may be used to calculate bond valences from bond lengths. Such parameters are listed by Brown (2002a, 2009, 2013) from a wide variety of sources, and are commonly used to validate experimentally derived crystal structures and to examine various crystal-chemical aspects of their atomic arrangements.

Brown and Shannon (1973) discussed the differences between the bond-valence model and the ionic model. In the bond-valence model, a structure consists of atom cores held together by valence electrons associated with the chemical bonds between the atoms, and they explicitly state that the valence electrons may be associated with chemical bonds in a symmetric (covalent) or asymmetric (ionic) manner. Thus a priori knowledge of the electron distribution is not required to use this approach. Burdett and Hawthorne (1993) showed that the form of the bond-valence curves may be derived algebraically from a molecular-orbital description of a solid in which there is a significant energy gap between the interacting orbitals on adjacent atoms, whereas Preiser et al. (1999) gave an ionic justification of the bond-valence model. One may conclude that the bond-valence model is not a theory of "ionic" bonds or "covalent" bonds. It is a simple yet quantitative method that allows us to examine and analyze the stereochemistry and physical properties of both simple and complex solids; it is used primarily for crystals, but also can be used for surfaces (Schindler et al. 2004a, 2004b; Bickmore et al. 2004, 2006), glasses, and liquids. Although the idea of bond valence grew out of Pauling's second rule, the wide variety of its application and subsequent examination of its theoretical underpinnings show that it is a theory of atomic arrangements in its own right, without any reference to specific models of the chemical bond. Its power lies in the fact that it is a back-of-the-envelope method in which the physical details are not obscured by complexities of computation. Each year sees new applications to an increasing array of problems as the bond-valence model takes a central role in our understanding of complex materials.

Bond-topological controls on the structure and chemical composition of oxysalt minerals

The valence-matching principle is a powerful method of assessing the stability (i.e., existence or otherwise) of potential chemical compounds, and we saw above how we can a priori predict the existence of Na_2SO_4 (thenardite), the non-existence of Na_4SiO_4, and the existence of $NaAlSiO_4$ (nepheline). For such simple structures, this approach is straightforward. However, for more complicated minerals, e.g., botryogen, $Mg_2(H_2O)_{10}[Fe^{3+}_2(SO_4)_4(OH)_2](H_2O)_2$ and metavoltine, $K_2Na_6Fe^{2+}(H_2O)_6[Fe^{3+}_3O(SO_4)_6(H_2O)_3]_2(H_2O)_6$, the approach is less transparent. Yet these complex minerals raise some very fundamental questions pertaining to the details of their chemical composition. Again: (1) why does botryogen have Mg rather than Ca or Ba as its divalent interstitial cation; (2) why does it have divalent interstitial cations, Mg_2, rather than monovalent interstitial cations, Na_4 or K_4; (3) why does it have 14 (H_2O) groups in its formula; why does not it have (for example) 12 (H_2O) groups; and (4) why does it have any (H_2O) groups at all in its formula; what is the role of these (H_2O) groups in the structure? How do the chemical formula and structural arrangement of botryogen relate to its stability as a function of

Eh and pH? We cannot say that we understand minerals until we understand what controls their chemical compositions at this level of detail.

To address this issue for complex structures, Hawthorne (1983, 1985) divided a structure into two components: the structural unit, the strongly bonded part of the structure, consisting of oxyanions and low-coordination-number cations; and the interstitial complex, the weakly bonded part of a structure, usually consisting of monovalent cations, large divalent cations and (H_2O) groups. To do this, we must define what we mean by "strongly bonded" and "weakly bonded." Many minerals contain octahedrally coordinated divalent cations, and many of these minerals, e.g., forsterite, enstatite, are stable at high temperature. Many minerals contain monovalent and divalent cations in higher coordination numbers, e.g., thenardite, gypsum, and many minerals are held together by hydrogen bonds; these minerals commonly crystallize from aqueous solution at ambient (or close to ambient) conditions. An appropriate boundary between "strongly bonded" and "weakly bonded" will be between 0.33 v.u. (for $^{[6]}Mg$) and 0.20 v.u. (for common hydrogen bonds, Ba, Pb^{2+}) or 0.23 v.u. (for Sr), and I will take it as 0.30 v.u., although the exact value will change depending on other bond valences in a structure.

If we can define Lewis acidities and Lewis basicities for the structural unit and the interstitial complex, we may examine their interaction using a mean-field version of the valence-matching principle. This binary representation of a complex structure is illustrated in Figure 8 for botryogen, $\{Mg_2(H_2O)_{10}\}[Fe^{3+}_2(SO)_4(OH)_2](H_2O)_2$. We have partitioned the structure into a structural unit: $[Fe^{3+}_2(SO)_4(H_2O)_2]$, a cluster of Fe^{3+} octahedra and sulfate tetrahedra (shown by cation-centered polyhedra in Fig. 8), and an interstitial complex: $\{Mg_2(H_2O)_{12}\}$, Mg cations together with their associated (H_2O) groups. We may calculate a Lewis basicity for the structural unit and a Lewis acidity for the interstitial complex as aggregate properties of the constituents of these two units (see Hawthorne and Schindler 2008), and their interaction may be examined in a manner similar to the application of the valence-matching principle to simple chemical compositions using the principle of correspondence of Lewis acidity-basicity (Hawthorne and Schindler 2008):

Stable structures will form where the Lewis-acid strength of the interstitial complex closely matches the Lewis-base strength of the structural unit.

As noted above, the principle of correspondence of Lewis acidity-basicity is thus the mean-field equivalent of the valence-matching principle. We may now use this principle in conjunction with the binary representation of complex structures to examine the reasons why minerals have the chemical compositions that they do, and to predict the possible chemical compositions of potential minerals.

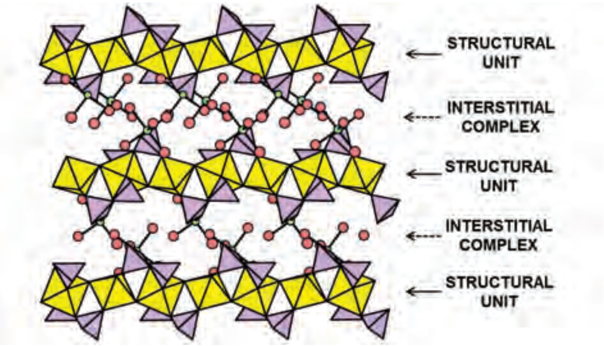


FIGURE 8. Partitioning of the crystal structure of botryogen, $Mg_2(H_2O)_{12}[Fe^{3+}_2(SO_4)_4(OH)_2](H_2O)_2$, into two units, the strongly bonded structural unit (shown as colored polyhedra) and the weakly bonded interstitial complex (shown as individual atoms and chemical bonds). Pink tetrahedra = (SO_4) groups; yellow octahedra = $(Fe^{3+}O_6)$ octahedra; large orange circles = O atoms; small blue circles = Mg atoms; black lines = Mg-O bonds.

The role of H_2O in crystal structures

There are several different major roles for hydrogen (H) in crystal structures (Hawthorne 1992; Hawthorne and Baur 1994). The (OH) and (H_2O) groups are very important because of their polar nature: on the O side, each group acts as an anion, whereas on the H side, the group acts as a cation. The hydrogen-bond interaction is extremely important; it moderates many biological interactions essential to life, and it imparts great diversity both to atomic arrangements in minerals and to atom interactions in minerals. An (H_2O) group may: (1) moderate Lewis acidity and Lewis basicity, and (2) control the dimensional polymerization of structural units. First, I will consider how (H_2O) can act as a moderator of bond valence.

(H_2O) bonded to one cation. Consider the atomic arrangements in Figures 9a and 9b: A cation, *M*, bonds to an anion *S* with a bond valence of v v.u., and a cation, *M*, bonds to an (H_2O) group, and the (H_2O) group bonds to an anion, *S*. In Figure 9a, the anion receives one bond of bond valence v v.u. from the cation *M*. In Figure 9b, the O atom of the (H_2O) group receives a bond valence of v v.u. from the cation; the bond-valence requirements of the central O atom are satisfied by two short O-H bonds of strength $(1 – v/2)$ v.u. Each H forms a hydrogen bond with the *S* anion to satisfy its own bond-valence requirements, and the *S* anion thus receives a bond valence one half (Fig. 9b) of what it received where it was bonded directly to the *M* cation (Fig. 9a). The (H_2O) group is functioning as a bond-strength transformer, dividing one bond (bond strength = v v.u.) into two bonds of half the strength (bond valence = v/2 v.u.); this type of (H_2O) group is called a transformer (H_2O) group (Hawthorne and Schindler 2008).

