

Structural complexity of minerals: information storage and processing in the mineral world

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ABSTRACT

Structural complexity of minerals is characterized using information contents of their crystal structures calculated according to the modified Shannon formula. The crystal structure is considered as a message consisting of atoms classified into equivalence classes according to their distribution over crystallographic orbits (Wyckoff sites). The proposed complexity measures combine both size- and symmetry-sensitive aspects of crystal structures. Information-based complexity parameters have been calculated for 3949 structure reports on minerals extracted from the Inorganic Crystal Structure Database. According to the total structural information content, $I_{G,total}$, mineral structures can be classified into very simple (0–20 bits), simple (20–100 bits), intermediate (100–500 bits), complex (500–1000 bits), and very complex (> 1000 bits). The average information content for mineral structures is calculated as 228(6) bits per structure and 3.23(2) bits per atom. Twenty most complex mineral structures are ($I_{G,total}$ in bits): paulingite (6766.998), fantappieite (5948.330), sacrofanite (5317.353), mendeleevite-(Ce) (3398.878), bouazzerite (3035.201), megacyclite (2950.928), vanderiesscheite (2835.307), giuseppite (2723.097), stilpnomelane (2483.819), stavelotite-(La) (2411.498), rogermitchellite (2320.653), parsettensite (2309.820), apjohnite (2305.361), antigorite ($m = 17$ polysome) (2250.397), tounkite (2187.799), tschoertnerite (2132.228), farneseite (2094.012), kircherite (2052.539), bannisterite (2031.017), and mutinaite (2025.067). The following complexity-generating mechanisms have been recognized: modularity, misfit relationships between structure elements, and presence of nanoscale units (clusters or tubules). Structural complexity should be distinguished from topological complexity. Structural complexity increases with decreasing temperature and increasing pressure, though at ultra-high pressures, the situation may be different. Quantitative complexity measures can be used to investigate evolution of information in the course of global and local geological processes involving formation and transformation of crystalline phases. The information-based complexity measures can also be used to estimate the ‘ease of crystallization’ from the viewpoint of simplicity principle proposed by J.R. Goldsmith (1953) for understanding of formation of simple and complex mineral phases under both natural and laboratory conditions. According to the proposed quantitative approach, the crystal structure can be viewed as a reservoir of information encoded in its complexity. Complex structures store more information than simple ones. As erasure of information is always associated with dissipation of energy, information stored in crystal structures of minerals must have an important influence upon natural processes. As every process can be viewed as a communication channel, the mineralogical history of our planet on any scale is a story of accumulation, storage, transmission and processing of structural information.

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Introduction

RECENT contributions to the studies of mineral evolution on the Earth (Hazen *et al.*, 2008, 2009, 2011, 2012) and Mars (Bilbring *et al.*, 2006; Chevrier and Mathe, 2006) have attracted considerable attention to the problems of mineral diversity and complexity and their evolution through space and time. Whereas mineral diversity can be understood as the number of different mineral species present in an association, the concept of mineral complexity still lacks an exact and quantitative definition. The fact that mineralogy has not yet dealt with the complexity of minerals is in great contrast with the development of complexity theory that spans many different areas of natural and social sciences (Avery, 2003; Bonchev and Rouvray, 2005; Davies and Gregersen, 2010; Graham, 2011; etc.). The modern definitions of complexity of a system are based upon the amount of information that the system is able to register and process. In this aspect, the theory of complexity has strong links to information theory in its various forms. However, information theorists have never considered minerals or crystals as a subject of scientific endeavour. They usually refer to ideal crystals as ‘intuitively simple objects’ (Bennet, 1990), which is evidently a consequence of their limited experience with crystal structures. On the other hand, many experimentalists working with crystal structures of minerals often describe them or parts of them as ‘complex’ or ‘complicated’, which implies the existence of a certain intuitive feeling and appreciation of structural complexity (Buerger and Venkatakrishnan, 1974; Moore and Araki, 1974, 1977, 1978; Rinaldi, 1978; Ghose and Wan, 1979; Moore *et al.*, 1982; Moore and Shen, 1983; Hawthorne *et al.* 1993; Cooper and Hawthorne, 1994a,b; Burns and Hawthorne, 1994, 1995; Grew *et al.*, 1996; Grice *et al.*, 1996; Moelo *et al.*, 1997; Burns, 1999a; Pushcharovsky, 2000; Kolitsch, 2004; Rastsvetaeva *et al.*, 2010; Cooper *et al.*, 2010; Rumsey *et al.*, 2012). However, a quantitative definition of crystal-structure complexity was not formulated until recently (Krivovichev, 2012a,b). In this paper, I provide an outline of structural complexity theory of minerals from basic definitions to possible applications and directions for further development.

