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REVISION 1

Toward theoretical mineralogy: a bond-topological approach

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ABSTRACT

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

37 The moments approach to the electronic-energy density-of-states provides a bond-
38 topological interpretation of the energetics of a structure. When comparing structures, the most
39 important structural differences involve the first few disparate moments of the electronic-energy
40 density-of-states. We may classify chemical reactions according to the lowest-order moment of
41 the electronic-energy density-of-states that is conserved, which allows us to identify the principal
42 structural changes that drive chemical change: (a) coordination number for discontinuous

43 reactions; (b) short-range order for continuous reactions. This relation between the bond
44 topology of a structure and its enthalpy of formation from constituent oxides is indicated by a
45 correlation between change in anion-coordination number and reduced enthalpy of formation for
46 the reactions $^{[6]}Mg_m^{[4]}Si_nO_{(m+2n)} = mMgO + nSiO_2$.

47

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

50

INTRODUCTION

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

64

65 **Established theoretical methods**

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

74 compositions, mineral stability and chemical reactions. We have gained significant
75 understanding of minerals, mineral stability and mineral reactions through crystal chemistry,
76 thermodynamics and computational mineralogy. However, these methods have tended to dictate
77 the questions that we ask about minerals—we ask questions to which these methods can give us
78 answers. There are many other questions of scientific interest which resist our current theoretical
79 approaches. Such questions tend to be ignored as they are seen as intractable, or even irrelevant
80 to current issues in Petrology, Geochemistry, Geophysics, etc. Let us consider some of these
81 questions: (1) Why do minerals have the chemical formulae that they do? (2) Why do they have
82 their specific structural arrangements? (3) Why are minerals stable over specific ranges of pH,
83 Eh, temperature, pressure and activities of their various constituents? (4) What are the relations
84 between crystal structure and both enthalpy and Gibbs free energy of formation? Many of these
85 questions are fundamental to our understanding of minerals and their behavior, and yet have
86 tended to be ignored in the past because they are not susceptible to established theoretical
87 techniques in Physics and Chemistry.

88 We conventionally represent a crystal structure as a space group plus a set of unit-cell
89 dimensions plus a list of atom coordinates (and displacement parameters), and we use these
90 parameters together with techniques in computational mineralogy to calculate various properties
91 of the crystal. This general approach is extremely successful in understanding the physical
92 properties of materials, and it is successful for a reason. The underlying theories deal with
93 electron sharing between atoms fairly rigorously, and many physical properties of crystals are
94 dependent on the details of electron sharing between atoms. However, what the underlying
95 theory does not do is explain the origin of translational (and quasi-crystal) symmetry in crystals.
96 Moreover, crystal-structure arrangements can be surprisingly insensitive to major variations in
97 electron delocalization and corresponding variations in physical properties. For example, the

98 NaCl structure is adopted both by the insulator LiF, with a band gap of 13.6 eV, and the
99 semiconductor PbS, with a band gap of 0.37 eV. Here, structure type is rather insensitive to bond
100 type (although other semiconductors with small band gaps do adopt the sphalerite and wurtzite
101 arrangements).

102 What is also interesting is that our perceptions of crystal structure are very insensitive to
103 the structural parameters used for such calculations. We cannot generally appreciate the salient
104 features of a crystal structure from its space group, unit-cell dimensions and atom coordinates;
105 we need a picture of that structure to recognize these features. This has been obvious since the
106 dawn of crystal-structure determination, and crystal structures have been classified and
107 interpreted according to the details of their atom connectivity as expressed visually (e.g., Barlow
108 1883, 1898; Bragg 1930; Belov 1961; Moore 1970, 1974; Burns 1999, 2005; Krivovichev 2004,
109 2008, 2009; Krivovichev et al. 1998; Hawthorne 1985, 1986, 1990, 2014; Grice et al. 1999;
110 Hawthorne and Huminicki 2002; Huminicki and Hawthorne 2002). This suggests (at least to me)
111 that if we wish to understand why crystal structures have the atom arrangements that they do, we
112 should not seek this understanding *via* calculations that involve the sharing of electrons between
113 atoms/ions; we need to understand the commonalities and differences in atom connectivity in
114 crystal structures (cf. Bowen 1928).

115

116 **Mineral chemistry and structure**

117 Consider the hydrated magnesium-sulfate compounds, $\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})_n$ where $n = 0-7$,
118 11: synthetic $\text{Mg}(\text{SO}_4)$, kieserite, sanderite, synthetic $\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})_3$, starkeyite,
119 $\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})_4$, cranswickite, $\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})_4$, pentahydrate, hexahydrate, epsomite and
120 meridianiite, $\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})_{11}$. The $\text{Mg}(\text{SO}_4)$ part of the chemical formulae is fixed by the
121 electroneutrality principle, but other factors control the degree of hydration of each mineral.

122 With increasing (H₂O) content, there is a gradual depolymerization of the (MgΦ₆) and (SO₄)
123 polyhedra (Φ = O, H₂O) as the valence-sum rule (Brown 2002a) prevents linkage of these
124 polyhedra through (H₂O) ligands (Hawthorne 1992; Hawthorne and Sokolova 2012). We know
125 that (H₂O) tends to depolymerize the structures of minerals (and synthetic inorganic solids).
126 However, we have little idea of (1) how such depolymerization is quantitatively related to
127 increasing (H₂O) content, and (2) what is the effect of interstitial cations on the bond topologies
128 of the resulting structures.

129 Consider structurally and chemically complicated minerals such as botryogen,
130 Mg₂(H₂O)₁₂[Fe³⁺₂(SO₄)₄(OH)₂](H₂O)₂, or metavoltine, K₂Na₆Fe²⁺(H₂O)₆[Fe³⁺₃O(SO)₄]₆(H₂O)₃]₂
131 (H₂O)₆. Their chemical formulae are constrained by the requirement of electroneutrality, but
132 what dictates the other details of their chemical formulae? Why does botryogen have Mg₂ as its
133 interstitial cation, and not Ca₂ or Na₄? Why does botryogen have 14 (H₂O) groups in its formula?
134 Why doesn't it have (for example) 8 (H₂O) groups? Why does botryogen contain any (H₂O)
135 groups at all and what are the roles of these (H₂O) groups in the structure? How do these aspects
136 of chemistry and structure relate to the stability of botryogen as a function of Eh and pH?

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

146

147

GRAPH THEORY

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

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

168

169

170 **The handshaking lemma**

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

173 Each edge in a graph contributes two degrees to the sum of the degrees of all the vertices of a
174 graph, and hence this sum must be even. This relation is known as the *handshaking lemma*
175 (Wilson 1979) for obvious reasons: each edge involves two vertices, just as a handshake involves
176 two hands, and hence the sum of the degrees of all vertices in a graph is even, as is the number of
177 hands shaken, independent of the number of vertices in the graph or the number of people
178 shaking hands. The handshaking lemma is extremely powerful in dealing with problems
179 involving coordination number and connectivity in structures, particularly where the vertex set is
180 partitioned into two subsets, as is the case where there are significant differences in
181 electronegativity of the constituent atoms in a structure, and atoms of the same set do not bond to
182 one another. For example, in AB compounds, the coordination numbers of A and B must be
183 equal (e.g., [6] in NaCl and [8] in CsCl), whereas in AB₂ compounds, the coordination number
184 of A must be twice that of B (e.g., [6] and [3] in TiO₂ and [8] and [4] in CaF₂).

185

186 **Graphs with multiple edges**

187 The definition of a graph given above is that of a *simple graph*; that is, a graph where
188 there cannot be more than one edge connecting two vertices. We may define a *general graph* (or
189 more simply, a graph) as a nonempty set of elements, V(G), called vertices, and a nonempty
190 *family* of unordered pairs of these vertices, E(G), called edges. A family is a collection of
191 elements, some of which may occur several times in that collection. The existence of family
192 (rather than a set) in the definition of a general graph allows multiple edges between a pair of

193 vertices, and this gives us much greater flexibility in applying graph theory to crystal structures
194 than would otherwise be the case.

195

196 **Graphical representation of linkage between polyhedra**

197 Above, we were using simple graphs to represent the linkage of individual atoms by
198 chemical bonds. However, complicated crystal structures are widely considered as (and
199 represented by) arrangements of linked coordination polyhedra. We may assign different
200 coordination polyhedra to different vertices of a (general) graph, and the capability of having
201 multiple edges allows us to efficiently denote the details of linkage between different
202 coordination polyhedra (Hawthorne 1983). Polyhedra may be represented by coloured vertices of
203 a labelled graph in which different colors represent different coordination and labels denote
204 chemically and crystallographically distinct polyhedra. Linkage is indicated by an edge or edges
205 between vertices, and the number of edges between two vertices denotes the number of atoms
206 common to both polyhedra (Fig. 3, M = octahedrally coordinated cation; T = tetrahedrally
207 coordinated cation; ϕ = unspecified ligand); round brackets and curly brackets denote a
208 polyhedron or a group, e.g., (SO₄), (H₂O); square brackets denote linked polyhedra, e.g.,
209 [M(TO₄)₂φ₄]. For two vertices, no edge denotes disconnected polyhedra (Fig. 3a), one edge
210 denotes corner-sharing between two polyhedra (Fig. 3b), and two edges denote edge-sharing
211 between two polyhedra (Fig. 3c). Figure 3d shows the cluster [M₂(Tφ₄)₂φ₈] and its graphical
212 representation. In a graphical representation, geometrical information is lost. This is illustrated in
213 Figure 3e which shows two different possible arrangements of the corner-linked cluster
214 [M(Tφ₄)₂φ₄]. Both these clusters are described by the same graph; such clusters are called
215 *geometrical isomers* (Hawthorne 1983). It is very useful to represent the FBB (Fundamental
216 Building Block) of a mineral in this graphical fashion as the hierarchical aspects of the

217 classification are immediately grasped from the arrangement of the constituent graphs. This type
218 of graphical representation is used quite commonly to consider the bond topology of complex
219 structures (e.g., Hawthorne 1983, 1994; Hawthorne et al. 2000a; Krivovichev 2008, 2009; Burns
220 1995, 1999, 2005; Burns et al. 1995).

221

222

BOND-VALENCE THEORY

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

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

236 In the late 1960s, it became apparent from the large amount of crystal-structure data
237 (made available by the development of automated X-ray diffractometers) that there are relations
238 between the lengths of chemical bonds (for specific pairs of atoms) and the strengths of those
239 bonds, and many schemes were put forward to relate these variables in a quantitative manner.
240 Pauling (1929) introduced the term *bond strength* to represent the strength of a bond between a

241 cation and an anion as measured by the cation valence divided by the cation coordination
242 number. It became apparent in the 1970s that a new term was needed for the strength of a bond,
243 where this strength is a function of bond length, in order to distinguish it from the Pauling bond-
244 strength, and the term *bond valence* was introduced. Bond valence is defined as the strength of a
245 chemical bond where, for any pair of bonded atoms, that strength is inversely proportional to the
246 distance between those atoms. Brown and Shannon (1973) introduced their widely used bond-
247 valence parameters; these have been (and are continually being) refined (e.g., Brown 2002a,
248 2009, 2013) and are now almost universally used to check the validity of refined crystal
249 structures.

250

251 **The bond-valence model: background**

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

260 There has been extensive work relating the form and numerical parameters of bond-
261 valence curves to different models of chemical bonding (e.g., Burdett and Hawthorne 1993;
262 Preiser et al. 1999; Gibbs et al. 2014), and it has become apparent that this approach is quite
263 general in that it applies equally well to structures with predominantly ionic bonds and with
264 predominantly covalent bonds. Brown (1981, 2002a, 2002b, 2009, 2013) has systematically

265 developed this approach into a comprehensive model, the *Bond-Valence Model*, that addresses
266 many aspects of chemical bonding in inorganic crystals. The bond-valence model actually
267 consists of two distinct parts, *Bond-Valence Theory* and empirical *bond-valence curves* (Fig. 4).
268 Most scientists have tended to ignore bond-valence theory and focus solely on using empirical
269 bond-valence curves for (1) validating the stereochemical details resulting from crystal-structure
270 refinement, and (2) various crystal-chemical purposes. It does not seem to be generally realized
271 that bond-valence theory is formally independent of the analytical bond-valence curves used
272 extensively in crystallography and crystal chemistry.

273

274 **Bond-valence theory**

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

277

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

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

288

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

291

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

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

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

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

308 The above definition of Lewis basicity is often not very useful, as variations in bond-
309 valence around anions are much greater than variations in bond-valence around cations, and any
310 characteristic bond-valence that is assigned has too large a dispersion to be useful. For example,
311 in dravite (Hawthorne et al. 1993), Na is [9]-coordinated and the O atoms to which it is bonded
312 receive on average 0.11 v.u. from each Na-O bond. In CrO₃ (Stephens and Cruickshank 1970),

313 which consists of pyroxene-like chains of $^{[4]}\text{CrO}_3$, one O is bonded only to Cr^{6+} and receives 2.00
314 v.u. from the Cr-O bond. With this amount of variation in bond valence, 0.11–2.00 v.u., it is not
315 useful to define a Lewis-base strength for O^{2-} . Consider a complex oxyanion such as $(\text{SO}_4)^{2-}$
316 (Fig. 7): The central S^{6+} cation provides 1.5 v.u. to each coordinating O atom and these need an
317 additional 0.5 v.u. from other neighbouring cations. If the coordination number of O^{2-} is [n], then
318 the average valence of the bonds to O^{2-} (exclusive of the S-O bond) is $0.5 / (n - 1)$ v.u.; where n
319 = 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
320 average bond-valence received by the $(\text{SO}_4)^{2-}$ group is the same as the average bond-valence
321 received by each individual O^{2-} anion, and allows us to define a Lewis basicity for the oxyanion
322 group. For the $(\text{SO}_4)^{2-}$ oxyanion, the possible average bond-valences are quite tightly constrained
323 (0.50–0.11 v.u.) and we may calculate a useful Lewis basicity. Tables 1 and 2 list Lewis acidities
324 and Lewis basicities for geochemically common cations and oxyanions.

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

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

334 Consider the composition Na_4SiO_4 . The Lewis basicity of the (SiO_4) group is 0.33 v.u.
335 (Table 2) and the Lewis acidity of Na is 0.17 v.u. The Lewis basicity of the anion does not match

336 the Lewis acidity of the cation, the valence-matching principle is not satisfied, and Na_4SiO_4 is
337 not a mineral (or stable structure).

338 Consider the composition $\text{Na}[\text{AlSiO}_4]$. The Lewis basicity of the $[\text{AlSiO}_4]$ group is 0.13
339 v.u. and the Lewis acidity of Na is 0.17 v.u. The Lewis basicity of the anion matches
340 (approximately) the Lewis acidity of the cation, the valence-matching principle is satisfied, and
341 nepheline, Na AlSiO_4 is a stable structure. Moreover, nepheline shows incommensurate
342 behaviour (e.g., Angel et al. 2008), perhaps reflecting the slight mismatch between the Lewis
343 basicity and acidity of its constituents.