(H_2O) bonded to two cations. Consider the atomic arrangement in Figure 9c: two cations bond to an (H_2O) group, which bonds to two anions. The O atom receives a bond valence of 2v v.u. from the cations, and the valence-sum rule at this O anion is satisfied by two short O-H bonds of strength $(1 – v)$ v.u. Each H forms a hydrogen bond with a neighboring anion, which receives the same bond valence (v v.u., Fig. 9c) as where it is bonded directly to one *M* cation (Fig. 9a). The (H_2O) group does not act as a bond-valence transformer, is a non-transformer (H_2O) group.

(H_2O) not bonded to any cation. Consider the atomic arrangement in Figure 9d: (H_2O) is involved only in a hydrogen-bond network. In such an environment, the O atom is usually [4]-coordinated, and the (H_2O) group participates in two O-H (donor-hydrogen) bonds and two H···O hydrogen bonds. Two hydrogen bonds of strength v v.u. are incident at the O atom of the (H_2O) group, the bond-valence requirements of the central O atom are satisfied by two O-H bonds of strength (1 – v) v.u., and each H atom forms a hydrogen bond of strength v v.u. to another anion (Fig. 9d). Hence an (H_2O) group not bonded to any cation does not modify the strengths of its exident chemical bonds, it merely propagates them to more distant anions, as is the case where the (H_2O) group is bonded to two cations (Fig. 9c); this type of (H_2O) is designated non-transformer (H_2O).

(H_2O) as a component of the interstitial complex. As a component of an interstitial complex, (H_2O) groups have two principal functions: (1) to satisfy the bond-valence requirements of an interstitial cation where there are not enough anions to do so from adjacent structural units, and (2) to function as a bond-valence transformer between interstitial cations and the structural unit. The first case involves only propagating bond valence through space, and hence may involve non-transformer (H_2O) groups. The second case involves transformer (H_2O) groups, and these will moderate the Lewis acidity of the interstitial complex. Hence the transformer (H_2O) groups of the interstitial complex affect the stability of a chemical composition through the operation of the principle of correspondence of Lewis acidity-basicity. Below I will show how this approach to understanding the role of (H_2O) groups can give us a quantitative understanding of the chemical compositions of interstitial complexes.

Controls on the amount of (H_2O) in minerals: The principle of correspondence of Lewis acidity-basicity

Calculation of Lewis basicity

The Lewis basicity of a structural unit is the average bond valence of bonds to that structural unit from adjacent interstitial complexes and structural units (Hawthorne and Schindler 2008). The bonds received by the structural unit must balance the charge of the structural unit, and hence we may define the Lewis basicity of the structural unit as the charge on the structural unit divided by the number of bonds to the structural unit. So we need to know: (1) the effective charge on the structural unit, and (2) the number of bonds (from the interstitial complex and adjacent structural units) needed by the structural unit.

What is the effective charge of the structural unit? The formal charge is not necessarily appropriate to use in this context, particularly for structures with formally neutral structural units as then there is no mechanism for the structure to link together. Consider lizardite, $Mg_3Si_2O_5(OH)_4$ (Fig. 10). $[Mg_3Si_2O_5(OH)_4]^0$ sheets link to each other via hydrogen bonds from the (OH) groups in the layer of octahedra of one sheet to the bridging O atoms in the layer of tetrahedra of the adjacent sheet. The hydrogen bonds transfer charge from one sheet to the next, and impart a polar character to the sheet; the sheet has cation character on the (OH) side and anion character on the silicate side (shown by + and – signs in Fig. 10). To correctly describe the interaction between adjacent structural units, we must factor this transfer of charge into our calculation of the charge of the structural unit. The effective charge of lizardite is 0 (the formal charge of the structural unit) + 4 × 0.20 (the charge transferred by hydrogen bonding, assuming a hydrogen bond valence of 0.20 v.u., Brown 1981) = 0.80^-. Note that such a transfer of charge can only involve cations with very asymmetric coordinations (commonly H^+, less commonly stereoactive-lone-pair cations such as Pb^{2+} or Bi^{3+}). Note that minerals with formally charged structural units may still be polar, and this transfer of charge must be built in to the calculation of Lewis basicity. For metavoltine, $K_2Na_6Fe^{2+}(H_2O)_6[Fe^{3+}_3O(SO_4)_6(H_2O)_3]_2(H_2O)_6$, the effective charge of the structural unit (in square parentheses) is 10 (the formal charge) + 12 × 0.20 (the charge transferred by 12 hydrogen bonds) = 12.4^+. We define

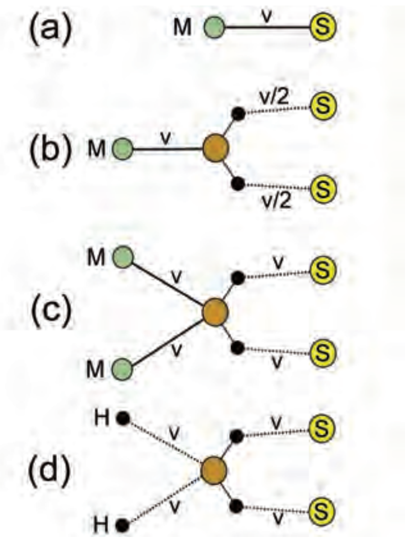


FIGURE 9. The bond-valence structure around (H_2O) as a function of local bond-topology; (**a**) a cation, C (green) bonded to an anion, S (yellow) with bond valence v v.u.; (**b**) a cation bonded to an (H_2O) group (O = orange; H = black) with bond valence v v.u.; the H atoms hydrogen-bond to the anions S with bond valence v/2 v.u. per bond; (**c**) two cations bonded to an (H_2O) group with bond valence v v.u. per bond; the H atoms hydrogen-bond to the anions S with bond valence v v.u. per bond; (**d**) two H atoms hydrogen-bonded to an (H_2O) group with bond valence v v.u. per bond; the H atoms of the (H_2O) group hydrogen-bond to the anions S with bond valence v v.u. per bond.

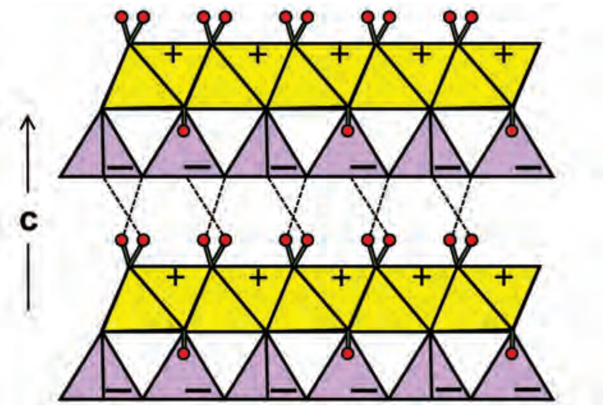


FIGURE 10. Representation of the crystal structure of lizardite, showing the polar nature of the structural unit; yellow = Mg octahedra; lilac = Si tetrahedra; red circles = H atoms; thick black lines = O_{donor}-H bonds; broken lines = hydrogen bonds. The acidic (+) and basic (–) parts of the structural unit are indicated.

the effective charge of the structural unit as the formal charge as modified by charge transferred by hydrogen bonding from donor anions within the structural unit.

What is the number of bonds needed by the structural unit?

First, I will show how we can calculate this quantity if everything is known about the crystal structure. The total number of chemical bonds in a structure is the sum of the products of the cation-coordination numbers and the numbers of those cations in the formula unit. We may similarly calculate the number of bonds in the structural unit. The difference between these two values is the number of bonds needed by the structural unit. This calculation is trivial if the details of the crystal structure are known. However, we wish to predict information about crystal structures, and we do not know such stereochemical details. We must be able to predict this information if we want a priori analysis of crystal structures; how to do this is covered in the next few sections.

The charge deficiency per anion: CDA

Schindler et al. (2000b) defined average basicity as the average bond valence per O atom contributed by the interstitial species and adjacent structural units. Average basicity correlates with the average O-coordination number of the structural unit, and this correlation plays a critical role in stereochemical prediction. As indicated by its definition, this quantity is the additional average incident bond valence required from the interstitial complex by each O atom of the structural unit to satisfy the principle of correspondence of Lewis acidity-basicity, and Schindler et al. (2006) renamed this quantity the charge deficiency per anion, or CDA. Below we will see that the CDA of a structural unit correlates strongly with the numbers of bonds to those structural units from the interstitial complex and neighboring structural units. It is these correlations that play a major role in a priori prediction of structural features.

The CDA of a structural unit is the effective charge of the structural unit divided by the number of O atoms in the structural unit. For bloedite, $Na_2[Mg(SO_4)_2(H_2O)_4]$, the effective charge of the structural unit is $2 + 0.2 \times 8 = 3.6^-$ and the number of O atoms in the structural unit is 12; thus the CDA = 3.6/12 = 0.30 v.u.

The number of bonds required by the structural unit

The CDA is a measure of the bond valence required by each O atom of the structural unit from the interstitial complex and adjacent structural units. Schindler et al. (2006) showed that there is a positive correlation between the CDA of the structural unit and the average number of bonds received by O atoms of the structural unit from the interstitial complex and adjacent structural units, $\langle NB \rangle_{in}$. This relation, shown for sulfate minerals in Figure 11, is very important as it allows us to predict a range for the number of bonds from the interstitial complex and adjacent structural units to a specific structural unit. In turn, we may then calculate the range in Lewis basicity for that structural unit.