Historical remarks

Probably, the first consideration of structural complexity, at least in the published literature, should be assigned to Linus Pauling’s paper on ‘The principles determining the structure of complex ionic crystals’ (Pauling, 1929). Among his five rules, the fifth rule of parsimony deals directly with structural complexity. In its original formulation, it says that “the number of different types of constituents in a crystal tends to be small.” Hawthorne (2006) argues that

“This is not what the rule states, and many minerals (and high-temperature superconductors) do not accord with this interpretation. There are many minerals with a large number of chemical constituents (e.g. amphibole-group minerals, tourmaline-group minerals, graphite). The rule emphasizes that the number of topochemically different environments in a structure tends to be small. ... This rule has not seen much use, apart from in teaching, but it certainly seems to hold reasonably well, and its underlying cause is certainly of interest.”

Pauling (1929) did not provide any quantitative procedure to evaluate structural parsimony (he did not even mention this rule in the first edition of *The Nature of the Chemical Bond* (Pauling, 1939)), and this was done by Baur *et al.* (1983), who proposed two types of *parsimony indices* in order to describe topological and geometrical complexity in crystal structures.

The *topological parsimony index*, I_t , was defined by Baur *et al.* (1983) as

$$I_t = (t - e)/t \quad (1)$$

where t is the number of topologically distinct atom sites in the asymmetric unit, and e is the number of different chemical elements.

The crystallographic parsimony index, I_c , can be calculated as

$$I_c = (c - e)/c \quad (2)$$

where c is the number of crystallographically distinct atom sites. Within this approach, topological and crystallographic equivalence of atoms are understood in terms of *topological* and *crystallographic* symmetry groups, respectively. The topological symmetry group of an atomic arrangement is the highest symmetry group that the arrangement may adopt by continuous

transformation that does not involve breaking of any bonds between atoms. Crystallographic symmetry corresponds to the space group of the structure. Topological symmetry may be either higher or identical to (but not lower than) the crystallographic symmetry. This distinction between crystallographic and topological symmetry will be used in the following throughout the paper.

Baur *et al.* (1983) pointed out that the topological parsimony index is of primary importance and suggested subdividing structures into lavish ($I_t > 0.66$), intermediate ($0.66 > I_t > 0.33$) and parsimonious ($I_t < 0.33$). However, this index has little discriminative power: for instance, $I_t = I_c = 0$ for cubic halite (NaCl), tetragonal rutile (TiO₂), and cubic BaTiO₃. Neither index is sensitive either to chemical complexity or symmetry and both reflect only relations between the number of chemical elements and the number of topologically distinct atom sites. It is obvious that, for some complex minerals, it may happen that $e > t$, and therefore $I_t < 0$. Though parsimony is generally related to structural complexity, the parsimony indices proposed by Baur *et al.* (1983) cannot be used as complexity measures of crystal structures.

Mackay (2001) discussed various approaches to complexity of inorganic crystal structures. He suggested that it may be possible to estimate structural complexity in terms of algorithms by considering a structure as the result of the computer program necessary to generate it, where the complexity of a structure and the amount of information is measured by the length of this program. This approach, known in information theory as a Kolmogorov (or Kolmogorov-Chaitin) complexity (Kolmogorov, 1965; Chaitin, 1969, 1987) or algorithmic complexity, was further developed by Estevez-Rams and González-Férez (2009). These authors discussed the use of algorithmic complexity to define the notion of crystallinity. They proposed calculating the *Kolmogorov (or algorithmic) complexity* $K(s|N)$ of the structure s consisting of N atoms according to the following formula:

$$K(s|N) = |r^*| + |v^*| + |a^*| \quad (3)$$

where r^* is the set of generators of the space group, v^* are atom coordinates, and a^* is the algorithm to compute all atomic positions from r^* and v^* . The notation $|s|$ means 'the length of the string s '. In this definition, $K(s|N)$ provides a universal measure of the process of generating

crystal structures from lattice parameters, space-group generators and atomic coordinates. The measure can be applied to any crystal structure without regard to chemical composition and topology. However, there is no clear way to calculate the $K(s|N)$ value; in particular, Estevez-Rams and González-Férez (2009) provided no example of (or clear procedure for) such a calculation, which makes this parameter impractical in its present form. In addition, structural parameters can be determined with different level of precision, which would result in different amounts of information assigned to the same structure studied by different methods.