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

349

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

356

357 **Bond-valence curves**

358 For any pair of bonded atoms, bond valence is inversely proportional to the length of the
359 bond: large bond-valences are associated with short bonds, and small bond-valences are

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

369 Brown and Shannon (1973) discussed the differences between the bond-valence model
370 and the ionic model. In the bond-valence model, a structure consists of atom cores held together
371 by valence electrons associated with the chemical bonds between the atoms, and they explicitly
372 state that the valence electrons may be associated with chemical bonds in a symmetric (covalent)
373 or asymmetric (ionic) manner. Thus *a priori* knowledge of the electron distribution is not
374 required to use this approach. Burdett and Hawthorne (1993) showed that the form of the bond-
375 valence curves may be derived algebraically from a molecular-orbital description of a solid in
376 which there is a significant energy gap between the interacting orbitals on adjacent atoms,
377 whereas Preiser et al. (1999) gave an ionic justification of the bond-valence model. One may
378 conclude that the bond-valence model is not a theory of “ionic” bonds or “covalent” bonds. It is a
379 simple yet quantitative method that allows us to examine and analyze the stereochemistry and
380 physical properties of both simple and complex solids; it is used primarily for crystals, but also
381 can be used for surfaces (Schindler et al. 2004a, 2004b; Bickmore et al. 2004, 2006), glasses and
382 liquids. Although the idea of bond valence grew out of Pauling’s second rule, the wide variety of
383 its application and subsequent examination of its theoretical underpinnings show that it is a

384 theory of atomic arrangements in its own right, without any reference to specific models of the
385 chemical bond. Its power lies in the fact that it is a back-of-the-envelope method in which the
386 physical details are not obscured by complexities of computation. Each year sees new
387 applications to an increasing array of problems as the bond-valence model takes a central role in
388 our understanding of complex materials.

389

390 **BOND-TOPOLOGICAL CONTROLS ON THE STRUCTURE AND**
391 **CHEMICAL COMPOSITION OF OXYSALT MINERALS**

392 The valence-matching principle is a powerful method of assessing the stability (i.e.,
393 existence or otherwise) of potential chemical compounds, and we saw above how we can *a priori*
394 predict the existence of Na₂SO₄ (thenardite), the non-existence of Na₄SiO₄, and the existence of
395 NaAlSiO₄ (nepheline). For such simple structures, this approach is straightforward. However, for
396 more complicated minerals, e.g., botryogen, Mg₂(H₂O)₁₀[Fe³⁺₂(SO₄)₄(OH)₂](H₂O)₂ and
397 metavoltine, K₂Na₆Fe²⁺(H₂O)₆[Fe³⁺₃O(SO₄)₆(H₂O)₃]₂(H₂O)₆, the approach is less transparent.
398 Yet these complex minerals raise some very fundamental questions pertaining to the details of
399 their chemical composition. Again, (1) why does botryogen have Mg rather than Ca or Ba as its
400 divalent interstitial cation; (2) why does it have divalent interstitial cations, Mg₂, rather than
401 monovalent interstitial cations, Na₄ or K₄; (3) why does it have 14 (H₂O) groups in its formula;
402 why doesn't it have (for example) 12 (H₂O) groups; (4) why does it have any (H₂O) groups at all
403 in its formula; what is the role of these (H₂O) groups in the structure? How do the chemical
404 formula and structural arrangement of botryogen relate to its stability as a function of Eh and
405 pH? We cannot say that we understand minerals until we understand what controls their
406 chemical compositions at this level of detail.

407 In order to address this issue for complex structures, Hawthorne (1983, 1985) divided a
408 structure into two components: the *structural unit*, the strongly bonded part of the structure,
409 consisting of oxyanions and low-coordination-number cations; and the *interstitial complex*, the
410 weakly bonded part of a structure, usually consisting of monovalent cations, large divalent
411 cations and (H₂O) groups. To do this, we must define what we mean by “strongly bonded” and
412 “weakly bonded”. Many minerals contain octahedrally coordinated divalent cations, and many of
413 these minerals, e.g., forsterite, enstatite, are stable at high temperature. Many minerals contain
414 monovalent and divalent cations in higher coordination numbers, e.g., thenardite, gypsum, and
415 many minerals are held together by hydrogen bonds; these minerals commonly crystallize from
416 aqueous solution at ambient (or close to ambient) conditions. An appropriate boundary between
417 “strongly bonded” and “weakly bonded” will be between 0.33 v.u. (for ⁶Mg) and 0.20 v.u. (for
418 common hydrogen bonds, Ba, Pb²⁺) or 0.23 v.u. (for Sr), and I will take it as 0.30 v.u., although
419 the exact value will change depending on other bond-valences in a structure.

420 If we can define Lewis acidities and Lewis basicities for the structural unit and the
421 interstitial complex, we may examine their interaction using a mean-field version of the valence-
422 matching principle. This *binary representation* of a complex structure is illustrated in Figure 8
423 for botryogen, {Mg₂(H₂O)₁₀} [Fe³⁺₂(SO)₄(OH)₂](H₂O)₂. We have partitioned the structure into a
424 structural unit: [Fe³⁺₂(SO)₄(H₂O)₂], a cluster of Fe³⁺ octahedra and sulfate tetrahedra (shown by
425 cation-centered polyhedra in Fig. 8), and an interstitial complex: {Mg₂(H₂O)₁₂}, Mg cations
426 together with their associated (H₂O) groups. We may calculate a Lewis basicity for the structural
427 unit and a Lewis acidity for the interstitial complex as aggregate properties of the constituents of
428 these two units (see Hawthorne and Schindler 2008), and their interaction may be examined in a
429 manner similar to the application of the valence-matching principle to simple chemical

430 compositions using the *principle of correspondence of Lewis acidity-basicity* (Hawthorne and
431 Schindler 2008):

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

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

439

440 **The role of H₂O in crystal structures**

441 There are several different major roles for hydrogen (H) in crystal structures (Hawthorne
442 1992; Hawthorne and Baur 1994). The (OH) and (H₂O) groups are very important because of
443 their polar nature: on the O side, each group acts as an anion, whereas on the H side, the group
444 acts as a cation. The hydrogen-bond interaction is extremely important; it moderates many
445 biological interactions essential to life, and it imparts great diversity both to atomic arrangements
446 in minerals and to atom interactions in minerals. An (H₂O) group may (1) moderate Lewis
447 acidity and Lewis basicity, and (2) control the dimensional polymerization of structural units.
448 First, I will consider how (H₂O) can act as a moderator of bond valence.

449

450 **(H₂O) bonded to one cation.** Consider the atomic arrangements in Figures 9a and 9b: A
451 cation, *M*, bonds to an anion *S* with a bond valence of *v* v.u., and a cation, *M*, bonds to an (H₂O)
452 group, and the (H₂O) group bonds to an anion, *S*. In Figure 9a, the anion receives one bond of
453 bond valence *v* v.u. from the cation *M*. In Figure 9b, the O atom of the (H₂O) group receives a

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

461

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

469

470 **(H_2O) not bonded to any cation.** Consider the atomic arrangement in Figure 9d: (H_2O)
471 is involved only in a hydrogen-bond network. In such an environment, the O atom is usually [4]-
472 coordinated, and the (H_2O) group participates in two O-H (donor-hydrogen) bonds and two
473 H...O hydrogen bonds. Two hydrogen bonds of strength v v.u. are incident at the O atom of the
474 (H_2O) group, the bond-valence requirements of the central O atom are satisfied by two O-H
475 bonds of strength $(1 - v)$ v.u., and each H atom forms a hydrogen bond of strength v v.u. to
476 another anion (Fig. 9d). Hence an (H_2O) group not bonded to any cation does not modify the
477 strengths of its existent chemical bonds, it merely propagates them to more distant anions, as is

478 the case where the (H₂O) group is bonded to two cations (Fig. 9c); this type of (H₂O) is
479 designated *non-transformer* (H₂O).

480

481 **(H₂O) as a component of the interstitial complex.** As a component of an interstitial
482 complex, (H₂O) groups have two principal functions: (1) to satisfy the bond-valence
483 requirements of an interstitial cation where there are not enough anions to do so from adjacent
484 structural units; (2) to function as a bond-valence transformer between interstitial cations and the
485 structural unit. The first case involves only propagating bond valence through space, and hence
486 may involve non-transformer (H₂O) groups. The second case involves transformer (H₂O) groups,
487 and these will moderate the Lewis acidity of the interstitial complex. Hence the transformer
488 (H₂O) groups of the interstitial complex affect the stability of a chemical composition through
489 the operation of the principle of correspondence of Lewis acidity-basicity. Below I will show
490 how this approach to understanding the role of (H₂O) groups can give us a quantitative
491 understanding of the chemical compositions of interstitial complexes.

492

493 **CONTROLS ON THE AMOUNT OF (H₂O) IN MINERALS:**

494 **THE PRINCIPLE OF CORRESPONDENCE OF LEWIS ACIDITY-BASICITY**

495 **Calculation of Lewis basicity**

496 The Lewis basicity of a structural unit is the average bond-valence of bonds to that
497 structural unit from adjacent interstitial complexes and structural units (Hawthorne and Schindler
498 2008). The bonds received by the structural unit must balance the charge of the structural unit,
499 and hence we may define the Lewis basicity of the structural unit as *the charge on the structural*
500 *unit divided by the number of bonds to the structural unit*. So we need to know (1) the effective

501 charge on the structural unit, and (2) the number of bonds (from the interstitial complex and
502 adjacent structural units) needed by the structural unit.

503 What is the effective charge of the structural unit? The formal charge is not necessarily
504 appropriate to use in this context, particularly for structures with formally neutral structural units
505 as then there is no mechanism for the structure to link together. Consider lizardite,
506 $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ (Fig. 10). $[\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]^0$ sheets link to each other via hydrogen bonds from
507 the (OH) groups in the layer of octahedra of one sheet to the bridging O atoms in the layer of
508 tetrahedra of the adjacent sheet. The hydrogen bonds transfer charge from one sheet to the next,
509 and impart a polar character to the sheet; the sheet has cation character on the (OH) side and
510 anion character on the silicate side (shown by + and – signs in Fig. 10). In order to correctly
511 describe the interaction between adjacent structural units, we must factor this transfer of charge
512 into our calculation of the charge of the structural unit. The effective charge of lizardite is 0 (the
513 formal charge of the structural unit) + 4 x 0.20 (the charge transferred by hydrogen bonding,
514 assuming a hydrogen bond-valence of 0.20 v.u., Brown 1981) = 0.80^- . Note that such a transfer
515 of charge can only involve cations with very asymmetric coordinations (commonly H^+ , less
516 commonly stereoactive-lone-pair cations such as Pb^{2+} or Bi^{3+}). Note that minerals with formally
517 charged structural units may still be polar, and this transfer of charge must be built in to the
518 calculation of Lewis basicity. For metavoltine, $\text{K}_2\text{Na}_6\text{Fe}^{2+}(\text{H}_2\text{O})_6[\text{Fe}^{3+}_3\text{O}(\text{SO}_4)_6(\text{H}_2\text{O})_3]_2(\text{H}_2\text{O})_6$,
519 the effective charge of the structural unit (in square brackets) is 10 (the formal charge) + 12 x
520 0.20 (the charge transferred by twelve hydrogen bonds) = 12.4^+ . We define the *effective charge*
521 of the structural unit as *the formal charge as modified by charge transferred by hydrogen*
522 *bonding from donor anions within the structural unit.*

523

524

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

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

535

536 **The charge deficiency per anion: CDA**

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

547 The CDA of a structural unit is the effective charge of the structural unit divided by the
548 number of O atoms in the structural unit. For bloedite, $\text{Na}_2[\text{Mg}(\text{SO}_4)_2(\text{H}_2\text{O})_4]$, the effective

549 charge of the structural unit is $2 + 0.2 \times 8 = 3.6^-$ and the number of O atoms in the structural unit
550 is 12; thus the CDA = $3.6 / 12 = 0.30$ v.u.

551

552 **The number of bonds required by the structural unit**

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

561 For bloedite, $\text{Na}_2[\text{Mg}(\text{SO}_4)_2(\text{H}_2\text{O})_4]$, the CDA = 0.30 v.u. (see above). Using Figure 11,
562 we may read off the range for the number of bonds to anions of the structural unit: 1.55 to 2.44.
563 The corresponding range in the total number of bonds to the structural unit is $(1.55 \text{ to } 2.44) \times 12$
564 = 18.6 to 29.3, and the resulting range in Lewis basicity of the $[\text{Mg}(\text{SO}_4)_2(\text{H}_2\text{O})_4]^{2-}$ structural
565 unit is the effective charge divided by the range in the number of bonds to the structural unit:
566 $3.6 / (18.6 \text{ to } 29.3) = 0.12 \text{ to } 0.19$ v.u.

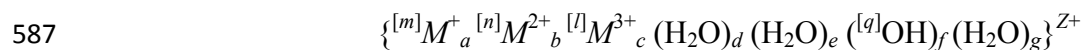
567 The parameter $\langle \text{NB} \rangle_{in}$ is required to establish a relation between O-coordination number
568 and CDA. To have predictive power, we need to be able to derive the number of bonds required
569 by O atoms *a priori*, without reference to an atomic arrangement, and the type of relation in
570 Figure 11 allows such a prediction. There is another important issue: the data in Figure 11 form a
571 band rather than a linear trend, indicating that the structural units can accommodate a range in
572 the number of bonds from the interstitial complex. It seems apparent that *structural units*

573 *maintain their stability as the pH of the environment changes by varying the number of bonds*
574 *they accept from the interstitial complex and adjacent structural units.* Thus the range in
575 numbers of bonds from the interstitial complex and adjacent structural units to the structural unit
576 reflects the range in pH over which the mineral is stable (Hawthorne and Schindler 2008). As
577 shown above, Figure 11 allows calculation of the range of possible Lewis-base strength for a
578 specific structural unit (see example for bloedite given above).

579

580 **FACTORS AFFECTING THE COMPOSITION OF THE INTERSTITIAL COMPLEX**

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



588 where M are interstitial cations of different coordination number $[m]$, $[n]$ and $[l]$, and valence; d
589 is the amount of transformer (H_2O); e is the amount of non-transformer (H_2O); and g is the
590 amount of (H_2O) not bonded to any interstitial cation (Schindler and Hawthorne 2001a). The
591 Lewis acidity of the interstitial complex may be represented graphically as a function of the
592 variables a to g , l to n , q and Z in the above expression (Fig. 12): the ordinate is the Lewis acidity
593 of the interstitial complex, the abscissa is the number of transformer (H_2O) groups per cation,
594 and the curved lines show the variation in Lewis acidity as a function of the number of
595 transformer (H_2O) groups per cation for interstitial cations of different coordination number and
596 formal charge (the corresponding cation charges and coordinations are shown to the left of the

597 curves). Monovalent anions (OH, Cl) may also be incorporated into this procedure (see
598 Hawthorne and Schindler 2008 for details).

599 Figure 13 shows the operation of the principle of correspondence of Lewis acidity-
600 basicity. The range in Lewis basicity of the structural unit is plotted on the graph of the Lewis-
601 acidity function (Fig. 12). Where the functions representing the properties of the interstitial
602 complexes and the structural unit do not intersect (i.e., outside the yellow band in Fig. 13a),
603 structures of those compositions are not stable as the Lewis acidities of these interstitial
604 complexes are not within the Lewis-basicity range of the interstitial complex represented on the
605 graph; the principle of correspondence of Lewis acidity-basicity is not satisfied, and structures of
606 these compositions will not form. Where the functions representing the properties of the
607 interstitial complexes and the structural unit do intersect (i.e., within the yellow band in Fig.
608 13a), structures of those compositions are potentially stable as the Lewis acidities of these
609 interstitial complexes are within the Lewis-basicity range of the interstitial complex represented
610 on the graph; the principle of correspondence of Lewis acidity-basicity is satisfied, and structures
611 of these compositions may form. Let us look at what we can do with this approach for a subset of
612 the sulfate minerals.

613

614 **Hydroxy-hydrated sulfate minerals**

615 The structural hierarchy developed for sulfate minerals by Hawthorne et al. (2000a)
616 forms a general framework for the examination of sulfate structures from a bond-topologic
617 perspective. Schindler et al. (2006) examined sulfate structures in this way and showed that
618 many crystal-chemical features of sulfate minerals may be understood in terms of the principle of
619 correspondence of Lewis acidity-basicity, in parallel with similar work on borate minerals
620 (Hawthorne et al. 1996a; Schindler and Hawthorne 2001a, 2001b, 2001c), vanadate minerals

621 (Schindler et al. 2000b) and uranyl minerals (Burns 2005, Schindler and Hawthorne 2004, 2008).
622 We will look at two structural units in this group and use the principle of correspondence of
623 Lewis acidity-basicity to derive possible interstitial complexes and compare them with what is
624 observed in minerals.