For bloedite, $Na_2[Mg(SO_4)_2(H_2O)_4]$, the CDA = 0.30 v.u. (see above). Using Figure 11, we may read off the range for the number of bonds to anions of the structural unit: 1.55 to 2.44. The corresponding range in the total number of bonds to the structural unit is (1.55 to 2.44) × 12 = 18.6 to 29.3, and the resulting range in Lewis basicity of the $[Mg(SO_4)_2(H_2O)_4]^{2-}$ structural unit is the effective charge divided by the range in the number of bonds to the structural unit: 3.6/(18.6 to 29.3) = 0.12 to 0.19 v.u.

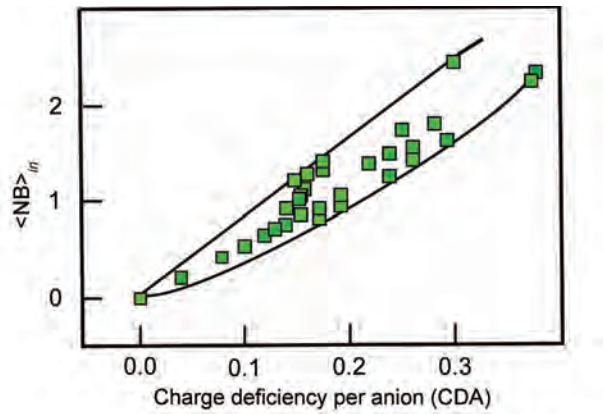


FIGURE 11. Correlation between the CDA of structural units and the average number of bonds from the interstitial complex and adjacent structural units, $\langle NB \rangle_{in}$, to O atoms in the corresponding structural units of sulfate minerals. The upper and lower bounds of the distribution are used to define the characteristic range in the number of bonds accepted by a specific structural unit.

The parameter $\langle NB \rangle_{in}$ is required to establish a relation between O-coordination number and CDA. To have predictive power, we need to be able to derive the number of bonds required by O atoms a priori, without reference to an atomic arrangement, and the type of relation in Figure 11 allows such a prediction. There is another important issue: the data in Figure 11 form a band rather than a linear trend, indicating that the structural units can accommodate a range in the number of bonds from the interstitial complex. It seems apparent that structural units maintain their stability as the pH of the environment changes by varying the number of bonds they accept from the interstitial complex and adjacent structural units. Thus the range in numbers of bonds from the interstitial complex and adjacent structural units to the structural unit reflects the range in pH over which the mineral is stable (Hawthorne and Schindler 2008). As shown above, Figure 11 allows calculation of the range of possible Lewis-base strength for a specific structural unit (see example for bloedite given above).

Factors affecting the composition of the interstitial complex

It is useful to represent the variation in Lewis-acid strength of an interstitial complex as a function of chemical composition and structure in a graphical fashion, as this facilitates use of the principle of correspondence of Lewis acidity-basicity to examine the interaction between the structural unit and interstitial complex as a function of varying chemical composition of each component of a structure. The chemical formula of a generalized interstitial complex may be written as

$$\{^{[m]}M^{+}_{a}{}^{[n]}M^{2+}_{b}{}^{[l]}M^{3+}_{c}(H_2O)_d(H_2O)_e(^{[q]}H_2O)_f(H_2O)_g\}^{2+}$$

where M are interstitial cations of different coordination number $[m]$, $[n]$, and $[l]$, and valence; d is the amount of transformer (H_2O); e is the amount of non-transformer (H_2O); and g is the amount of (H_2O) not bonded to any interstitial cation (Schindler and Hawthorne 2001a). The Lewis acidity of the interstitial complex may be represented graphically as a function of the variables a to g, l to n, q and Z in the above expression (Fig. 12): the ordinate is the Lewis acidity of the interstitial complex, the abscissa is the number of transformer (H_2O) groups per cation, and the curved lines show the variation in Lewis acidity as a function of the number of transformer (H_2O) groups per cation for interstitial cations of different coordination number and formal charge (the corresponding cation charges and coordinations are shown to the left of the curves). Monovalent anions (OH, Cl) may also be incorporated into this procedure (see Hawthorne and Schindler 2008 for details).

Figure 13 shows the operation of the principle of correspondence of Lewis acidity-basicity. The range in Lewis basicity of the structural unit is plotted on the graph of the Lewis-acidity function (Fig. 12). Where the functions representing the properties of the interstitial complexes and the structural unit do not intersect (i.e., outside the yellow band in Fig. 13a), structures of those compositions are not stable as the Lewis acidities of these interstitial complexes are not within the Lewis-basicity range of the interstitial complex represented on the graph; the principle of correspondence of Lewis acidity-basicity is not satisfied, and structures of these compositions will not form. Where the functions representing the properties of the interstitial complexes and the structural unit do intersect (i.e., within the yellow band in Fig. 13a), structures of those compositions are potentially stable as the Lewis acidities of these interstitial complexes are within the Lewis-basicity range of the interstitial complex represented on the graph; the principle of correspondence of Lewis acidity-basicity is satisfied, and structures of these compositions may form. Let us look at what we can do with this approach for a subset of the sulfate minerals.

Hydroxy-hydrated sulfate minerals

The structural hierarchy developed for sulfate minerals by Hawthorne et al. (2000a) forms a general framework for the examination of sulfate structures from a bond-topologic perspective. Schindler et al. (2006) examined sulfate structures in this way and showed that many crystal-chemical features of sulfate minerals may be understood in terms of the principle of correspondence of Lewis acidity-basicity, in parallel with similar work on borate minerals (Hawthorne et al. 1996a; Schindler and Hawthorne 2001a, 2001b, 2001c), vanadate minerals (Schindler et al. 2000b), and uranyl minerals (Burns 2005; Schindler and Hawthorne 2004, 2008). We will look at two structural units in this group and use the principle of correspondence of Lewis acidity-basicity to derive possible interstitial complexes and compare them with what is observed in minerals.

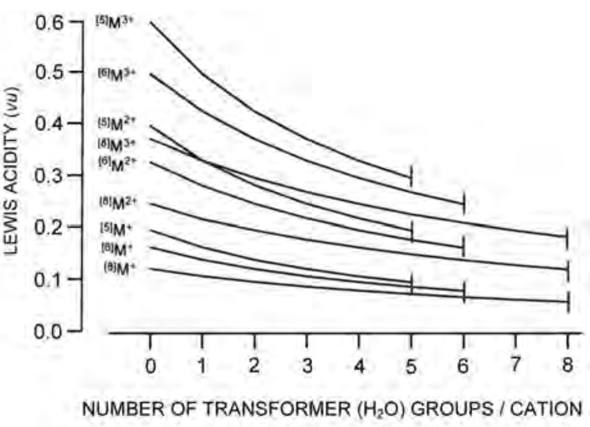


FIGURE 12. Variation in Lewis acidity of a general interstitial complex as a function of the number of transformer (H_2O) groups per cation. The lines shown are for interstitial cations with formal charges and coordination numbers shown to the left of the plot. After Hawthorne and Schindler (2008).

$[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$ (M = Mg, Ni, Zn, Fe^{2+}). The structural unit $[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$ occurs in bloedite, $\{Na_2\}[Mg(SO_4)_2(H_2O)_4]$, nickelbloedite, $\{Na_2\}[Ni(SO_4)_2(H_2O)_4]$, leonite, $\{K_2\}[Mg(SO_4)_2(H_2O)_4]$, changoite, $\{Na_2\}[Zn(SO_4)_2(H_2O)_4]$, mereiterite, $\{K_2\}[Fe(SO_4)_2(H_2O)_4]$, and roemerite, $\{Fe^{2+}(H_2O)_6\}[Fe^{2+}(SO_4)_2(H_2O)_4]$ (Hawthorne et al. 2000a). Above, we calculated a range in Lewis basicity for this structural unit (in bloedite): 0.12–0.19 v.u.