625

626 $[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$ ($M = Mg, Ni, Zn, Fe^{2+}$). The structural unit $[M^{2+}(SO_4)_2(H_2O)_4]^{2-}$
627 occurs in bloedite, $\{Na_2\}[Mg(SO_4)_2(H_2O)_4]$, nickelbloedite, $\{Na_2\}[Ni(SO_4)_2(H_2O)_4]$, leonite,
628 $\{K_2\}[Mg(SO_4)_2(H_2O)_4]$, changoite, $\{Na_2\}[Zn(SO_4)_2(H_2O)_4]$, mereiterite, $\{K_2\}[Fe(SO_4)_2(H_2O)_4]$,
629 and roemerite, $\{Fe^{2+}(H_2O)_6\}[Fe^{2+}(SO_4)_2(H_2O)_4]$ (Hawthorne et al. 2000a). Above, we calculated
630 a range in Lewis basicity for this structural unit (in bloedite): 0.12–0.19 v.u.

631 Values of Lewis acidity for interstitial monovalent cations with coordination numbers [6]
632 to [8] intersect the range in Lewis basicity for 0–2, 0–1 and 0 transformer (H_2O) groups per
633 cation, respectively. With regard to divalent interstitial cations, $^{[6]}M^{2+}$ can occur with 4–6
634 transformer (H_2O) groups and $^{[8]}M^{2+}$ can occur with 2–8 transformer (H_2O) groups. With regard
635 to trivalent interstitial cations, $^{[8]}M^{3+}$ can occur only with 8 transformer (H_2O) groups, $^{[7]}M^{3+}$ and
636 $^{[6]}M^{3+}$ cannot occur at all. All minerals of this group conform to these predictions: bloedite,
637 nickelbloedite and changoite have an interstitial complex $\{^{[6]}Na_2(H_2O)_0\dots\}$, leonite and
638 mereiterite have an interstitial complex $\{^{[6]}K_2(H_2O)_0\dots\}$, and roemerite has an interstitial
639 complex $\{^{[6]}Fe^{2+}(H_2O)_6\dots\}$.

640

641 $[Fe^{3+}(OH)(SO_4)_2]^{2-}$. The structural unit $[Fe^{3+}(OH)(SO_4)_2]^{2-}$ occurs in sideronatrite,
642 $\{Na_2(H_2O)_3\}[Fe^{3+}(SO_4)_2(OH)]$, metasideronatrite, $\{Na_4(H_2O)_3\}[Fe^{3+}(SO_4)_2(OH)]_2(H_2O)_3$,
643 chaidamuite, $\{^{[6]}Zn(H_2O)_4\}[Fe^{3+}(SO_4)_2(OH)]$, and guildite, $\{^{[4+2]}Cu^{2+}(H_2O)_4\}[Fe^{3+}(SO_4)_2(OH)]$.
644 The effective charge of this structural unit is $(2 + 0.2 \times 1)^- = 2.2^-$, the number of O atoms in the

645 structural unit is 9, and the CDA of the structural unit is $2.2 / 9 = 0.24$ v.u. With this value, we
646 may derive the lower and upper bounds for $\langle \text{NB} \rangle_{in}$ using Figure 11: 1.10–1.75. The resultant
647 range in the number of bonds required by the structural unit is $1.14\text{--}1.97 \times 9 = 10.3\text{--}17.7$.
648 Dividing the effective charge by the number of bonds required, $2.2 / (10.3\text{--}17.7)$, gives the range
649 in Lewis basicity: 0.12–0.22 v.u. As before, we plot this range in Lewis basicity on the graph of
650 the Lewis-acidity function, Fig. 13b, and can predict the range in chemical composition for
651 possible interstitial complexes.

652 Values of Lewis acidity for interstitial monovalent cations with coordination numbers [5]
653 to [7] intersect the range in Lewis basicity for 0–2, 0–1 and 0 transformer (H_2O) groups per
654 cation, respectively. With regard to divalent interstitial cations, $^{[6]}M^{2+}$ can occur with 3–6
655 transformer (H_2O) groups, $^{[7]}M^{2+}$ can occur with 2–7 transformer (H_2O) groups, $^{[8]}M^{2+}$ can occur
656 with 1–8 transformer (H_2O) groups, and $^{[8]}M^{3+}$ can occur with 5–8 transformer (H_2O) groups.
657 All minerals of this group conform to these predictions: sideronatrite and metasideronatrite have
658 an interstitial complex $\{^{[6]}\text{Na}_2(\text{H}_2\text{O})_0\dots\}$, guildite has an interstitial complex $\{^{[6]}\text{Cu}^{2+}(\text{H}_2\text{O})_4\}$,
659 and chaidamuite has an interstitial complex $\{^{[6]}\text{Zn}(\text{H}_2\text{O})_4\}$ (Schindler et al. 2006).

660 The approach described above provides significant understanding of what factors affect
661 the chemical compositions of minerals, and some prediction of the details of interstitial cations
662 and anions in minerals. For some structural units, the predicted interstitial complexes vary over a
663 wide range of cations or transformer (H_2O) groups, which in terms of prediction, is not
664 satisfactory. This indicates the need for further development along these lines. It seems likely
665 that the compositions of interstitial complexes in these circumstances are also affected by the pH
666 of their environment during crystallization. Some very interesting questions now emerge
667 concerning the nature of the crystallization process. Does the pH of the environment have a
668 strong effect on the form of the structural unit or the amount of (H_2O) incorporated into the

669 structure? Does the form of the structural unit dictate the identity of the interstitial cations, or
670 does the availability of a particular interstitial cation dictate the form of the structural unit? Are
671 there synergetic interactions between these factors? We can begin to investigate some of these
672 questions using this bond topology approach.

673

674 **Other applications**

675 This approach has also been used to examine the structure, chemical composition and
676 stability of vanadate (Schindler et al. 2000a, 2000b), borate (Schindler and Hawthorne 2001a,
677 2001b, 2001c) and uranyl-oxysalt minerals (Schindler and Hawthorne 2004, 2008), and has the
678 potential to be applied to other low-temperature oxysalt minerals. It has also been used to
679 consider crystal morphology and surface features (Schindler et al. 2004a, 2004b) and
680 crystallization-dissolution of minerals in aqueous solutions (Hawthorne and Schindler 2014). An
681 important aspect of this approach is that it relates bond topology and bond valence to processes
682 involved in crystallization, and it may also be applicable to chemical reactions. The valence-sum
683 rule is used for atoms in crystals, glasses and aqueous fluids. It seems reasonable that atoms in
684 transition between these various states of matter also tend to obey the valence-sum rule. This led
685 Hawthorne (2012) to propose the *Reaction Principle*:

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

691

692 It also suggests that the arrangements of atoms in the reactants may significantly affect the
693 arrangements of atoms in the products, as many mineral reactions will tend to occur by breaking
694 the weaker chemical bonds in the reactants and maintaining the stronger chemical bonds, thus
695 giving us a possible mechanism for explaining Ostwald's Step Rule¹ (see Morse and Casey 1988
696 for an excellent description of this rule in geochemical reactions). An example of this mechanism
697 was given by Gaskell et al. (1991) who showed that a CaSiO₃ glass has short- and medium-range
698 structure very similar to that of wollastonite. This suggests that in a CaSiO₃ melt close to the
699 liquidus, the product in the crystallization of wollastonite is already templated in the reactant,
700 and the atoms in the system obey the Reaction Principle, and crystallize as wollastonite. It is
701 unfortunate that the structures of magmas are not well-characterized at medium range, but the
702 possibility that such templating of minerals occurs in magmas provides additional incentive to
703 learn more about the structures of magma and the details of crystallization processes at the
704 atomic scale in magmatic systems.

705

706 **LEWIS BASICITY OF THE STRUCTURAL UNIT, AND THE FORMATION OF ROCKS**

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

708 Above, we defined the boundary between the bonds of the structural unit and the bonds
709 of the interstitial complex as 0.30 v.u. The strength of the bonds involving the interstitial
710 complex is thus less than 0.30 v.u., and hence its Lewis acidity is less than 0.30 v.u. As the
711 principle of correspondence of Lewis acidity-basicity requires that the Lewis basicity of the
712 structural unit match the Lewis acidity of the interstitial complex, *the Lewis basicity of the*
713 *structural unit must also be less than 0.30 v.u.* This is an extremely important statement as it

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.

714 must exert stringent controls on the possible chemical compositions and atomic arrangements of
715 structural units in minerals.

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

726 First, let us consider divalent-metal phosphates with structural units of the form
727 $M^{2+}_N(PO_4)(OH)_m$. The variation in Lewis basicity as a function of N, the number of octahedrally
728 coordinated M^{2+} cations, and m, the number of (OH) groups, is shown in Figure 14a for N = 2 to
729 4 and m = 0 to 25 (the method of calculation is explained in the Appendix). For
730 $M^{2+}_2(PO_4)(OH)_{0-15}$, the Lewis basicity increases with increasing values of m, the amount of
731 (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.
732 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
733 high values of m, and increases dramatically with decreasing values of m. Above, we showed
734 that the Lewis basicity of the structural unit must be less than 0.30 v.u. if it is to satisfy the
735 principle of correspondence of Lewis acidity-basicity. If we mark this boundary on Figure 14a,
736 we see that most compositions of the general form $M^{2+}_N(PO_4)(OH)_m$ lie to the higher side of the
737 0.30 v.u. boundary, and hence cannot occur as structural units in minerals. Only for N = 2 and m

738 ≤ 2 do we have Lewis basicities less than 0.30 v.u.: $[M^{2+}_2(PO_4)(OH)_2]^-$ and $[M^{2+}_2(PO_4)(OH)]^0$. If
739 we look at minerals (Table 3), we see selected minerals of this form: farringtonite, sarcopside
740 and zavalíaite ($N = 1.5, m = 0$), althausite ($N = 2, m = 1$), holtedahlite ($N = 2, m = 1$) and
741 wagnerite ($N = 2, m = 1$). Moreover, there are no minerals of the form $M^{2+}_N(PO_4)(OH)_m$ with
742 Mg^{2+} or OH^- greater than two ions per phosphate group.

743 Next, let us consider divalent-metal sulfates with structural units of the form
744 $M^{2+}_N(SO_4)(OH)_m$. The variation in Lewis basicity as a function of N and is shown in Figure 14b
745 for $N = 1$ to 5 and $m = 0$ to 18. For $M^{2+}(SO_4)(OH)_{0-4}$, the Lewis basicity increases rapidly from
746 $m = 4$ to 6, but then levels off at higher values of m , the amount of (OH) , and overlaps with the
747 curve for $N = 3$ for larger values of m . For $M^{2+}_3(SO_4)(OH)_{4-18}$, the Lewis basicity increases
748 rapidly from $m = 4$ to 6, but then gradually levels off with increasing values of m . For
749 $M^{2+}_4(SO_4)(OH)_{0-18}$, the Lewis basicity is constant at 0.50 v.u. for all values of m . For
750 $M^{2+}_5(SO_4)(OH)_{0-18}$, the Lewis basicity increases with decreasing values of m at large values of m
751 (>12). Only for $N = 1, m \leq 4$ and $N = 3, m \leq 6$ are the Lewis basicity values below the cut-off
752 value of 0.30 v.u. Selected minerals of this form are listed in Table 3: zincosite ($N = 1, m = 0$),
753 linarite and chlorothionite ($N = 1, m = 2$), antlerite ($N = 3, m = 4$) and christelite ($N = 2, m = 3$
754 for $(SO_4)_1$), plus the synthetic $Mg_3(SO_4)_2(OH)_2$ ($N = 1.5, m = 1$ per (SO_4) group).

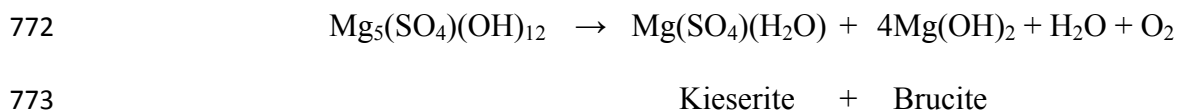
755

756 **The distribution of mineral stoichiometries and the existence of rocks**

757 The above calculations and Figure 14 suggest that many stoichiometries cannot exist as
758 structures as there are strong bond-topological controls on their possible compositions and
759 structures. Indeed, Figure 14 suggests that stoichiometries of structural units cannot exceed a
760 value of $N \approx 4$ as the resulting Lewis basicity of the structural unit is too high to form a stable
761 structure. Let us examine this point using the stoichiometries of oxysalt minerals. Figure 15

762 shows a frequency diagram for minerals whose formulae involve octahedrally coordinated (M)
763 and tetrahedrally coordinated (T) cations. The number of minerals is a maximum at an M:T ratio
764 of 1:1, and falls off to close to zero beyond the range $4:1 \leq M:T \leq 1:4$ except for $M:T = \infty:1$ and
765 $M:T = 1:\infty$. All the oxysalt minerals occur in the central region; oxides occur at $M:T = \infty:1$ and
766 tetrahedron-framework structures (e.g., quartz, feldspars) occur at $M:T = 1:\infty$.

767 Thus the stoichiometry of minerals is extremely restricted. What “happens” to all those
768 other chemical compositions that cannot occur as single minerals (the yellow regions in Fig. 15)?
769 Let us consider a simple example. The composition $[Mg_5(SO_4)(OH)_{12}]^{4+}$ has a Lewis basicity of
770 0.67 v.u. (Fig. 14b) and hence cannot form a structural unit. So what will happen to such a
771 composition?



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

784

785

786 **HYDROGEN, POLYMERIZATION OF THE STRUCTURAL UNIT, AND THE DISTRIBUTION OF**
787 **STRUCTURAL COMPLEXITY OF MINERALS WITHIN THE EARTH**

788 Above, we saw that both (H₂O) and (OH) groups are extremely polar: on the O side, each
789 functions as an anion, whereas on the H side, each functions as a cation. The metal(M)-O bonds
790 are commonly relatively strong [~ 0.40 v.u. for (H₂O); 0.80 v.u. for (OH)], whereas the H...O
791 (hydrogen) bonds are much weaker [~ 0.20 v.u. for both (H₂O) and (OH)]. Hence the M-O bonds
792 are commonly part of the structural unit, whereas the hydrogen bonds are *not* part of the
793 structural unit (Hawthorne 1985). The net result of this asymmetric arrangement of bond
794 valences is commonly to terminate the structural unit at the (H₂O) and (OH) groups.

795 Consider the structure of newberyite (Sutor 1967), Mg₃(PO₃OH)(H₂O)₃ (Fig. 16), in
796 which (OH) and (H₂O) play significant roles in limiting polymerization of polyhedra in the
797 structure. Newberyite contains an acid-phosphate group, (PO₃OH). Each tetrahedron links to
798 three (Mgφ₆) octahedra, forming a sheet in the **ac** plane (Fig. 16), and the fourth vertex of the
799 tetrahedron points in the $\pm\mathbf{b}$ direction. In a (PO₄) group, the fourth vertex of the tetrahedron
800 would link to another polyhedron of the structural unit in order to satisfy the valence-sum rule at
801 that anion. However, in newberyite, H is attached to the O anion at this vertex, and the valence-
802 sum rule prevents linkage to another tetrahedron or octahedron, preventing polymerization of the
803 structural unit in the **b** direction through the phosphate group. Newberyite also contains
804 {MgO₃(H₂O)₃} octahedra that are linked by the tetrahedra into a sheet (Fig. 16) by each
805 tetrahedron sharing three vertices with adjacent tetrahedra. This linkage leaves three vertices of
806 the octahedron that can potentially link in the third dimension to form a framework structure.
807 However, each of the O anions occupying these three vertices also link to two H atoms, forming
808 (H₂O) groups; the H atoms satisfy the bond-valence requirements of the anions at these three
809 vertices, and prevent linkage in the **b** direction.

810 Although the presence of H prevents all intra-unit linkage at the (OH) and (H₂O) groups
811 in newberyite, this is not necessarily the case in all H-bearing minerals: both (OH) and (H₂O) can
812 allow linkage of a structural unit in some directions and prevent such linkage in other directions.
813 The structural unit in artinite, [Mg₂(CO₃)(OH)₂(H₂O)₃] (Akao and Iwai 1977), consists of a
814 ribbon of edge-sharing (MgO₆) octahedra, flanked by (CO₃) triangles (Fig. 17). In the centre of
815 the ribbon, the anions bond to three Mg cations, receiving $0.36 \times 3 = 1.08$ v.u. from Mg. The
816 additional bond valence required by these anions is provided by their associated H atoms which
817 weakly hydrogen-bond (bond-valence approximately 0.08 v.u.) to an adjacent ribbon. The (OH)
818 group *prevents* linkage of the structural unit in the Z- direction but *allows* linkage in the X- and
819 Y-directions. The anions along the edge of the ribbon bond to either one Mg, two Mg, or one Mg
820 and one C, with incident bond-valence values of ~0.3, 0.6 and 1.7 v.u. The first two anions must
821 be (H₂O) groups and cannot propagate linkage of the structural unit. The (H₂O) group bonded to
822 one Mg prevents further polymerization of the structural unit in all three directions, whereas the
823 (H₂O) group bonded to two Mg atoms allows polymerization of the structural unit in the Y-
824 direction but prevents polymerization in the X- and Z-directions. Thus in artinite, the (OH)
825 groups allow polymerization of the structural unit in two directions, the two types of (H₂O)
826 group allow polymerization in one and no directions, respectively, and all linkage between
827 structural units is through hydrogen bonding via the (OH) and (H₂O) groups of the structural
828 unit.

829 In summary, H as (OH) and (H₂O) can control *the dimensional polymerization of a*
830 *structural unit*, limiting it in one or more directions. This is the principal single chemical feature
831 that leads to the amazing structural diversity in oxygen-based minerals. Moreover, the
832 distribution of H throughout the Earth, together with the anharmonic nature of the hydrogen

833 bond, is a major factor in accounting for the systematic distribution of mineral species from the
834 core to the surface of the Earth.

835

836 THE METHOD OF MOMENTS

837 There is little intuitive connection between the essential features of a crystal structure, the
838 relative positions of the atoms and the disposition of the chemical bonds, and the usual methods
839 for deriving the electronic energy density-of-states (Hawthorne 2012). However, the electronic
840 energy density-of-states may be derived from the bond-topological aspects of a structure using
841 the method of moments (Burdett et al. 1984). I will give a brief outline of the method; the reader
842 should consult their paper for mathematical details.

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

$$848 \quad E = (\int \psi^* H^{\text{eff}} \psi \, d\tau) / (\int \psi^* \psi \, d\tau) = (\langle \psi^* H^{\text{eff}} \psi \rangle) / (\langle \psi^* \psi \rangle) \quad (1)$$

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

853 Substitution for $\psi (= \sum c_i \phi_i)$ gives

$$854 \quad E = (\sum_i \sum_j c_i c_j (\langle \phi_i | H^{\text{eff}} | \phi_j \rangle)) / (\sum_i \sum_j c_i c_j \langle \phi_i | \phi_j \rangle) \quad (2).$$

855 Equation (2) may be simplified thus: (a) $\langle \phi_i | \phi_j \rangle$ is the overlap integral between atomic orbitals
856 on different atoms, and is written as S_{ij} , which is always ≤ 1 ; where $i = j$, $\langle \phi_i | \phi_j \rangle = 1$ for a

857 normalized (atomic) basis set of orbitals; (b) $\langle \varphi_i | H^{eff} | \varphi_j \rangle = H_{ij}$; this represents the energy of an
 858 electron in orbital φ_i and can be approximated by the orbital ionization potential; (c) $\langle \varphi_i | H^{eff} | \varphi_j \rangle$
 859 $= H_{ij}$; this is the resonance integral. Minimizing the energy with respect to the coefficients c_i ,
 860 equation (2) gives the molecular-orbital energies. The eigenvalues of the following *secular*
 861 *determinant equation* give the molecular-orbital energy levels:

$$862 \quad |H_{ij} - S_{ij}E| = 0 \quad (3).$$

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

$$867 \quad \begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad (4).$$

868 Compare the structure of Figure 1b with the matrix entries in equation (4). Where atoms
 869 are bonded together (i.e., atoms 1 and 2 in Fig. 1b), there is a nonzero value at the corresponding
 870 (1,2) entry in the secular determinant; where atoms are not bonded together (i.e., atoms 1 and 3
 871 in Fig. 1b), the corresponding entry in the secular determinant (1,3) is zero. Note also the
 872 correspondence of the zero off-diagonal matrix entries in the adjacency matrix of the graph of
 873 this molecule (Fig. 2) with the zero off-diagonal matrix entries in equation (4).

874 We cannot use this sort of calculation to deal with a crystal containing approximately
 875 Avogadro's number of atoms. Instead, we use Bloch orbitals (Ziman 1965) which assume a unit
 876 cell and constrain the orbital content of the unit cell to the translational periodicity of the crystal.
 877 Using the special-points method, the secular determinant is solved at a representative set of
 878 points within the Brillouin zone, giving a representative sampling of the orbital energy levels that

879 may be smoothed to give the electronic-energy density-of-states. The total orbital energy is
880 obtained by integrating the electronic energy density-of-states up to the Fermi level.
881 To solve equation (4), we diagonalize the Hamiltonian matrix. The trace of this matrix may be
882 written as follows:

$$Tr(H^n) = \sum_i \sum_{j,k,\dots,n} H_{ij} H_{jk} \dots H_{ni} \quad (5).$$

883

884 A topological interpretation of one term in this sum is shown in Figure 18. H_{ij} is the interaction
885 integral between orbitals i and j ; we may simplify the situation without loss of topological
886 content by adopting the Huckel approximation: $H_{ij} = \beta$ where the atoms are bonded, $H_{ij} = 0$
887 where the atoms are not bonded, and $\alpha = 0$ where $i = j$. In equation (5), as each single term $\{H_{ij}$
888 $H_{ik} \dots H_{ni}\}$ is a product, the term is nonzero only if all individual H_{ij} values in the term, e.g.,
889 $\{H_{12}H_{23}H_{34}H_{41}\}$, are nonzero. The last H_{ij} in each product is H_{ni} , the interaction between the n th
890 orbital and the first orbital, and hence the product $\{H_{ij} H_{jk} \dots H_{ni}\}$ represents a closed path in the
891 graph of the orbitals (molecule). If one (or more) of the terms in the product is zero (e.g., H_{31} in
892 Fig. 18), that product is zero, i.e., $\{H_{12}H_{23}H_{31}\} = 0$, and does not contribute to the trace of the
893 Hamiltonian matrix. Hence the double-summation in equation (5) contains all closed paths
894 through the graph of (the orbital structure of) the array of atoms.

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

$$Tr(H^n) = Tr(E^n) = \mu_n \quad (6)$$

896

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

$$\mu_n = \sum_i E_i^n \quad (7).$$

899

900 The density-of-states may be obtained by inverting the collection of moments $\{\mu_n\}$ (Burdett et al.
901 1984). The result is that we can evaluate $Tr(H^n)$ directly from the bond topology, and, in so
902 doing, derive the electronic energy density-of-states.

903 This method generalizes to infinite systems (i.e., crystals) in a straightforward manner.

904 We may define the n th moment of E as

$$905 \quad \mu_n = \int E^n \rho(E) dE \quad (8)$$

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

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

915

916 **Low-order moments and crystal chemistry**

917 The number of edges in a path through the bonded atoms in a structure is the *moment* of
918 that path, and each path corresponds to a crystal-chemical feature of the structure. We will now
919 consider the structural features corresponding to the lower-order moments that are the most
920 energetically important. A *zero-moment path* has no steps and corresponds to remaining still
921 (called a “walk in place”); as such, it specifies the identity of the atom at that vertex of the graph
922 of the structure. Thus the complete set of zero-moment paths defines the chemical composition
923 of the structure. A *second-moment path* is a walk from one vertex to an adjacent vertex and back

924 again, and the set of second-moment paths from a single vertex defines the coordination number
925 of the atom corresponding to that vertex. A *fourth-moment path* is a walk from an atom (e.g., a
926 cation) to an anion to another cation to another anion and back to the first cation, and specifies
927 the linkage of two coordination polyhedra. Higher-moment paths describe more complicated
928 linkages of polyhedra, but these are less important from an energetic perspective than the low-
929 moment linkages. *Here is our energetic rationale for traditional crystal chemistry:* we focus on
930 chemical composition (zero moment), coordination number (second moment), and local linkage
931 between coordination polyhedra (fourth moment) as the most important differences between
932 structures, as differences in low-order moments are the most energetically important differences
933 between structures.

934

935 **Mineral reactions**

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

939

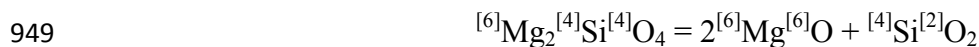
940 **Zero-moment changes.** Zero-moment changes involve changes in the chemical
941 composition of the system, i.e., a reaction in which the constituents are not conserved. This can
942 be a *metasomatic reaction* and involve open-system behavior.

943

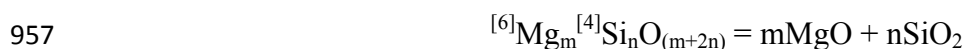
944 **Second-moment changes.** Second-moment changes involve changes in coordination
945 number in the constituent phases. A change in coordination number usually involves a
946 *discontinuous reaction*. Consider:

947

948 Forsterite = Periclase + Quartz



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



958 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
959 al. (1992), using fictive enthalpies of formation. However, (change in) coordination number is an
960 intensive variable whereas enthalpy of formation is an extensive variable. We must transform the
961 enthalpy of formation into an intensive variable, and I do this by dividing the enthalpy of
962 formation by the molecular weight of the reactant to produce the intensive variable $\Delta H/\text{MW}$
963 which I will call the *reduced enthalpy* of formation. There is a strong correlation between the
964 reduced enthalpy of formation and the change in anion-coordination number (details of this
965 calculation will be given in a later paper) through the reaction (Fig. 19) in accord with the
966 influence of coordination number on the energetics of structures indicated by the moment
967 arguments given above. A similar relation for the hydrated magnesium sulfates $\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})_n$
968 (where $n = 0-7, 11$) was shown by Hawthorne and Sokolova (2012).

969 These second-moment changes throw considerable light on why the additive-fictive
970 approach to predicting enthalpies of formation from oxides works so well. The relation
971 $^{[6]}\text{Mg}_m^{[4]}\text{Si}_n\text{O}_{(m+2n)} = m\text{MgO} + n\text{SiO}_2$ has no experimentally determined quantities; the

972 coordination numbers are assumed (and hence have no experimental uncertainty attached to
973 them) and the relation is exact. Consider the relation $\Delta H([{}^6\text{Mg}_m[{}^4\text{Si}_n\text{O}_{(m+2n)}]) = m\Delta H(\text{MgO}) +$
974 $n\Delta H(\text{SiO}_2)$ where $\Delta H(\text{MgO})$ and $\Delta H(\text{SiO}_2)$ are the fictive enthalpies for MgO and SiO₂,
975 respectively. This relation is also exact; $\Delta H([{}^6\text{Mg}_m[{}^4\text{Si}_n\text{O}_{(m+2n)}])$ is calculated from $\Delta H(\text{MgO})$ and
976 $n\Delta H(\text{SiO}_2)$. Hence $\Delta H([{}^6\text{Mg}_m[{}^4\text{Si}_n\text{O}_{(m+2n)}])$ *must* correlate with change in anion-coordination
977 number; this is an algebraic requirement. However, there is no algebraic requirement that change
978 in anion-coordination number must correlate with *experimental* enthalpies of formation from the
979 oxides. We know that the enthalpies calculated from the fictive enthalpies of the oxides correlate
980 with their experimental analogues; this is the whole point of using fictive enthalpies. Therefore
981 we may conclude that changes in anion-coordination number correlate with experimental
982 enthalpies of formation from the oxides, in accord with our prediction from the moments
983 approach to the electronic-energy density-of-states. In this regard, I should also emphasize that
984 using enthalpies of formation calculated from fictive enthalpies does not replace the
985 measurement of enthalpies of formation. One expects subtle differences in energetics with
986 higher-moment changes in bond topology, and this will not be reflected in enthalpies of
987 formation calculated using the fictive approach; they will only be apparent in measured
988 enthalpies of formation.

989

990 **Fourth-moment changes.** Fourth-moment changes involve maintaining chemical
991 composition and both cation- and anion-coordination numbers while changing the identities of
992 next-nearest-neighbor atoms. Such changes hence involve the nature of local (short-range)
993 clusters of ions. Such changes are common in amphiboles (e.g., Hawthorne et al. 1996b, 1996c,
994 1997, 2000b; Della Ventura et al. 1999; Hawthorne and Della Ventura 2007), and the short-range

995 version of the valence-sum rule (Hawthorne 1997, see above) suggests that such short-range
996 order should be common in all solid solutions involving polyvalent substitutions.

997 Major chemical variations in amphiboles in metabasic rocks involve the change from
998 tremolite, $\square\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$, to sadanagaite, $\text{NaCa}_2(\text{Mg}_3\text{Al}_2)(\text{Si}_5\text{Al}_3)\text{O}_{22}(\text{OH})_2$, with
999 increasing grade of metamorphism. In this reaction, the bond topology of the amphibole is
1000 conserved, and any energetic differences with regard to the amphiboles involve atom identities
1001 and their relative locations, i.e., short-range order-disorder. End-member tremolite is completely
1002 ordered whereas end-member sadanagaite must show extensive short-range order/disorder. Such
1003 short-range order/disorder must have a major effect on the energetics of the resulting minerals
1004 and their reactions with other phases.

1005

1006

SUMMARY

1007 The theoretical approach outlined above examines the structure and chemical
1008 composition of minerals based on their bond topology, aspects of graph theory and bond-valence
1009 theory, and the moments approach to the electronic-energy density of states. Below, I identify
1010 the principal features of this approach, and some of its uses:

1011 [1] An arrangement of atoms and chemical bonds may be represented by a weighted
1012 polychromatic digraph, and the handshaking principle may be used to examine many
1013 aspects of atom coordination and the linkage of coordination polyhedra.

1014 [2] The moments approach to the electronic-energy density-of-states provides a bond-
1015 topological interpretation of the energetics of a structure.

1016 [3] When comparing structures, the most important structural differences involve the first
1017 few disparate moments of the electronic-energy density-of-states.