Values of Lewis acidity for interstitial monovalent cations with coordination numbers [6] to [8] intersect the range in Lewis basicity for 0–2, 0–1, and 0 transformer (H_2O) groups per cation,

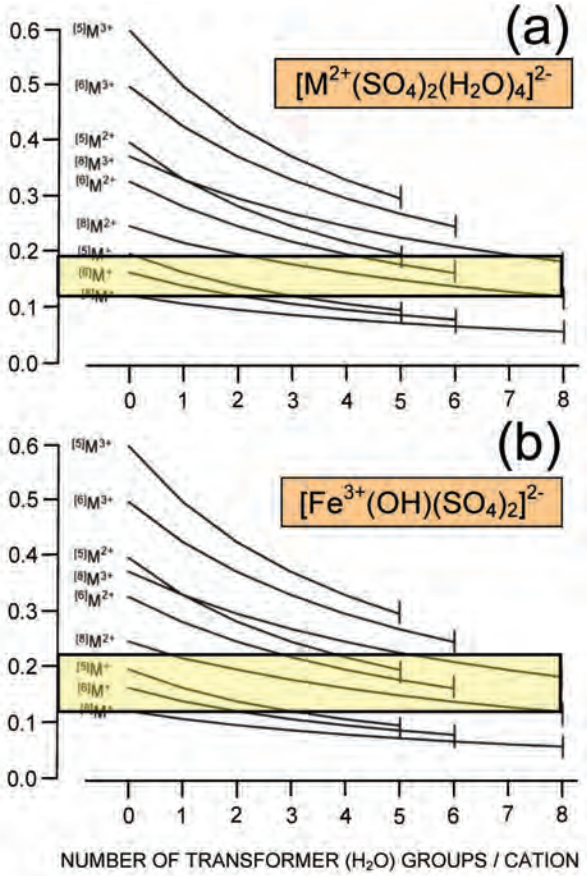


FIGURE 13. Variation in Lewis acidity with the number of transformer (H_2O) groups per cation for different interstitial-cation charges and coordination numbers for a general interstitial complex; the range in Lewis basicity of the structural units for selected sulfate minerals are shown by the yellow fields: (**a**) $[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$; (**b**) $[Fe^{3+}(OH)(SO_4)_2]^{2-}$.

respectively. With regard to divalent interstitial cations, $^{[6]}M^{2+}$ can occur with 4–6 transformer (H_2O) groups and $^{[8]}M^{2+}$ can occur with 2–8 transformer (H_2O) groups. With regard to trivalent interstitial cations, $^{[8]}M^{3+}$ can occur only with 8 transformer (H_2O) groups, $^{[7]}M^{3+}$ and $^{[6]}M^{3+}$ cannot occur at all. All minerals of this group conform to these predictions: bloedite, nickelbloedite and changoite have an interstitial complex $\{^{[6]}Na_2(H_2O)_0\ldots\}$, leonite and mereiterite have an interstitial complex $\{^{[6]}K_2(H_2O)_0\ldots\}$, and roemerite has an interstitial complex $\{^{[6]}Fe^{2+}(H_2O)_6\ldots.\}$.

$[Fe^{3+}(OH)(SO_4)_2]^{2-}$. The structural unit $[Fe^{3+}(OH)(SO_4)_2]^{2-}$ occurs in sideronatrite, $\{Na_2(H_2O)_3\}[Fe^{3+}(SO_4)_2(OH)]$, metasideronatrite, $\{Na_4(H_2O)_3\}[Fe^{3+}(SO_4)_2(OH)]_2(H_2O)_3$, chaidamuite, $\{^{[6]}Zn(H_2O)_4\}[Fe^{3+}(SO_4)_2(OH)]$, and guildite, $\{^{[4+2]}Cu^{2+}(H_2O)_4\}[Fe^{3+}(SO_4)_2(OH)]$. The effective charge of this structural unit is $(2 + 0.2 \times 1)^- = 2.2^-$, the number of O atoms in the structural unit is 9, and the CDA of the structural unit is 2.2/9 = 0.24 v.u. With this value, we may derive the lower and upper bounds for $\langle NB\rangle_{in}$ using Figure 11: 1.10–1.75. The resultant range in the number of bonds required by the structural unit is 1.14–1.97 × 9 = 10.3–17.7. Dividing the effective charge by the number of bonds required, 2.2/(10.3–17.7), gives the range in Lewis basicity: 0.12–0.22 v.u. As before, we plot this range in Lewis basicity on the graph of the Lewis-acidity function, Figure 13b, and can predict the range in chemical composition for possible interstitial complexes.

Values of Lewis acidity for interstitial monovalent cations with coordination numbers [5] to [7] intersect the range in Lewis basicity for 0–2, 0–1, and 0 transformer (H_2O) groups per cation, respectively. With regard to divalent interstitial cations, $^{[6]}M^{2+}$ can occur with 3–6 transformer (H_2O) groups, $^{[7]}M^{2+}$ can occur with 2–7 transformer (H_2O) groups, $^{[8]}M^{2+}$ can occur with 1–8 transformer (H_2O) groups, and $^{[8]}M^{3+}$ can occur with 5–8 transformer (H_2O) groups. All minerals of this group conform to these predictions: sideronatrite and metasideronatrite have an interstitial complex $\{^{[6]}Na_2(H_2O)_0\ldots\}$, guildite has an interstitial complex $\{^{[6]}Cu^{2+}(H_2O)_4\}$, and chaidamuite has an interstitial complex $\{^{[6]}Zn(H_2O)_4\}$ (Schindler et al. 2006).

The approach described above provides significant understanding of what factors affect the chemical compositions of minerals, and some prediction of the details of interstitial cations and anions in minerals. For some structural units, the predicted interstitial complexes vary over a wide range of cations or transformer (H_2O) groups, which in terms of prediction, is not satisfactory. This indicates the need for further development along these lines. It seems likely that the compositions of interstitial complexes in these circumstances are also affected by the pH of their environment during crystallization. Some very interesting questions now emerge concerning the nature of the crystallization process. Does the pH of the environment have a strong effect on the form of the structural unit or the amount of (H_2O) incorporated into the structure? Does the form of the structural unit dictate the identity of the interstitial cations, or does the availability of a particular interstitial cation dictate the form of the structural unit? Are there synergetic interactions between these factors? We can begin to investigate some of these questions using this bond topology approach.

Other applications

This approach has also been used to examine the structure, chemical composition and stability of vanadate (Schindler et al. 2000a, 2000b), borate (Schindler and Hawthorne 2001a, 2001b, 2001c), and uranyl-oxysalt minerals (Schindler and Hawthorne 2004, 2008), and has the potential to be applied to other low-temperature oxysalt minerals. It has also been used to consider crystal morphology and surface features (Schindler et al. 2004a, 2004b) and crystallization-dissolution of minerals in aqueous solutions (Hawthorne and Schindler 2014). An important aspect of this approach is that it relates bond topology and bond valence to processes involved in crystallization, and it may also be applicable to chemical reactions. The valence-sum rule is used for atoms in crystals, glasses, and aqueous fluids. It seems reasonable that atoms in transition between these various states of matter also tend to obey the valence-sum rule. This led Hawthorne (2012) to propose the "reaction principle":

During a chemical reaction, atoms move relative to each other such that they continually minimize local deviations from the valence-sum rule. Thus as the atomic arrangements pass through their excited states, the atoms follow trajectories that are both consistent with those excited states and minimize the local deviations from the valence-sum rule at all stages of the reaction.

It also suggests that the arrangements of atoms in the reactants may significantly affect the arrangements of atoms in the products, as many mineral reactions will tend to occur by breaking the weaker chemical bonds in the reactants and maintaining the stronger chemical bonds, thus giving us a possible mechanism for explaining Ostwald's Step Rule[1] (see Morse and Casey 1988 for an excellent description of this rule in geochemical reactions). An example of this mechanism was given by Gaskell et al. (1991) who showed that a $CaSiO_3$ glass has short- and medium-range structure very similar to that of wollastonite. This suggests that in a $CaSiO_3$ melt close to the liquidus, the product in the crystallization of wollastonite is already templated in the reactant, and the atoms in the system obey the reaction principle, and crystallize as wollastonite. It is unfortunate that the structures of magmas are not well-characterized at medium range, but the possibility that such templating of minerals occurs in magmas provides additional incentive to learn more about the structures of magma and the details of crystallization processes at the atomic scale in magmatic systems.

LEWIS BASICITY OF THE STRUCTURAL UNIT AND THE FORMATION OF ROCKS

A major constraint on the chemistry and atomic arrangements of structural units

Above, we defined the boundary between the bonds of the structural unit and the bonds of the interstitial complex as 0.30 v.u. The strength of the bonds involving the interstitial complex is thus <0.30 v.u., and hence its Lewis acidity is less than 0.30 v.u. As the principle of correspondence of Lewis acidity-basicity requires that the Lewis basicity of the structural unit match the Lewis acidity of the interstitial complex, the Lewis basicity of the structural unit must also be <0.30 v.u. This is an extremely important statement as it must exert stringent controls on the possible chemical compositions and atomic arrangements of

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[1] There are many versions of Ostwald's step rule. Perhaps the most general states that there is a tendency for the least-stable product of a chemical reaction to crystallize first, and this phase subsequently reacts over time to form a sequence of progressively more stable phases.

structural units in minerals.

Let us examine this issue for structural units consisting of octahedrally and tetrahedrally coordinated cations (e.g., Mg,Al and transition-metal phosphates, sulfates, silicates). The Lewis basicity of a structural unit is affected by its chemical composition, aggregate formal charge, and the coordination numbers of its cations and anions. We may approximately calculate the Lewis basicity of a structural unit by proposing an average anion-coordination number [a more accurate but more complicated method is available, see Hawthorne and Schindler (2008)] and calculating the number of bonds required from the interstitial complex to produce this number; dividing the charge of the structural unit by this number gives the Lewis basicity of that structural unit. As will be apparent later, small inaccuracies in the calculated Lewis basicities do not affect the resulting arguments and understanding.

First, let us consider divalent-metal phosphates with structural units of the form $M^{2+}_N(PO_4)(OH)_m$. The variation in Lewis basicity as a function of N, the number of octahedrally coordinated M^{2+} cations, and m, the number of (OH) groups, is shown in Figure 14a for N = 2 to 4 and m = 0 to 25 (the method of calculation is explained in the Appendix). For $M^{2+}_2(PO_4)(OH)_{0–15}$, the Lewis basicity increases with increasing values of m, the amount of (OH), but levels off at m >7. For $M^{2+}_3(PO_4)(OH)_{0–25}$, the Lewis basicity is constant at 0.50 v.u. for all values of m. For $M^{2+}_4(PO_4)(OH)_{0–25}$, the Lewis basicity is somewhat above 0.50 v.u. at high values of m, and increases dramatically with decreasing values of m. Above, we showed that the Lewis basicity of the structural unit must be less than 0.30 v.u. if it is to satisfy the principle of correspondence of Lewis acidity-basicity. If we mark this boundary on Figure 14a, we see that most compositions of the general form $M^{2+}_N(PO_4)(OH)_m$ lie to the higher side of the 0.30 v.u. boundary, and hence cannot occur as structural units in minerals. Only for N = 2 and m ≤ 2 do we have Lewis basicities less that 0.30 v.u.: $[M^{2+}_2(PO_4)(OH)_2]^-$ and $[M^{2+}_2(PO_4)(OH)]^0$. If we look at minerals (Table 3), we see selected minerals of this form: farringtonite, sarcopside and zavalíaite (N = 1.5, m = 0), althausite (N = 2, m = 1), holtedahlite (N = 2, m = 1), and wagnerite (N = 2, m = 1). Moreover, there are no minerals of the form $M^{2+}_N(PO_4)(OH)_m$ with Mg^{2+} or OH^- greater than two ions per phosphate group.

Next, let us consider divalent-metal sulfates with structural units of the form $M^{2+}_N(SO_4)(OH)_m$. The variation in Lewis basicity as a function of N and is shown in Figure 14b for N = 1 to 5 and m = 0 to 18. For $M^{2+}(SO_4)(OH)_{0–4}$, the Lewis basicity increases rapidly from m = 4 to 6, but then levels off at higher values of m, the amount of (OH), and overlaps with the curve for N = 3 for larger values of m. For $M^{2+}_3(SO_4)(OH)_{4–18}$, the Lewis basicity increases rapidly from m = 4 to 6, but then gradually levels off with increasing values of m. For $M^{2+}_4(SO_4)(OH)_{0–18}$, the Lewis basicity is constant at 0.50 v.u. for all values of m. For $M^{2+}_5(SO_4)(OH)_{0–18}$, the Lewis basicity increases with decreasing values of m at large values of m (>12). Only for N = 1, m ≤ 4 and N = 3, m ≤ 6 are the Lewis basicity values below the cut-off value of 0.30 v.u. Selected minerals of this form are listed in Table 3: zincosite (N = 1, m = 0), linarite and chlorothionite (N = 1, m = 2), antlerite (N = 3, m = 4) and christelite [N = 2, m = 3 for $(SO_4)_1$], plus the synthetic $Mg_3(SO_4)_2(OH)_2$ [N = 1.5, m = 1 per (SO_4) group].

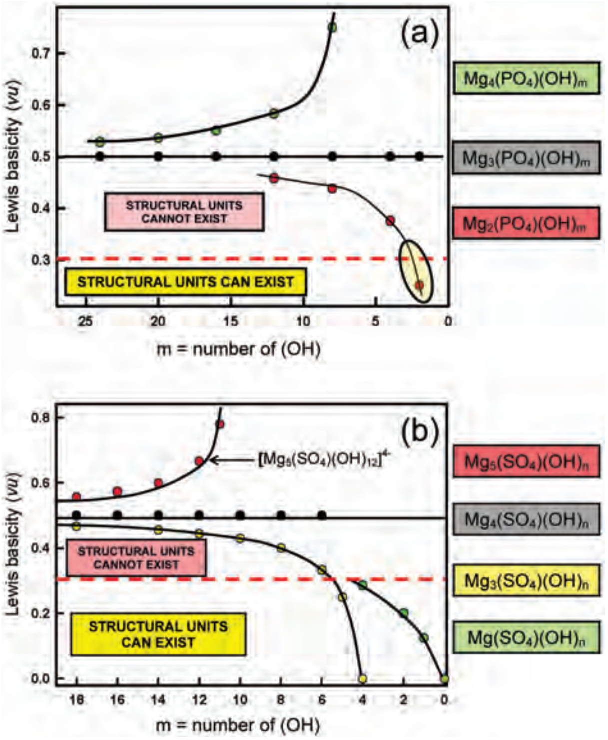

FIGURE 14. (**a**) Lewis basicity of structural units of the form $Mg_N(T^{5+}O_4)(OH)_n$ (T^{5+} = P, As, V) as a function of stoichiometry for N = 2, 3, 4; m = 1–24. (**b**) Lewis basicity of structural units of the form $Mg_N(T^{6+}O_4)(OH)_n$ (T^{6+} = S, Cr) as a function of stoichiometry for N = 1, 3, 4, 5; m = 1–18.

TABLE 3. Selected minerals with structural Units of the form $M^{2+}_N(TO_4)(OH)_m$, T = P,S

Farringtonite	$Mg_3(PO_4)_2$
Sarcopside	$Mn_3(PO_4)_2$
Zavalíaite	$Mn_3(PO_4)_2$
Althausite	$Mg_2(PO_4)(OH)$
Holtedahlite	$Mg_2(PO_4)(OH)$
Wagnerite	$Mn_2(PO_4)F$
Zincosite	$Zn(SO_4)$
Linarite	$Pb[Cu(SO_4)(OH)_2]$
Chlorothionite	$K_2[Cu(SO_4)Cl_2]$
Antlerite	$[Cu_3(SO_4)(OH)_4]$
Christelite	$Zn(H_2O)_4[Zn_2Cu_2(SO_4)_2(OH)_6]$

The distribution of mineral stoichiometries and the existence of rocks

The above calculations and Figure 14 suggest that many stoichiometries cannot exist as structures as there are strong bond-topological controls on their possible compositions and structures. Indeed, Figure 14 suggests that stoichiometries of structural units cannot exceed a value of N ≈ 4 as the resulting Lewis basicity of the structural unit is too high to form a stable structure. Let us examine this point using the stoichiometries of oxysalt minerals. Figure 15 shows a frequency diagram for minerals whose formulas involve octahedrally coordinated (M) and tetrahedrally coordinated (T) cations. The number of minerals is a maximum at an M:T ratio of 1:1, and falls off to close to zero beyond the range 4:1 ≤ M:T ≤ 1:4 except for M:T = ∞:1 and M:T = 1:∞. All the oxysalt minerals occur in the central region;

oxides occur at M:T = ∞:1 and tetrahedron-framework structures (e.g., quartz, feldspars) occur at M:T = 1:∞.

Thus the stoichiometry of minerals is extremely restricted. What "happens" to all those other chemical compositions that cannot occur as single minerals (the yellow regions in Fig. 15)? Let us consider a simple example. The composition $[Mg_5(SO_4)(OH)_{12}]^{4-}$ has a Lewis basicity of 0.67 v.u. (Fig. 14b) and hence cannot form a structural unit. So what will happen to such a composition?

$$Mg_5(SO_4)(OH)_{12} \rightarrow Mg(SO_4)(H_2O)+4Mg(OH)_2+H_2O+O_2$$

kieserite + brucite

It will crystallize as two different minerals, which in this example have Lewis basicities of 0.0 v.u. as there are no available large low-valence cations to form interstitial complexes. In the presence of potential interstitial cations (e.g., Na, K), other minerals of appropriate stoichiometry will form. Thus such stoichiometries as $M^{2+}_{N>2}(PO_4)(OH)_{m>2}$ will crystallize as mixtures of minerals, i.e., as rocks. For silicates, those compositions with M:T < 1:4 will form rocks containing significant amounts of framework silicates (e.g., granite, syenite), those compositions with 4:1 ≤ M:T ≤ 1:4 will form rocks dominated by ferromagnesian silicates (e.g., peridotite), and those compositions with M:T > 4:1 will contain major amounts of oxides and ferromagnesian silicates (e.g., iron formations). This is the principal reason why most chemical compositions do not crystallize as single minerals, but form rocks.