- 1018 [4] We may classify chemical reactions according to the lowest-order moment of the
1019 electronic-energy density-of-states that is conserved, which allows us to identify the
1020 principal structural changes that drive chemical change: (a) coordination number for
1021 discontinuous reactions, and (b) short-range order for continuous reactions.
- 1022 [5] It may be shown that the quantitative aspects of bond-valence theory arise from the
1023 topological (or graphical) characteristics of structures as arrangements of atoms and
1024 chemical bonds.
- 1025 [6] The principle of correspondence of Lewis acidity-basicity states that stable structures will
1026 form when the Lewis-acid strength of the interstitial complex closely matches the Lewis-
1027 base strength of the structural unit, and allows us to examine the factors that control the
1028 chemical composition and aspects of the structural arrangement of minerals.
- 1029 [7] (H₂O) groups in the structural unit limit the polymerization of the structural unit in one or
1030 more directions, controlling the polymerization of the structural unit. This is a major
1031 factor affecting structural diversity in oxygen-based minerals and the systematic
1032 distribution and relative complexity of mineral species from the core to the surface of the
1033 Earth.
- 1034 [8] Interstitial (H₂O) groups may (1) satisfy the bond-valence requirements around an
1035 interstitial cation where there are insufficient adjacent anions to do so from neighboring
1036 structural units, or (2) moderate the Lewis acidity of the interstitial complex and affect
1037 the stability of a chemical composition through the operation of the principle of
1038 correspondence of Lewis acidity-basicity.
- 1039
1040
1041

1042

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1043

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APPENDIX

1051 Consider the structural unit $[\text{Mg}_N(\text{PO}_4)(\text{OH})_m]$.

1052 The charge on the structural unit is $2N - 3 - m$.

1053 The number of bonds involving the structural unit is $6N$ (for $^{[6]}\text{Mg}_N$) + 4 (for the (PO_4) group) +
1054 $2m$ (for H, assuming a coordination number of [2]) = $6N + 4 + 2m$.

1055 If we assume an ideal coordination number of [4] for oxygen, the number of bonds needed to
1056 produce such a coordination = $4(4 + m)$.

1057 The number of bonds needed from the interstitial complex is the difference of these two values:
1058 $4(4 + m) - (6N + 4 + 2m) = 12 + 2m - 6N$.

1059 The Lewis basicity of the structural unit is the charge divided by the number of bonds needed
1060 from the interstitial complex: $(2N - 3 - m)/(12 + 2m - 6N)$.

1061 For $N = 2$, this expression reduces to $(1 - m)/2m$, and for $m = 1, 2, 4, 8$, the Lewis basicities =
1062 0.00, 0.25, 0.38, 0.44 *vu*, respectively.

1063 For $N = 3$, this expression reduces to $(3 - m)/(2m - 6) = 0.50$ *vu* independent of the value of m .

1064 For $N = 4$, this expression reduces to $(5 - m)/(2m - 12)$, and for $m = 8, 12, 16, 20$, the Lewis
1065 basicities = 0.75, 0.58, 0.55, 0.53 *vu*, respectively.

1066 The calculations for the structural unit $[\text{Mg}_N(\text{SO}_4)(\text{OH})_m]$ are similar, except that we assume an
1067 ideal coordination number of [3] for oxygen because of the higher bond-valence of the S-O bond.

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1261

FIGURE CAPTIONS

1262

Figure 1. (a) A weighted polychromatic digraph with the coloured vertex set $\{1, 2, 3, 4\}$

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and the directed weighted edge set $\{12, 32, 34, 14\}$; (b) a simple idealized square molecule

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consisting of four atoms labelled 1–4; different chemical types of atoms are indicated by

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different colours.

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

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Figure 3. Graphical representation of polyhedron clusters; octahedra are shown in

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yellow, tetrahedra are shown in orange. Each cluster of polyhedra is represented by a graph in

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which the yellow vertices represent octahedra, the orange vertices represent tetrahedra, and the

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edges represent the number of vertices common to pairs of polyhedra: (a) $(M\phi_6)_2$; (b) $[M_2\phi_{11}]$;

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(c) $[M_2\phi_{10}]$; (d) $[M_2(TO_4)_2\phi_8]$; (e) graphical isomers of $[M(TO_4)_2\phi_4]$.

1272

Figure 4. The two components of the bond-valence model: Bond-Valence Theory (left)

1273

and Bond-Valence Curves (right).

1274

Figure 5. The three axioms of Bond-Valence Theory.

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Figure 6. The valence-matching principle.

1276

Figure 7. The bond-valence structure of the $(SO_4)^{2-}$ oxyanion in thenardite, with the

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individual bond valences shown in valence units (after Hawthorne 1994).

1278

Figure 8. Partitioning of the crystal structure of botryogen,

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$Mg_2(H_2O)_{12}[Fe^{3+}_2(SO_4)_4(OH)_2](H_2O)_2$, into two units, the strongly bonded structural unit

1280

(shown as coloured polyhedra) and the weakly bonded interstitial complex (shown as individual

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atoms and chemical bonds). Pink tetrahedra: (SO_4) groups; yellow octahedra: $(Fe^{3+}O_6)$

1282

octahedra; large orange circles: O atoms; small blue circles: Mg atoms; black lines: Mg-O bonds.

1283

Figure 9. The bond-valence structure around (H_2O) as a function of local bond-topology;

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(a) a cation, C (green) bonded to an anion, S (yellow) with bond valence v v.u.; (b) a cation

1285 bonded to an (H₂O) group (O: orange; H: black) with bond valence v v.u.; the H atoms
1286 hydrogen-bond to the anions S with bond valence $v/2$ v.u. per bond; (c) two cations bonded to an
1287 (H₂O) group with bond valence v v.u. per bond; the H atoms hydrogen-bond to the anions S with
1288 bond valence v v.u. per bond; (d) two H atoms hydrogen-bonded to an (H₂O) group with bond
1289 valence v v.u. per bond; the H atoms of the (H₂O) group hydrogen-bond to the anions S with
1290 bond valence v v.u. per bond.

1291 **Figure 10.** Representation of the crystal structure of lizardite, showing the polar nature of
1292 the structural unit; yellow: Mg octahedra; lilac: Si tetrahedra; red circles: H atoms; thick black
1293 lines: O_{donor}-H bonds; broken lines: hydrogen bonds. The acidic (+) and basic (–) parts of the
1294 structural unit are indicated.

1295 **Figure 11.** Correlation between the CDA of structural units and the average number of
1296 bonds from the interstitial complex and adjacent structural units, $\langle \text{NB} \rangle_{in}$, to O-atoms in the
1297 corresponding structural units of sulfate minerals. The upper and lower bounds of the distribution
1298 are used to define the characteristic range in the number of bonds accepted by a specific
1299 structural unit.

1300 **Figure 12.** Variation in Lewis acidity of a general interstitial complex as a function of the
1301 number of transformer (H₂O) groups per cation. The lines shown are for interstitial cations with
1302 formal charges and coordination numbers shown to the left of the plot. From Hawthorne and
1303 Schindler (2008).

1304 **Figure 13.** Variation in Lewis acidity with the number of transformer (H₂O) groups per
1305 cation for different interstitial-cation charges and coordination numbers for a general interstitial
1306 complex; the range in Lewis basicity of the structural units for selected sulfate minerals are
1307 shown by the yellow fields: (a) $[M^{2+}(\text{SO}_4)_2(\text{H}_2\text{O})_4]^{2-}$; (b) $[\text{Fe}^{3+}(\text{OH})(\text{SO}_4)_2]^{2-}$.

1308 **Figure 14.** (a) Lewis basicity of structural units of the form $Mg_N(T^{5+}O_4)(OH)_n$ ($T^{5+} = P,$
1309 As, V) as a function of stoichiometry for $N = 2, 3, 4$; $m = 1-24$. (b) Lewis basicity of structural
1310 units of the form $Mg_N(T^{6+}O_4)(OH)_n$ ($T^{6+} = S, Cr$) as a function of stoichiometry for $N = 1, 3, 4,$
1311 5; $m = 1-18$.

1312 **Figure 15.** The distribution of mineral stoichiometries with regard to the ratio of
1313 octahedrally coordinated cations (M) and tetrahedrally and triangularly coordinated cations (T).
1314 The bars in pink show the numbers of minerals with M:T ratios approximately equal to 4:1,
1315 3:1...1:3, 1:4. The yellow areas denote compositions not corresponding to single minerals.

1316 **Figure 16.** The crystal structure of newberyite, $Mg_3(PO_3OH)(H_2O)_3$, projected onto
1317 (010); Mg octahedra are shown in yellow, P tetrahedra are shown in lilac, H atoms are shown as
1318 red circles, $O_{\text{donor}}-H$ bonds are shown as thick black lines.

1319 **Figure 17.** The crystal structure of artinite, $[Mg_2(CO_3)(OH)_2(H_2O)_3]$, projected onto
1320 (001); Mg octahedra are shown in yellow, C triangles are shown in lilac, H atoms are shown as
1321 red circles, $O_{\text{donor}}-H$ bonds are shown as thick black lines.

1322 **Figure 18.** Interpretation of paths through the molecule shown in Figure 1b; the path $1 \rightarrow$
1323 $2 \rightarrow 3 \rightarrow 4$ contains only non-zero H_{ij} terms and contributes to the trace of the matrix, whereas
1324 the path $1 \rightarrow 2 \rightarrow 4$ contains a zero H_{ij} term (H_{31}) and does not contribute to the trace of the
1325 matrix.

1326 **Figure 19.** Variation in reduced enthalpy of formation (from the oxides) *versus* change in
1327 anion-coordination number through the reaction $[^6]Mg_m [^4]Si_n O_{(m+2n)} = m [^6]MgO + n [^4]SiO_2$. Units
1328 on the ordinate are kJ/mol/Dalton.

1329

TABLE 1. Lewis acid strengths (ν) 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

Values taken from Brown (2002), except V⁵⁺ (Schindler et al., 2000) and Pb²⁺ which was estimated from several oxysalt mineral structures.

TABLE 2. Lewis basicities (ν) for selected oxyanions

$(\text{BO}_3)^{3-}$	0.33	$(\text{CO}_3)^{2-}$	0.22
$(\text{SiO}_4)^{4-}$	0.33	$(\text{NO}_3)^{3-}$	0.11
$(\text{AlO}_4)^{3-}$	0.42	$(\text{VO}_4)^{3-}$	0.25
$(\text{PO}_4)^{3-}$	0.25	$(\text{SO}_4)^{2-}$	0.17
$(\text{AsO}_4)^{3-}$	0.25	$(\text{CrO}_4)^{2-}$	0.17

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	$Mn_3(PO_4)_2$
Zavaliáite	$Mn_3(PO_4)_2$
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	$Zn(H_2O)_4[Zn_2Cu_2(SO_4)_2(OH)_6]$