Hydrogen, polymerization of the structural unit, and the distribution of structural complexity of minerals within the Earth

Above, we saw that both (H_2O) and (OH) groups are extremely polar: on the O side, each functions as an anion, whereas on the H side, each functions as a cation. The metal(M)-O bonds are commonly relatively strong [~0.40 v.u. for (H_2O); 0.80 v.u. for (OH)], whereas the H···O (hydrogen) bonds are much weaker [~0.20 v.u. for both (H_2O) and (OH)]. Hence the M-O bonds are commonly part of the structural unit, whereas the hydrogen bonds are not part of the structural unit (Hawthorne 1985). The net result of this asymmetric arrangement of bond valences is commonly to terminate the structural unit at the (H_2O) and (OH) groups.

Consider the structure of newberyite (Sutor 1967), $Mg_3(PO_3OH)(H_2O)_3$ (Fig. 16), in which (OH) and (H_2O) play significant roles in limiting polymerization of polyhedra in the structure. Newberyite contains an acid-phosphate group, (PO_3OH). Each tetrahedron links to three $(Mg\varphi_6)$ octahedra, forming a sheet in the **ac** plane (Fig. 16), and the fourth vertex of the tetrahedron points in the ±**b** direction. In a (PO_4) group, the fourth vertex of the tetrahedron would link to another polyhedron of the structural unit to satisfy the valence-sum rule at that anion. However, in newberyite, H is attached to the O anion at this vertex, and the valence-sum rule prevents linkage to another tetrahedron or octahedron, preventing polymerization of the structural unit in the **b** direction through the phosphate group. Newberyite also contains $\{MgO_3(H_2O)_3\}$ octahedra that are linked by the tetrahedra into a sheet (Fig. 16) by each tetrahedron sharing three vertices with adjacent tetrahedra. This linkage leaves three vertices of the octahedron that can potentially link in the third dimension to form a framework structure. However, each of the O anions occupying these three vertices also link to two H atoms, forming (H_2O) groups; the H atoms satisfy the bond-valence requirements of the anions at these three vertices, and prevent linkage in the **b** direction.

Although the presence of H prevents all intra-unit linkage at the (OH) and (H_2O) groups in newberyite, this is not necessarily the case in all H-bearing minerals: both (OH) and (H_2O) can allow linkage of a structural unit in some directions and prevent such linkage in other directions. The structural unit in artinite, $[Mg_2(CO_3)(OH)_2(H_2O)_3]$ (Akao and Iwai 1977), consists of a

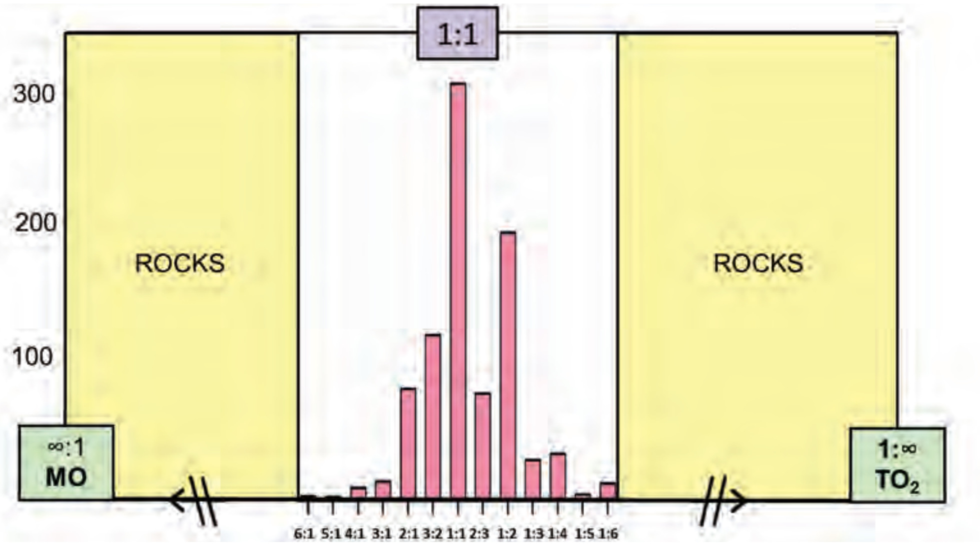

FIGURE 15. The distribution of mineral stoichiometries with regard to the ratio of octahedrally coordinated cations (M) and tetrahedrally and triangularly coordinated cations (T). The bars in pink show the numbers of minerals with M:T ratios approximately equal to 4:1, 3:1…1:3, 1:4. The yellow areas denote compositions not corresponding to single minerals.

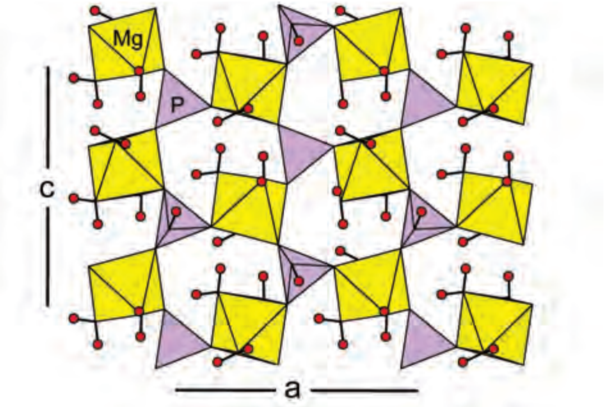

FIGURE 16. The crystal structure of newberyite, $Mg_3(PO_3OH)(H_2O)_3$, projected onto (010); Mg octahedra are shown in yellow, P tetrahedra are shown in lilac, H atoms are shown as red circles, O_{donor}-H bonds are shown as thick black lines.

ribbon of edge-sharing (MgO_6) octahedra, flanked by (CO_3) triangles (Fig. 17). In the center of the ribbon, the anions bond to three Mg cations, receiving 0.36 × 3 = 1.08 v.u. from Mg. The additional bond valence required by these anions is provided by their associated H atoms, which weakly hydrogen-bond (bond valence approximately 0.08 v.u.) to an adjacent ribbon. The (OH) group prevents linkage of the structural unit in the **c**-direction but allows linkage in the **a**- and **b**-directions. The anions along the edge of the ribbon bond to either one Mg, two Mg, or one Mg and one C, with incident bond-valence values of ~0.3, 0.6, and 1.7 v.u. The first two anions must be (H_2O) groups and cannot propagate linkage of the structural unit. The (H_2O) group bonded to one Mg prevents further polymerization of the structural unit in all three directions, whereas the (H_2O) group bonded to two Mg atoms allows polymerization of the structural unit in the **b**-direction but prevents polymerization in the **a**- and **c**-directions. Thus in artinite, the (OH) groups allow polymerization of the structural unit in two directions, the two types of (H_2O) group allow polymerization in one and no directions, respectively, and all linkage between structural units is through hydrogen bonding via the (OH) and (H_2O) groups of the structural unit.

In summary, H as (OH) and (H_2O) can control the dimensional polymerization of a structural unit, limiting it in one or more directions. This is the principal single chemical feature that leads to the amazing structural diversity in oxygen-based minerals. Moreover, the distribution of H throughout the Earth, together with the anharmonic nature of the hydrogen bond, is a major factor in accounting for the systematic distribution of mineral species from the core to the surface of the Earth.

The method of moments

There is little intuitive connection between the essential features of a crystal structure, the relative positions of the atoms and the disposition of the chemical bonds, and the usual methods for deriving the electronic energy density-of-states (Hawthorne 2012). However, the electronic energy density-of-states may be derived from the bond-topological aspects of a structure using the method of moments (Burdett et al. 1984). I will give a brief

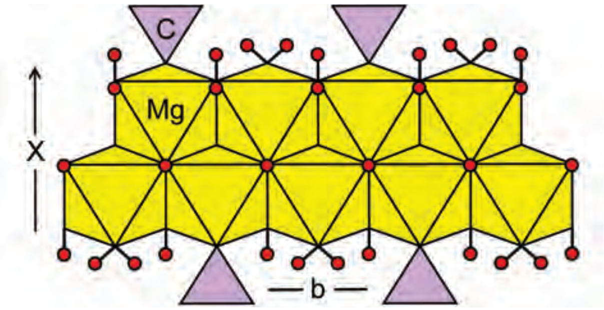

FIGURE 17. The crystal structure of artinite, $[Mg_2(CO_3)(OH)_2(H_2O)_3]$, projected onto (001); Mg octahedra are shown in yellow, C triangles are shown in lilac, H atoms are shown as red circles, O_{donor}-H bonds are shown as thick black lines.

outline of the method; the reader should consult their paper for mathematical details.