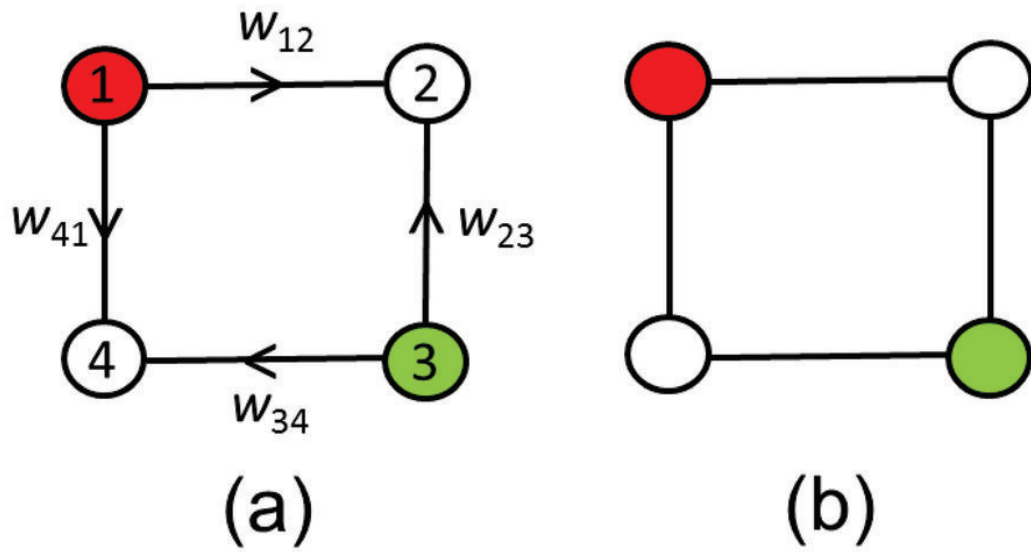


FIGURE 1

	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

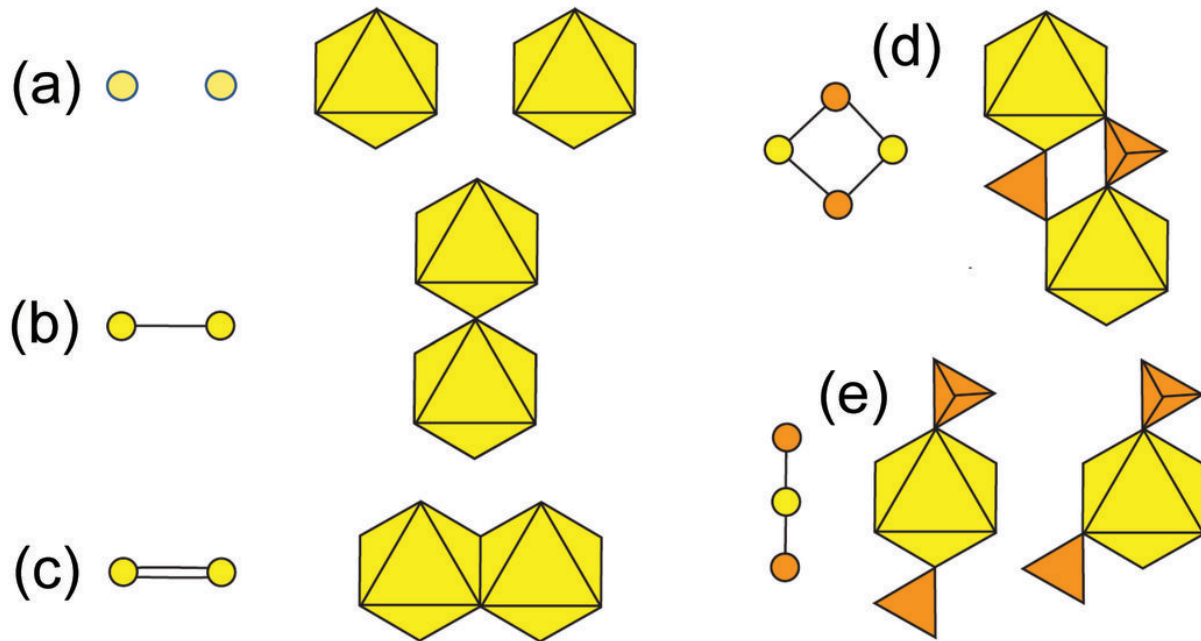


FIGURE 3

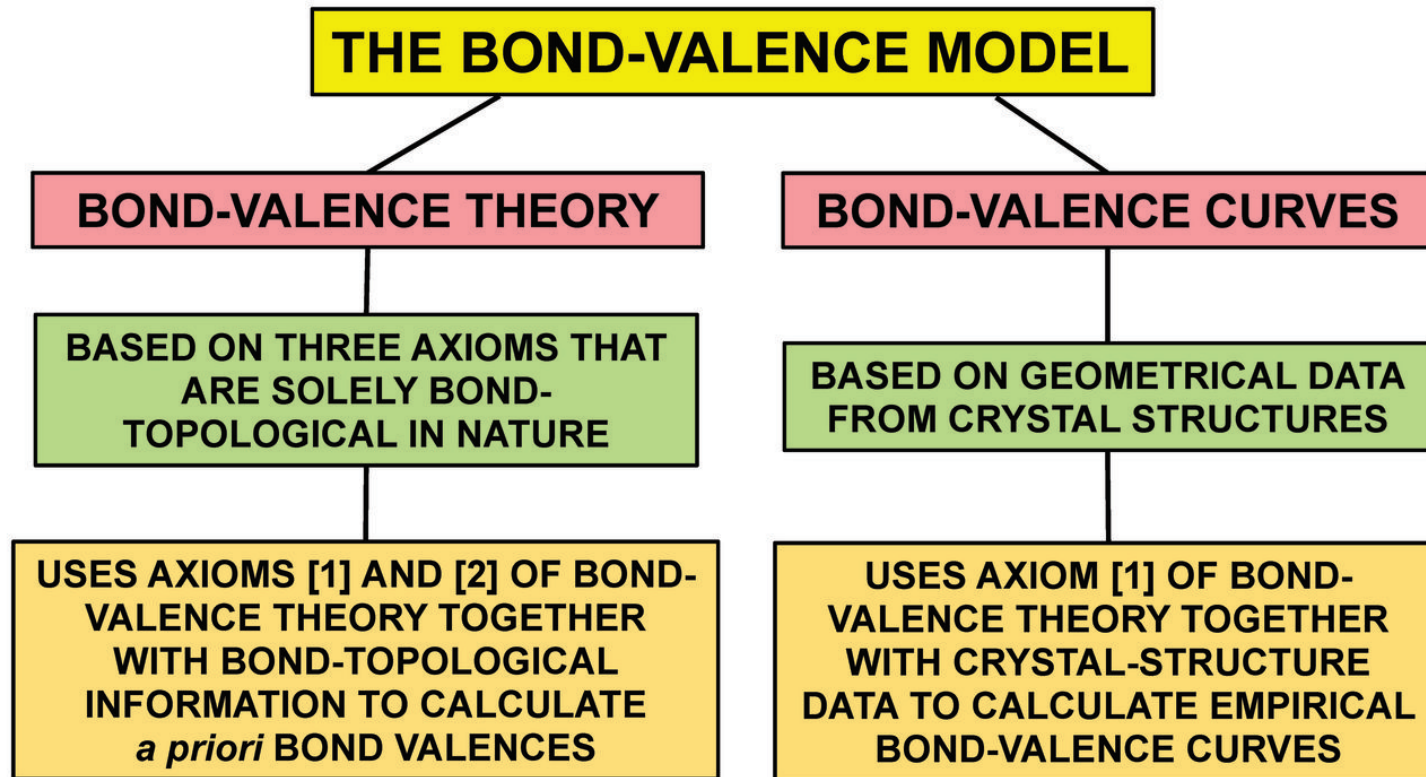


FIGURE 4

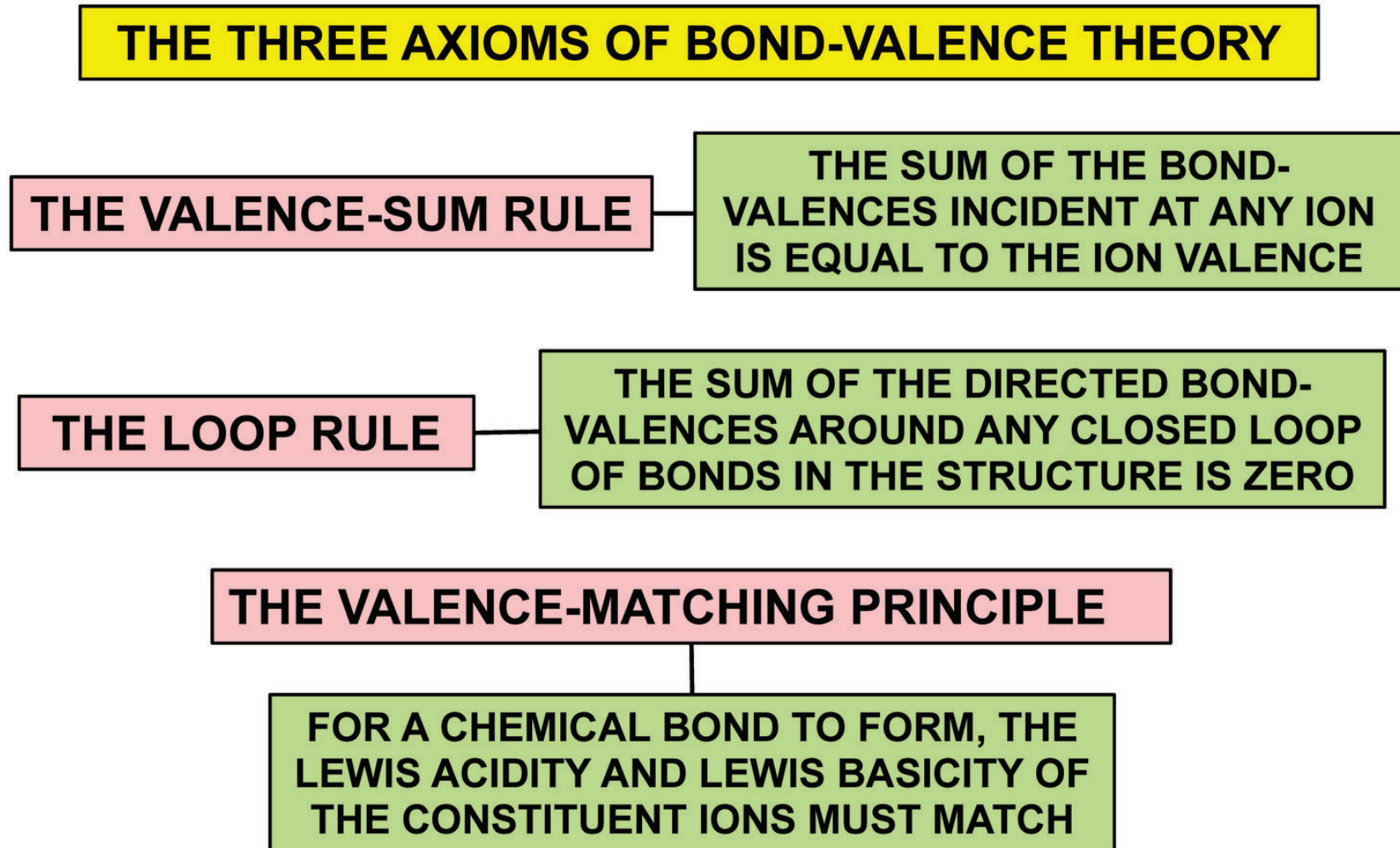


FIGURE 5

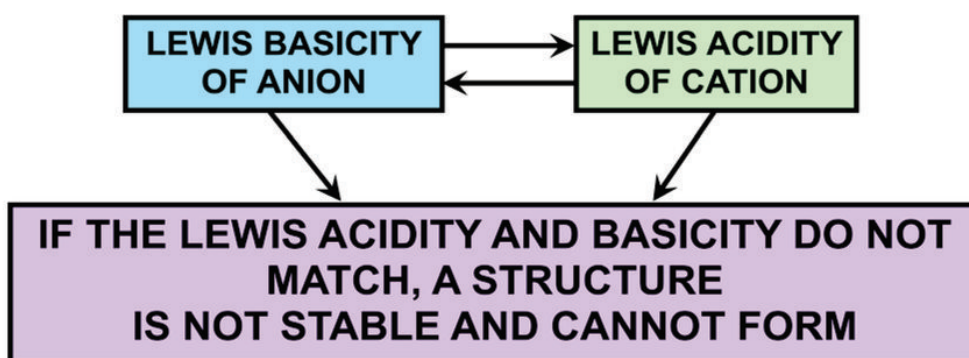


FIGURE 6

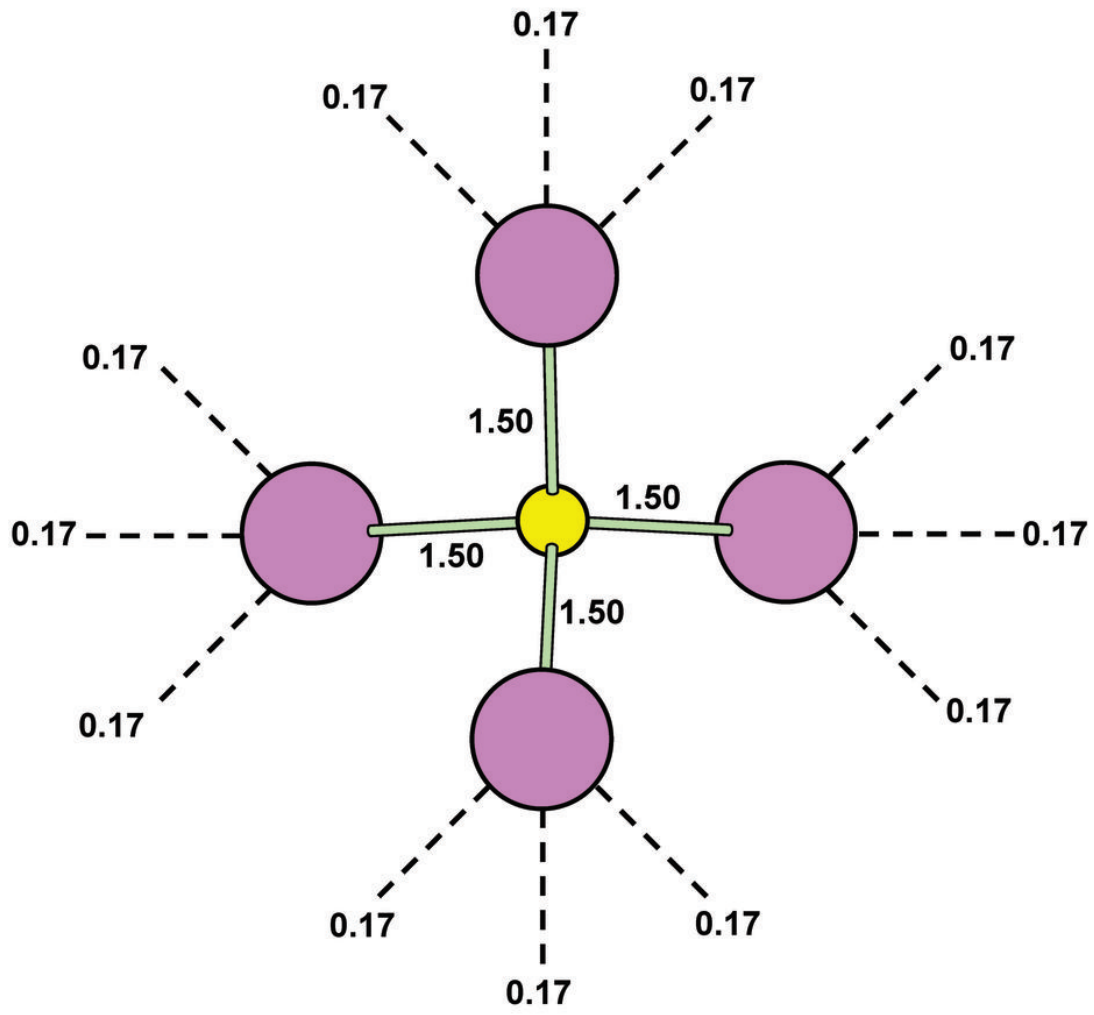


FIGURE 7

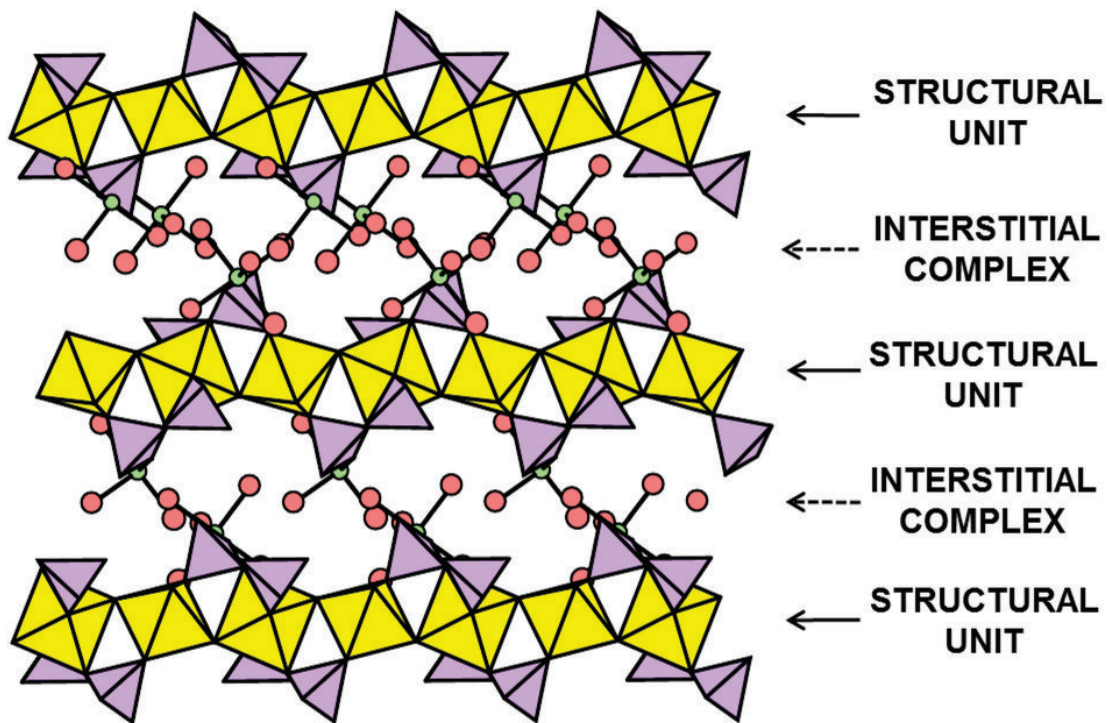


FIGURE 8

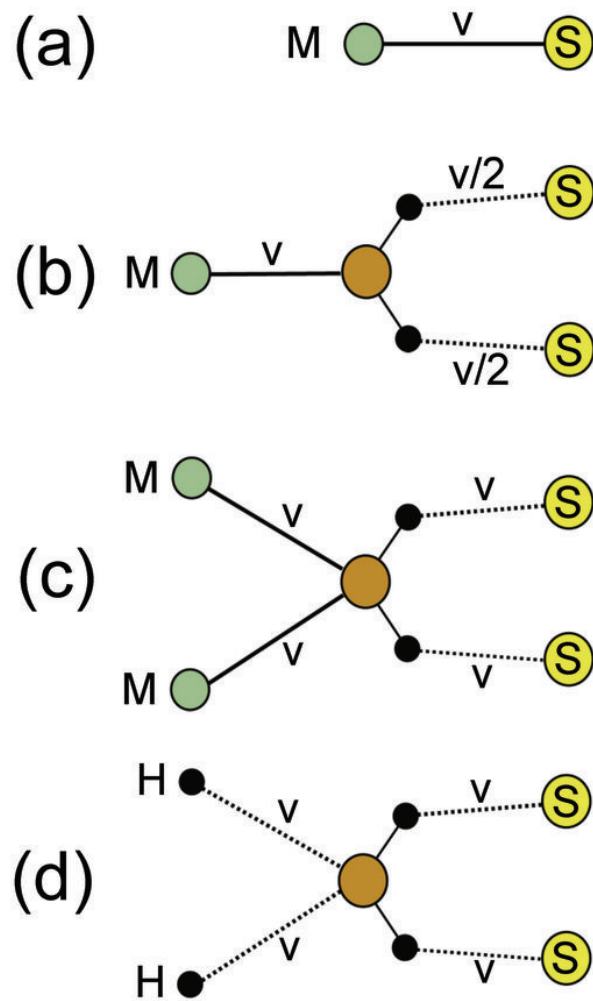


FIGURE 9

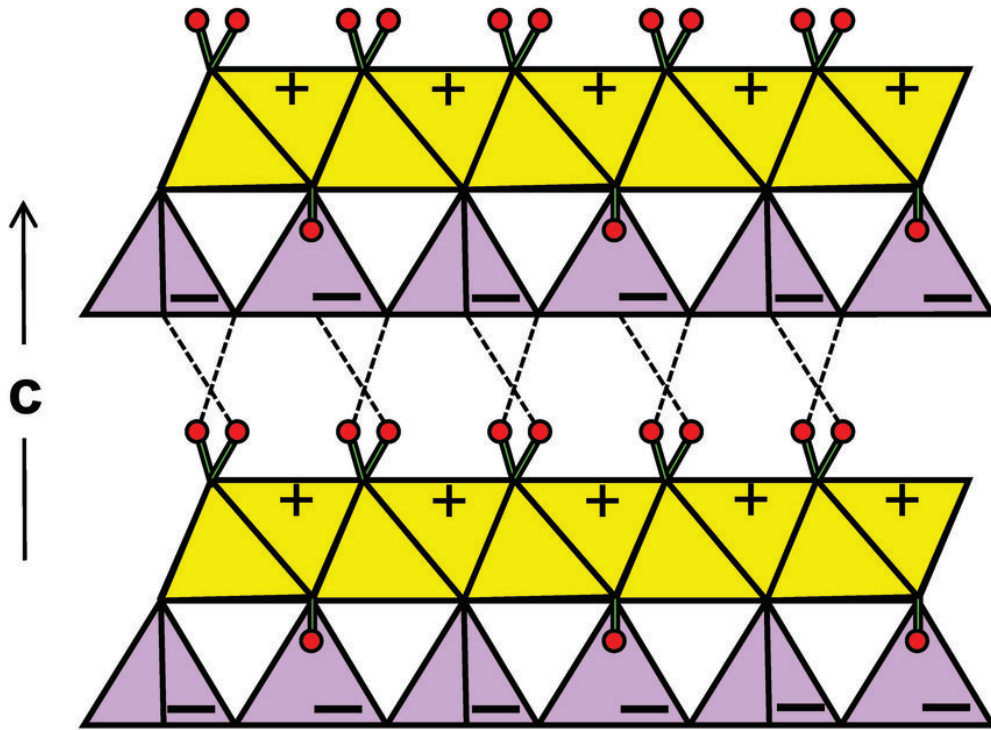


FIGURE 10

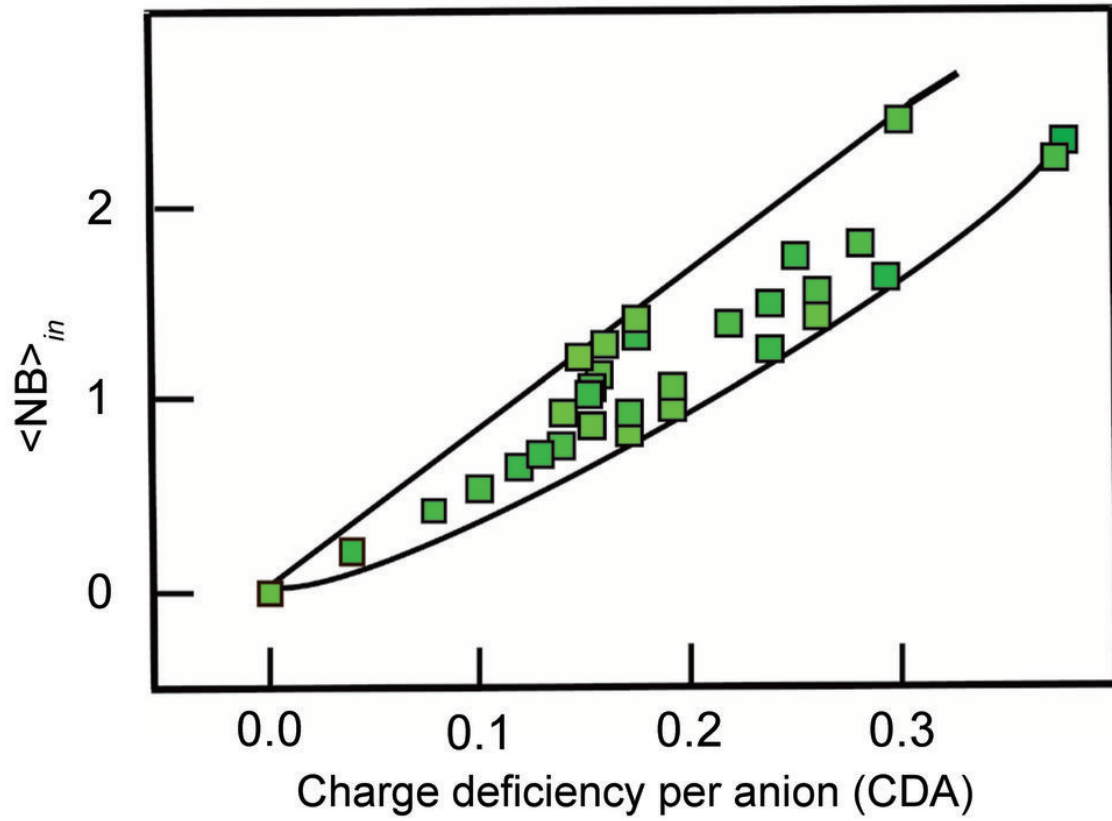


FIGURE 11

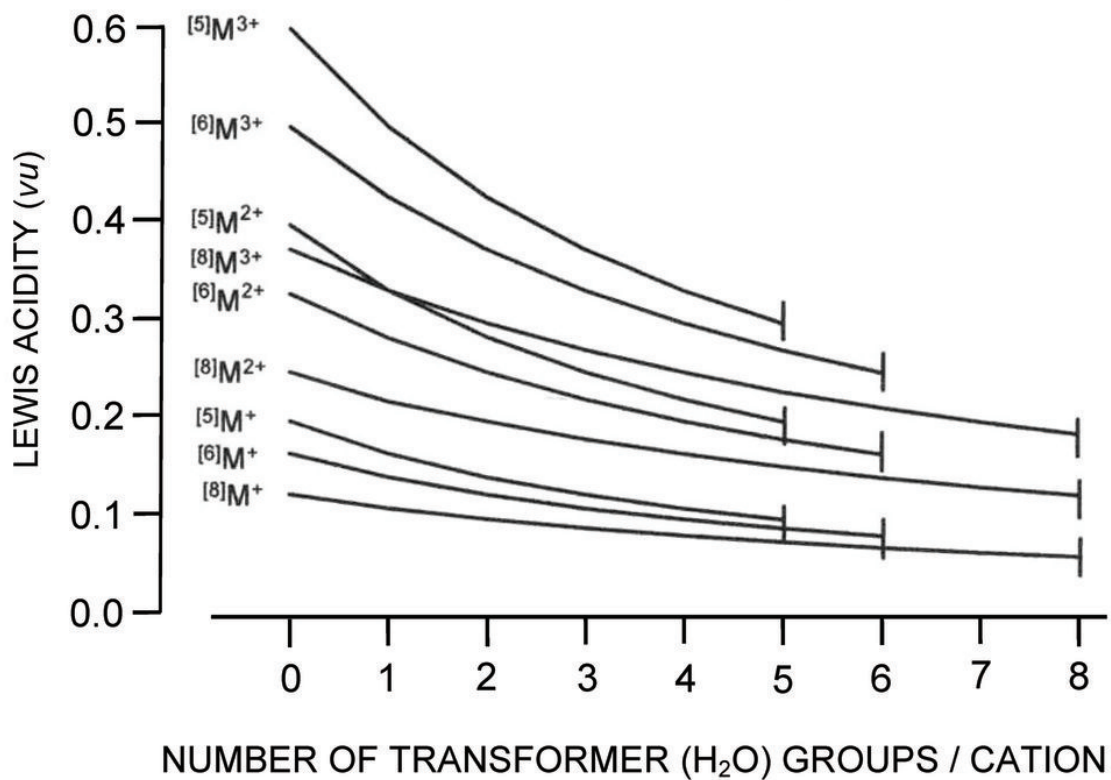


FIGURE 12

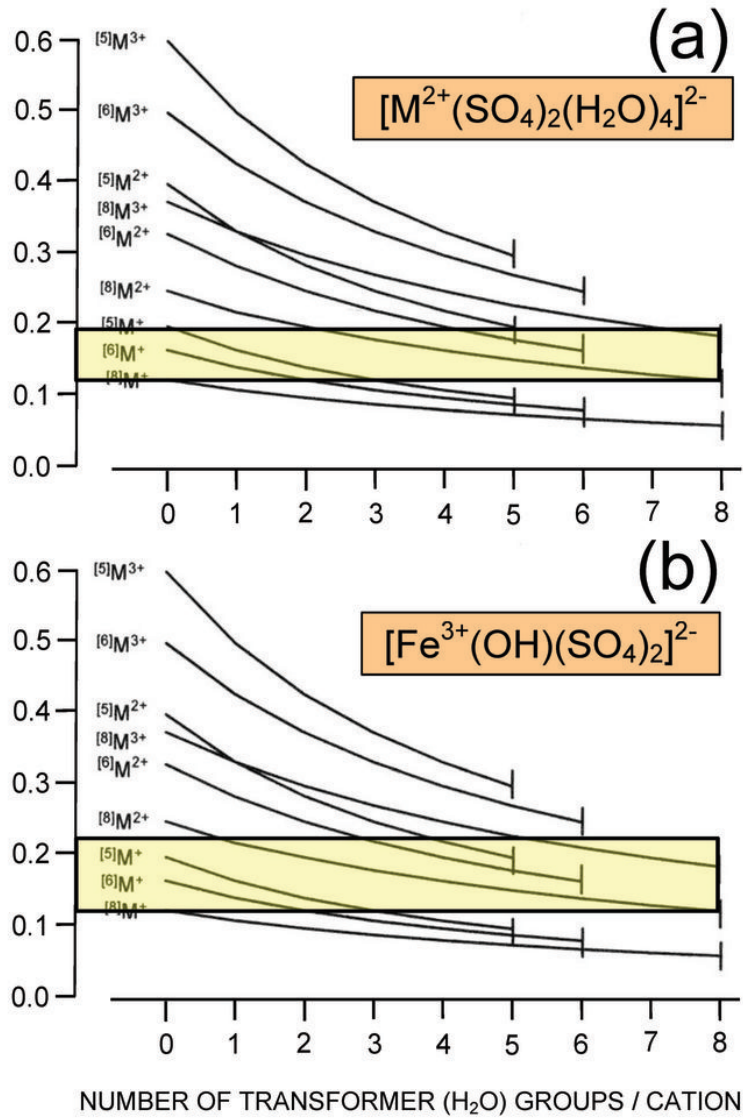


FIGURE 13

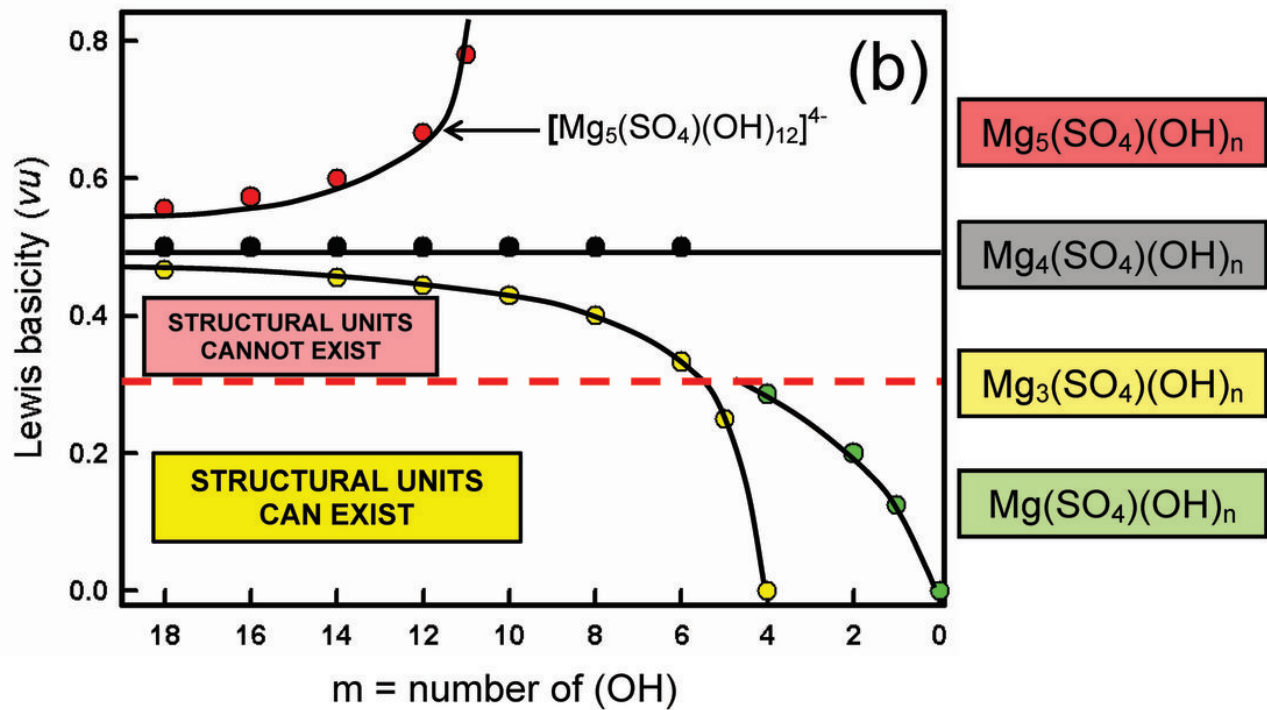
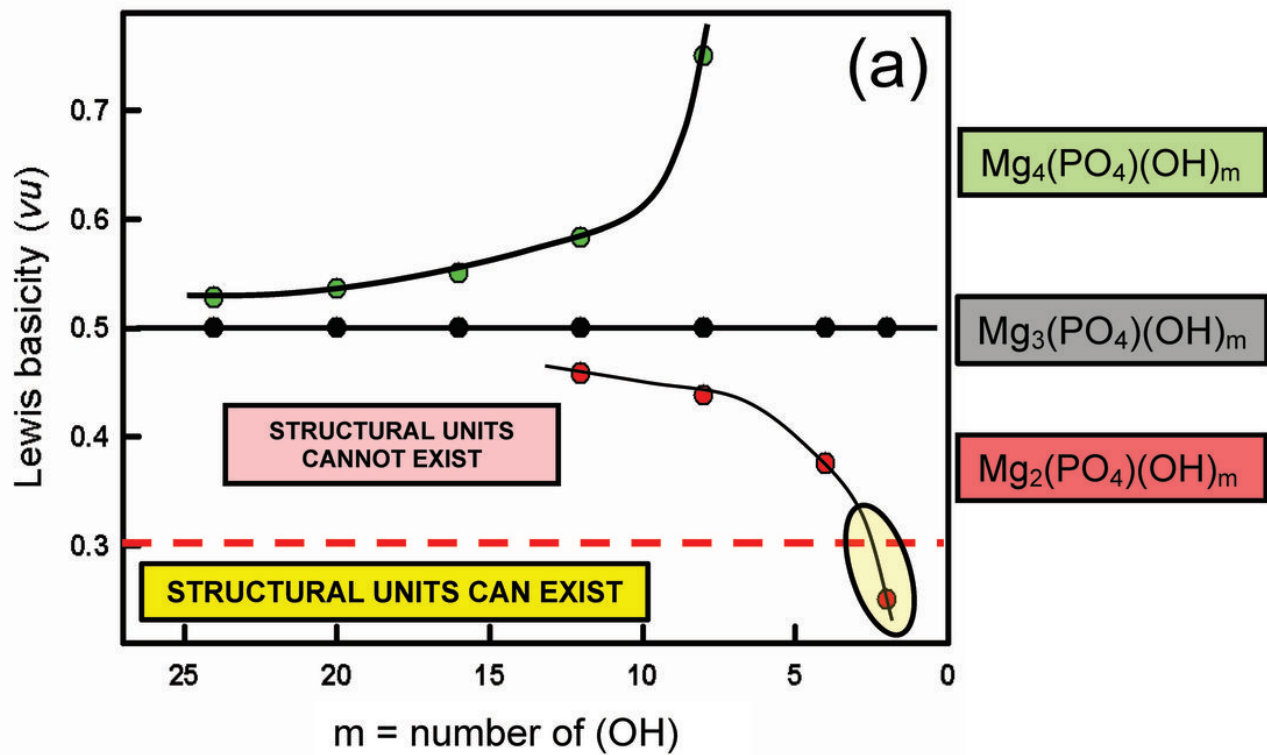