A simple way to consider the electronic structure of a molecule is to construct the molecular-orbital wavefunction as a linear combination of atomic orbitals. These wavefunctions are eigenstates of an effective one-electron Hamiltonian, H^{eff} that may be written as $H^{\text{eff}}\psi = E\psi$ where E is the energy associated with ψ. The total electron energy of the state described by the wavefunction is

$$E = (\int\psi\cdot H^{\text{eff}}\psi d\tau)/(\int\psi\cdot\psi d\tau) = (<\psi\cdot H^{\text{eff}}\psi d\tau>)/(<\psi\cdot\psi>) \qquad (1)$$

where the integration is over all space, H^{eff} is an effective one-electron Hamiltonian that may be written as $H^{\text{eff}}\psi = E\psi$ where E is the energy associated with ψ, and the molecular-orbital wavefunction is written as $\psi = \Sigma_i c_i\varphi_i$ where $\{\varphi_i\}$ are the valence orbitals of the atoms and c_i is the contribution of a specific atomic orbital to a specific molecular orbital (e.g., Gibbs 1980). Substitution for ψ $(= \Sigma c_i\varphi_i)$ gives

$$E = [\Sigma_i\Sigma_j c_i c_j(<\varphi_i|H^{eff}|\varphi_j>)]/(\Sigma_i\Sigma_j c_i c_j<\varphi_i|\varphi_j>) \qquad (2)$$

Equation 2 may be simplified thus: (1) $<\varphi_i|\varphi_j>$ is the overlap integral between atomic orbitals on different atoms, and is written as S_{ij}, which is always ≤1; where $i = j$, $<\varphi_i|\varphi_j> = 1$ for a normalized (atomic) basis set of orbitals; (2) $<\varphi_i|H^{eff}|\varphi_j> = H_{ii}$; this represents the energy of an electron in orbital φ_i and can be approximated by the orbital ionization potential; and (3) $<\varphi_i|H^{eff}|\varphi_j> = H_{ij}$; this is the resonance integral. Minimizing the energy with respect to the coefficients c_i, Equation 2 gives the molecular-orbital energies. The eigenvalues of the following secular determinant equation give the molecular-orbital energy levels:

$$|H_{ij}–S_{ij}E| = O \qquad (3)$$

The Hückel approximation (Trinajstic 1983) best shows the topological content of this approach: For the pπ orbitals, all H_{ii} values are set equal to α, all H_{ij} are set equal to β, and all S_{jj} $(i \neq j)$ are set equal to zero. The expanded secular determinant equation for the square molecule of Figure 1b is as follows:

$$\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix} = 0 \qquad (4)$$

Compare the structure of Figure 1b with the matrix entries in Equation 4. Where atoms are bonded together (i.e., atoms 1 and 2 in Fig. 1b), there is a nonzero value at the corresponding (1,2) entry in the secular determinant; where atoms are not bonded together (i.e., atoms 1 and 3 in Fig. 1b), the corresponding entry in the secular determinant (1,3) is zero. Note also the correspondence of the zero off-diagonal matrix entries in the adjacency matrix of the graph of this molecule (Fig. 2) with the zero off-diagonal matrix entries in Equation 4.

We cannot use this sort of calculation to deal with a crystal containing approximately Avogadro's number of atoms. Instead, we use Bloch orbitals (Ziman 1965), which assume a unit cell and constrain the orbital content of the unit cell to the translational periodicity of the crystal. Using the special-points method, the secular determinant is solved at a representative set of points within the Brillouin zone, giving a representative sampling of the orbital energy levels that may be smoothed to give the electronic-energy density-of-states. The total orbital energy is obtained by integrating the electronic energy density-of-states up to the Fermi level.

To solve Equation 4, we diagonalize the Hamiltonian matrix. The trace of this matrix may be written as follows:

$$Tr\left(H^{n}\right)=\sum_{i}\sum_{j,k\ldots n}H_{ij}H_{jk\ldots}H_{\mathrm{ni}} \tag{5}$$

A topological interpretation of one term in this sum is shown in Figure 18. H_{ij} is the interaction integral between orbitals i and j; we may simplify the situation without loss of topological content by adopting the Huckel approximation: $H_{ij} = \beta$ where the atoms are bonded, $H_{ij} = 0$ where the atoms are not bonded, and $\alpha = 0$ where $i = j$. In Equation 5, as each single term $\{H_{ij}\,H_{ik}\,\ldots\,H_{ni}\}$ is a product, the term is nonzero only if all individual H_{ij} values in the term, e.g., $\{H_{12}H_{23}H_{34}H_{41}\}$, are nonzero. The last H_{ij} in each product is H_{ni}, the interaction between the nth orbital and the first orbital, and hence the product $\{H_{ij}\,H_{jk}\,\ldots\,H_{ni}\}$ represents a closed path in the graph of the orbitals (molecule). If one (or more) of the terms in the product is zero (e.g., H_{31} in Fig. 18) that product is zero, i.e., $\{H_{12}H_{23}H_{31}\} = 0$, and does not contribute to the trace of the Hamiltonian matrix. Hence the double-summation in Equation 5 contains all closed paths through the graph of (the orbital structure of) the array of atoms.

The trace of a matrix remains invariant under diagonalization, and thus

$$Tr(H^n) = Tr(E^n) = \mu_n \tag{6}$$

where E is the diagonal matrix of eigenvalues (energy levels) and μ_n is the nth moment of E (Burdett et al. 1984), denoted by

$$\mu_n=\sum_i E_i^n\,. \tag{7}$$

The density-of-states may be obtained by inverting the collection of moments $\{\mu_n\}$ (Burdett et al. 1984). The result is that we can evaluate $Tr(H^n)$ directly from the bond topology, and, in so doing, derive the electronic energy density-of-states.

This method generalizes to infinite systems (i.e., crystals) in a straightforward manner. We may define the nth moment of E as

$$\mu_n = \int E^n \rho(E)dE \tag{8}$$

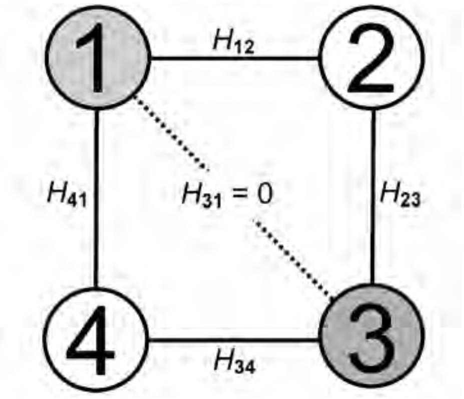

FIGURE 18. Interpretation of paths through the molecule shown in Figure 1b; the path 1 → 2 → 3 → 4 contains only non-zero H_{ij} terms and contributes to the trace of the matrix, whereas the path 1 → 2 → 4 contains a zero H_{ij} term (H_{31}) and does not contribute to the trace of the matrix.

where $\rho(E)$ is the density-of-states of the crystal. In this case, the moments may be evaluated in principle as above and inverted to give the electronic energy density-of-states.

Burdett (1986) introduced an extremely important idea: The energy difference between two structures may be expressed in terms of the first few disparate moments of their electronic-energy density-of-states. This means that the most important energetic differences between two structures involve the most local bond-topological differences between those structures. Also, in structures with bonds of different strength, each edge is weighted according to the strength of the analogous bond. Thus, closed paths of strongly bonded atoms will contribute more to the electronic energy density-of-states than closed paths of weakly bonded atoms.

Low-order moments and crystal chemistry

The number of edges in a path through the bonded atoms in a structure is the *moment* of that path, and each path corresponds to a crystal-chemical feature of the structure. We will now consider the structural features corresponding to the lower-order moments that are the most energetically important. A zero-moment path has no steps and corresponds to remaining still (called a "walk in place"); as such, it specifies the identity of the atom at that vertex of the graph of the structure. Thus the complete set of zero-moment paths defines the chemical composition of the structure. A second-moment path is a walk from one vertex to an adjacent vertex and back again, and the set of second-moment paths from a single vertex defines the coordination number of the atom corresponding to that vertex. A fourth-moment path is a walk from an atom (e.g., a cation) to an anion to another cation to another anion and back to the first cation, and specifies the linkage of two coordination polyhedra. Higher-moment paths describe more complicated linkages of polyhedra, but these are less important from an energetic perspective than the low-moment linkages. Here is our energetic rationale for traditional crystal chemistry: we focus on chemical composition (zero moment), coordination number (second moment), and local linkage between coordination polyhedra (fourth moment) as the most important differences between structures, as differences in low-order moments are the most energetically important differences between structures.

Mineral reactions

The moments approach tells us that the important energetic differences between two structures are the most local topological differences between the structures. What does this mean in terms of mineral reactions?

Zero-moment changes. Zero-moment changes involve changes in the chemical composition of the system, i.e., a reaction in which the constituents are not conserved. This can be a metasomatic reaction and involve open-system behavior.

Second-moment changes. Second-moment changes involve changes in coordination number in the constituent phases. A change in coordination number usually involves a discontinuous reaction. Consider

$$\begin{array}{ccccc} \text{forsterite} & = & \text{periclase} & + & \text{quartz} \\ {}^{[6]}Mg_2{}^{[4]}Si^{[4]}O_4 & = & 2^{[6]}Mg^{[6]}O & + & {}^{[4]}Si^{[2]}O_2 \end{array}$$

in which I include the coordination numbers of all the constituent atoms. Whereas the coordination numbers of $^{[6]}Mg$ and $^{[4]}Si$ are conserved in the reaction, the coordination numbers of O are not conserved. The lowest-moment changes in this reaction involve the changes in coordination number of O, and these changes are the major driver of this reaction, as these are the lowest-moment differences involved in the reaction. We may also express the driving force of this reaction in terms of the enthalpy of reaction, ΔH, suggesting a correlation between the changes in coordination number and the enthalpy of reaction. Consider the general reaction

$$^{[6]}Mg_m{}^{[4]}Si_nO_{(m+2n)} = mMgO + nSiO_2$$

for m,n = 2,1; 3,2; 1,1; 1,2; 2,5; 1,3. ΔH of reaction may be calculated with the model of Aja et al. (1992), using fictive enthalpies of formation. However, (change in) coordination number is an intensive variable whereas enthalpy of formation is an extensive variable. We must transform the enthalpy of formation into an intensive variable, and I do this by dividing the enthalpy of formation by the molecular weight of the reactant to produce the intensive variable ΔH/MW, which I will call the reduced enthalpy of formation. There is a strong correlation between the reduced enthalpy of formation and the change in anion-coordination number (details of this calculation will be given in a later paper) through the reaction (Fig. 19) in accord with the influence of coordination number on the energetics of structures indicated by the moment arguments given above. A similar relation for the hydrated magnesium sulfates $Mg(SO_4)(H_2O)_n$ (where n = 0–7, 11) was shown by Hawthorne and Sokolova (2012).

These second-moment changes throw considerable light on why the additive-fictive approach to predicting enthalpies of formation from oxides works so well. The relation $^{[6]}Mg_m{}^{[4]}Si_nO_{(m+2n)} = mMgO + nSiO_2$ has no experimentally determined quantities; the coordination numbers are assumed (and hence have no experimental uncertainty attached to them) and the relation is exact. Consider the relation $\Delta H(^{[6]}Mg_m{}^{[4]}Si_nO_{(m+2n)}) = m\Delta H(MgO) + n\Delta H(SiO_2)$ where $\Delta H(MgO)$ and $\Delta H(SiO_2)$ are the fictive enthalpies for MgO and SiO_2, respectively. This relation is also exact; $\Delta H(^{[6]}Mg_m{}^{[4]}Si_nO_{(m+2n)})$ is calculated from $\Delta H(MgO)$ and $n\Delta H(SiO_2)$. Hence $\Delta H(^{[6]}Mg_m{}^{[4]}Si_nO_{(m+2n)})$ must correlate with change in anion-coordination number; this is an algebraic requirement. However, there is no algebraic requirement that change in anion-coordination number must correlate with experimental enthalpies of formation from the oxides. We know that the enthalpies calculated from the fictive enthalpies of the oxides correlate with their experimental analogs; this is the whole point of using fictive enthalpies. Therefore we may conclude that changes in anion-coordination number correlate with experimental enthalpies of formation from the oxides, in accord with our prediction from the moments approach to the electronic-energy density-of-states. In this regard, I should also emphasize that using enthalpies of formation calculated from fictive enthalpies does not replace the measurement of enthalpies of formation. One expects subtle differences in energetics with higher-moment changes in bond topology, and this will not be reflected in enthalpies of formation calculated using the fictive approach; they will only be apparent in measured enthalpies of formation.

Fourth-moment changes. Fourth-moment changes involve maintaining chemical composition and both cation- and anion-coordination numbers while changing the identities of next-nearest-neighbor atoms. Such changes hence involve the nature of local (short-range) clusters of ions. Such changes are common in amphiboles (e.g., Hawthorne et al. 1996b, 1996c, 1997, 2000b; Della Ventura et al. 1999; Hawthorne and Della Ventura 2007), and the short-range version of the valence-sum rule (Hawthorne 1997, see above) suggests that such short-range order should be common in all solid solutions involving polyvalent substitutions.

Major chemical variations in amphiboles in metabasic rocks involve the change from tremolite, $\square Ca_2Mg_5Si_8O_{22}(OH)_2$, to sadanagaite, $NaCa_2(Mg_3Al_2)(Si_5Al_3)O_{22}(OH)_2$, with increasing grade of metamorphism. In this reaction, the bond topology of the amphibole is conserved, and any energetic differences with regard to the amphiboles involve atom identities and their relative locations, i.e., short-range order-disorder. End-member tremolite is completely ordered whereas end-member sadanagaite must show extensive short-range order/disorder. Such short-range order/disorder must have a major effect on the energetics of the resulting minerals and their reactions with other phases.

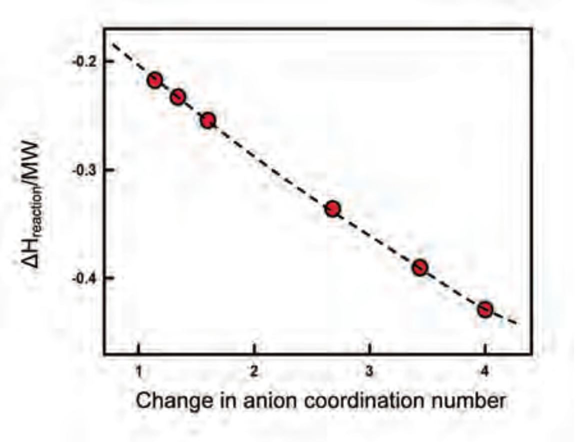

FIGURE 19. Variation in reduced enthalpy of formation (from the oxides) vs. change in anion-coordination number through the reaction $^{[6]}Mg_m{}^{[4]}Si_nO_{(m+2n)} = m^{[6]}MgO + n^{[4]}SiO_2$. Units on the ordinate are kJ/mol/Dalton.

SUMMARY

The theoretical approach outlined above examines the structure and chemical composition of minerals based on their bond topology, aspects of graph theory and bond-valence theory, and the moments approach to the electronic-energy density of states. Below, I identify the principal features of this approach, and some of its uses:

(1) An arrangement of atoms and chemical bonds may be represented by a weighted polychromatic digraph, and the handshaking principle may be used to examine many aspects of atom coordination and the linkage of coordination polyhedra.

(2) The moments approach to the electronic-energy density-of-states provides a bond-topological interpretation of the energetics of a structure.

(3) When comparing structures, the most important structural differences involve the first few disparate moments of the electronic-energy density-of-states.

(4) 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: (a) coordination number for discontinuous reactions, and (b) short-range order for continuous reactions.

(5) It may be shown that the quantitative aspects of bond-valence theory arise from the topological (or graphical) characteristics of structures as arrangements of atoms and chemical bonds.

(6) The principle of correspondence of Lewis acidity-basicity states that stable structures will form when the Lewis-acid strength of the interstitial complex closely matches the Lewis-base strength of the structural unit, and allows us to examine the factors that control the chemical composition and aspects of the structural arrangement of minerals.

(7) (H_2O) 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 factor affecting structural diversity in oxygen-based minerals and the systematic distribution and relative complexity of mineral species from the core to the surface of the Earth.

(8) Interstitial (H_2O) groups may (a) satisfy the bond-valence requirements around an interstitial cation where there are insufficient adjacent anions to do so from neighboring structural units, or (b) moderate the Lewis acidity of the interstitial complex and affect the stability of a chemical composition through the operation of the principle of correspondence of Lewis acidity-basicity.

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APPENDIX

Consider the structural unit $[Mg_N(PO_4)(OH)_m]$

The charge on the structural unit is 2N – 3 – m.

The number of bonds involving the structural unit is 6N (for $^{[6]}Mg_N$) + 4 [for the (PO_4) group] + 2m (for H, assuming a coordination number of [2]) = 6N + 4 + 2m.

If we assume an ideal coordination number of [4] for oxygen, the number of bonds needed to produce such a coordination = 4(4 + m).

The number of bonds needed from the interstitial complex is the difference of these two values: 4(4 + m) – (6N + 4 + 2m) = 12 + 2m – 6N.

The Lewis basicity of the structural unit is the charge divided by the number of bonds needed from the interstitial complex: (2N – 3 – m)/(12 + 2m – 6N).

For N = 2, this expression reduces to (1 – m)/2m, and for m = 1, 2, 4, 8, the Lewis basicities = 0.00, 0.25, 0.38, 0.44 v.u., respectively.

For N = 3, this expression reduces to (3 – m)/(2m – 6) = 0.50 v.u. independent of the value of m.

For N = 4, this expression reduces to (5 – m)/(2m – 12), and for m = 8, 12, 16, 20, the Lewis basicities = 0.75, 0.58, 0.55, 0.53 v.u., respectively.

The calculations for the structural unit $[Mg_N(SO_4)(OH)_m]$ are similar, except that we assume an ideal coordination number of [3] for oxygen because of the higher bond valence of the S-O bond.