FIGURE 14

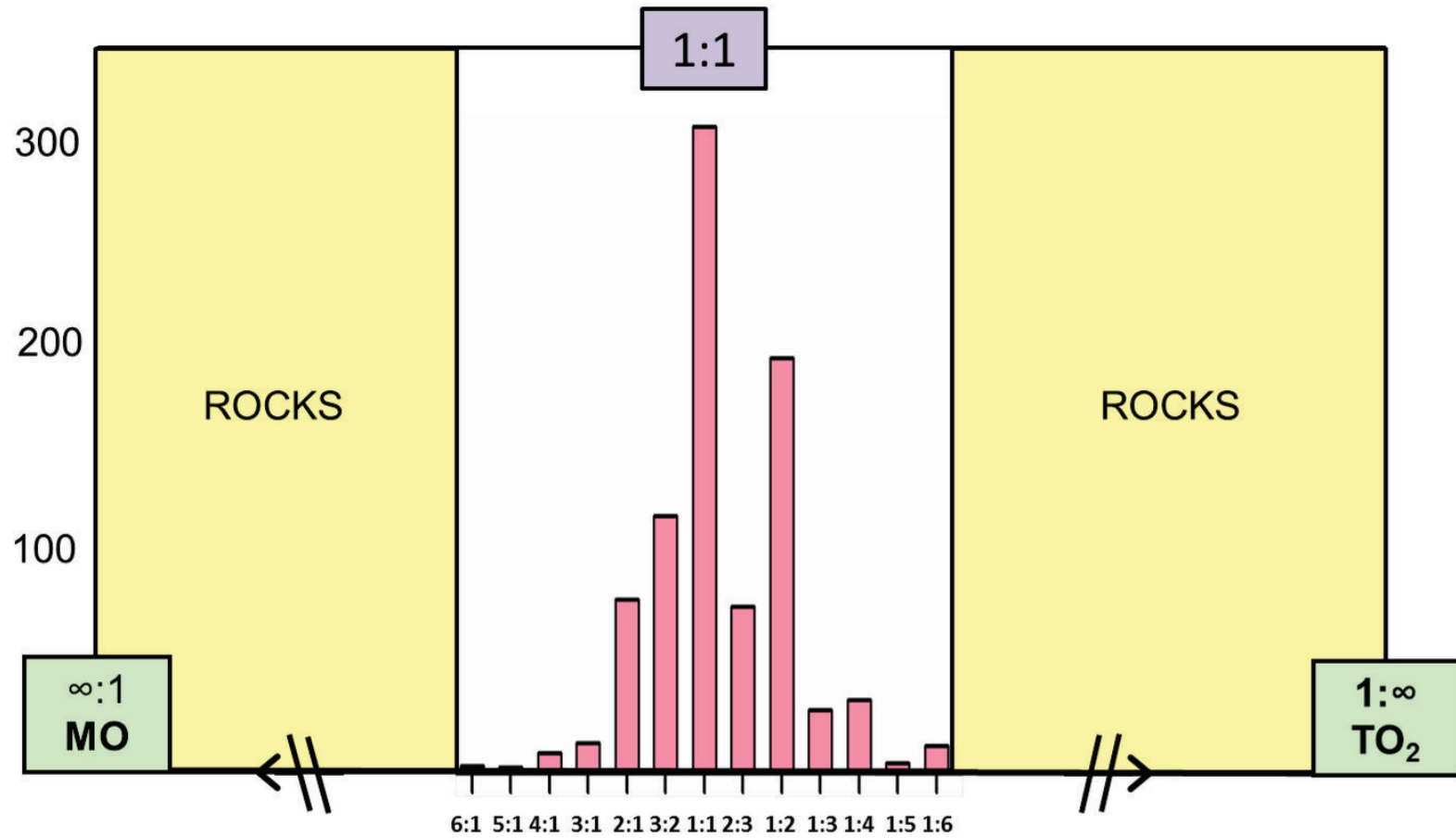


FIGURE 15

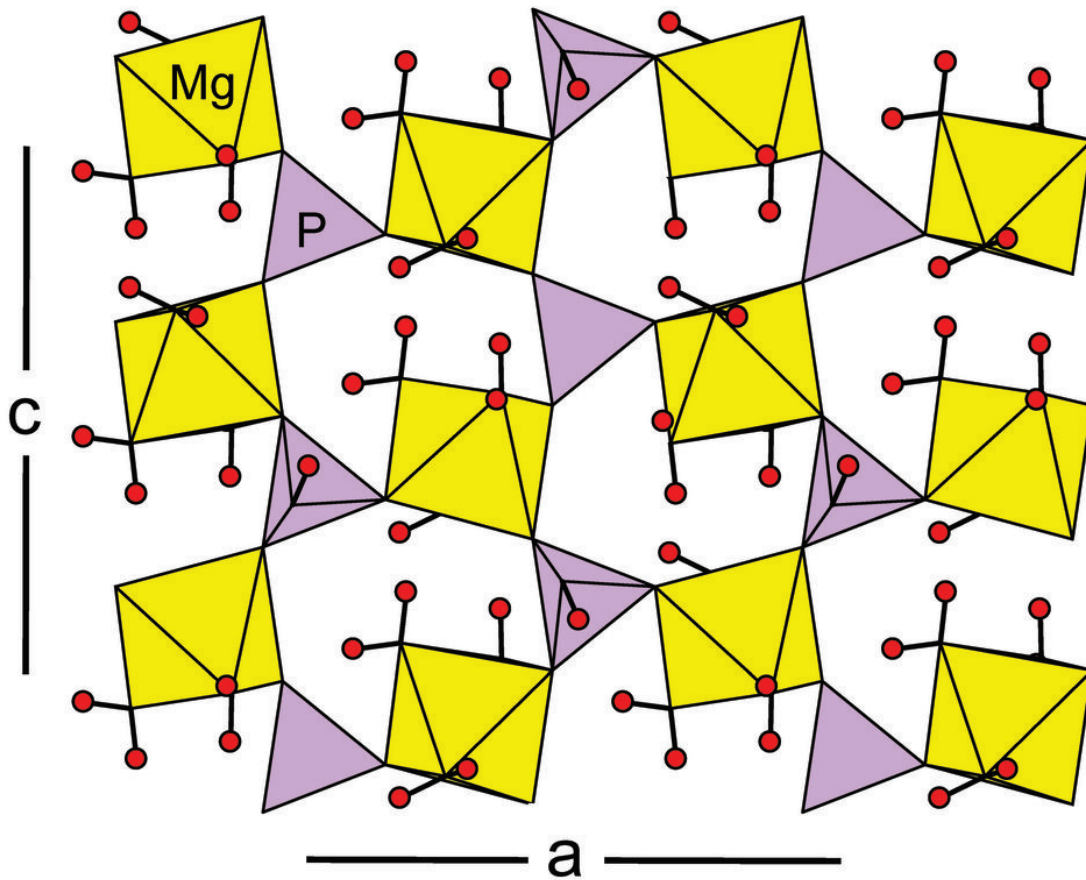


FIGURE 16

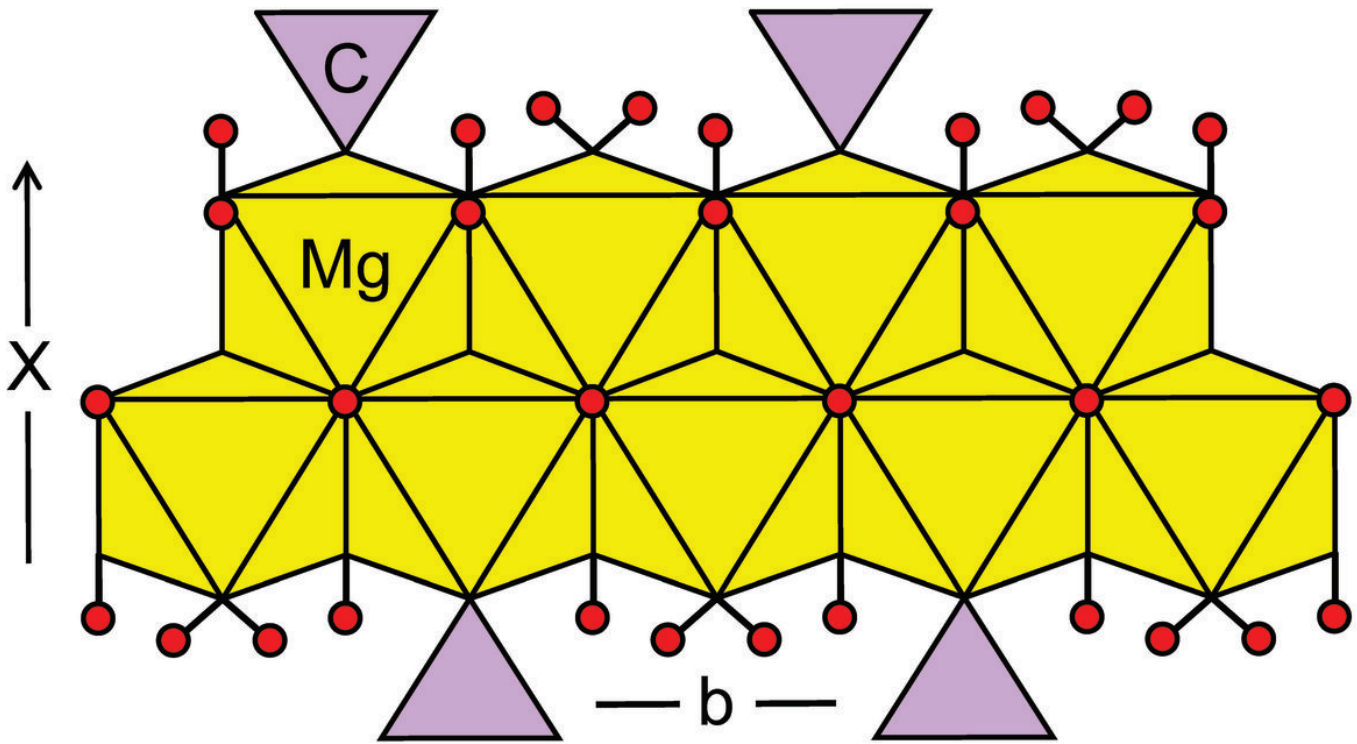


FIGURE 17

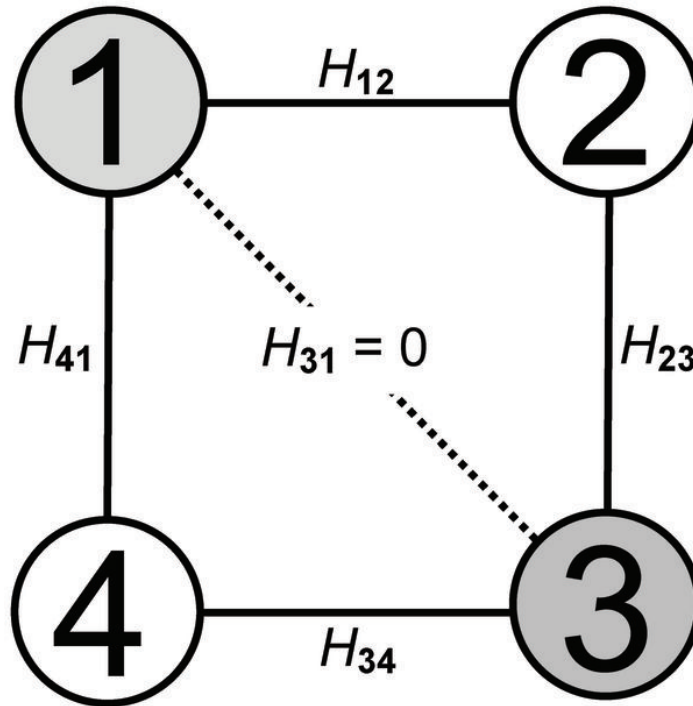


FIGURE 18

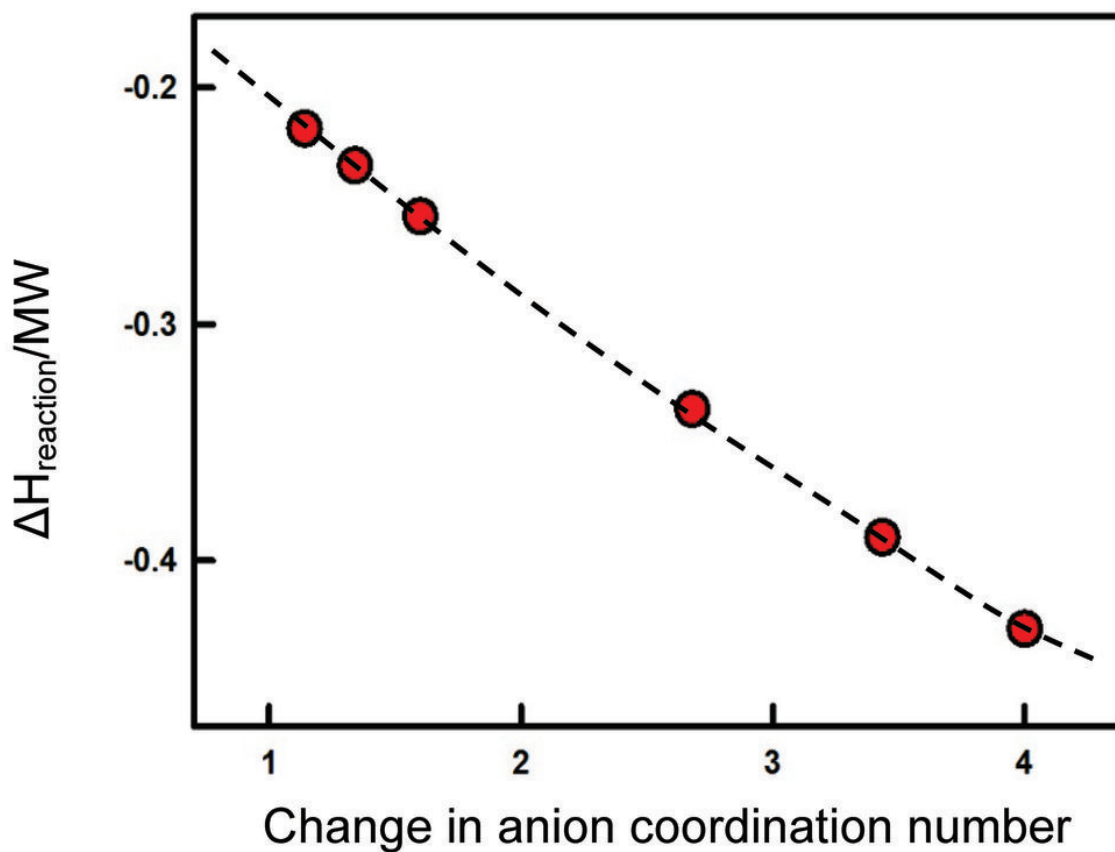


FIGURE 19