Mackay (2001) noted that many structures are hierarchical assemblies of smaller subunits, which contributes to their complexity. From the viewpoint of crystal-chemical classification of minerals, the subunits are coordination polyhedra with higher bond valences (Hawthorne, 1983, 1985, 1986, 1990, 1994, 1998; Sandomirskii and Belov, 1984; Liebau, 1985; Pushcharovsky *et al.*, 1998; Krivovichev and Filatov, 1999a), an approach that has been used since the earlier works on silicate structures (Machatschki, 1928; Pauling, 1929; Bragg, 1930, etc.). Many crystal structures can be described as assemblies of larger subunits of polyhedra (clusters, chains, layers), which can be derived from some simple parent structures and then recombined into structures with a higher level of complexity (Thompson, 1978; Makovicky, 1985, 1989, 1997; Egorov-Tismenko and Sokolova, 1990; Veblen, 1991; Ferraris, 1997; Merlino and Pasero, 1997; Egorov-Tismenko, 1998; Ferraris *et al.*, 2004, etc.). The hierarchical organization of crystal structures of minerals links structural mineralogy to the theory of complex hierarchical networks with the properties of clustering and modularity (Newman, 2006). The modular approach to the description of complex structural topologies and some other non-standard approaches (including cation arrays and anion-centred polyhedra (O'Keefe and Hyde, 1985; Krivovichev and Filatov, 1999a,b; Vegas and Jansen, 2002)) provided essential contributions to our understanding of the crystal-chemical reasons for the formation of complex structures, but did not result in the formulation of quantitative complexity measures. Complexity was destined to be "largely a qualitative, frequently intuitive, notion" (Burdett *et al.*, 1994). Large unit cells, low symmetries, distorted coordination environments, and the presence of chemically equivalent atoms

in different crystallographic sites were identified as indicators of structural complexity.

Different approaches to structural complexity of crystals were discussed by Steurer (2011). He proposed to distinguish between algorithmic (as defined by Estevez-Rams and González-Férez (2009)) and symbolic and combinatorial measures of complexity. *Symbolic complexity* is “a function of system size, which is a function of the repeat period” for periodic structures, whereas *combinatorial complexity* “...can best account for higher symmetries of structural subunits (clusters). The less probable (symmetric) a configuration is, the higher is its complexity” (Steurer, 2011). In other words, symbolic complexity is a function of unit-cell volume or the number of atoms in the unit cell, whereas combinatorial complexity is a function of symmetry. Steurer (2011) calls special attention to the establishment of a universal measure of complexity which could be applied equally to periodic structures, incommensurately modulated structures and quasicrystals. He concluded that “no single complexity concept alone is able to reflect all facets of structural complexity”. As most minerals are crystals, in the following, I develop an approach that may be thought of as a combination of symbolic and combinatorial complexities understood in the context outlined by Steurer (2011).

Basic concepts and definitions

Information content of a message

The concept of information content was developed in connection with the theory of communication (Hartley, 1928; Shannon and Weaver, 1949). Information is measured in bits, or binary digits. Suppose that we have a message consisting of n symbols taken from an alphabet $\mathbf{S}$ consisting of precisely s different symbols. If the probabilities, $p_1, p_2, \dots, p_{s-1}, p_s$, of appearance of symbols from $\mathbf{S}$ are equal,

$$p_1 = p_2 = p_{s-1} = p_s = s^{-1} \quad (4)$$

$$\sum_{i=1}^s p_i = 1 \quad (5)$$

and the amount of information, H , conveyed by the message can be calculated as

$$H = n \log_2 s \text{ (bits)} \quad (6a)$$

or

$$H = n \log_2 s \text{ (bits/symbol)} \quad (6b)$$

This formula, known as a *Hartley equation*, allows calculation of the amount of information

that can be adapted by the system as a result of a process with several possible outcomes. In the case of a single coin toss, there are two possible outcomes: head (0) or tail (1), and the amount of information is equal to 1 bit. In the case of two sequential coin tosses, there are four equally probable outcomes: 00, 01, 10, and 11, and the amount of information is equal to 2 bits. If a process has three equally probable outcomes, the amount of information registered by the system is $H = \log_2 3 = 1.585$ bits.

Where symbols in $\mathbf{S}$ have different probabilities, the information content of the message is calculated according to the *Shannon formula*

$$H = - \sum_{i=1}^s p_i \log_2 p_i \text{ (bits/symbol)} \quad (7)$$

where p_i is the probability of occurrence of the i th symbol from $\mathbf{S}$. Where the probabilities of all symbols are equal (i.e. equation 4 holds true), equation 7 transforms into the Hartley formula (equation 6).

Information content and complexity of a graph

A graph, G , is defined as a structure consisting of a set of objects $V = \{v_1, v_2, \dots\}$ called vertices, and a set of unordered pairs of vertices $E = \{v_i, v_j\}$, whose elements are called edges. Graphs have found extensive application in crystal chemistry and structural mineralogy, e.g. when atoms (or coordination polyhedra) are identified with vertices and bonds (or interpolyhedral links) with edges (Moore, 1974; Hawthorne, 1983).

Rashevsky (1955) was the first to apply the Shannon formula to the information content of topological and geometrical structures. He considered a graph as a message and its vertices as symbols. Two vertices of a graph G are equivalent if their permutation does not result in a graph topologically different from (= non-isomorphic to) G . For instance, the graph shown in Fig. 1a consists of five vertices, which can be subdivided into three equivalence classes, C_1 , C_2 and C_3 . The first class, C_1 , consists of vertices 3 and 4 ($C_1 = \{3, 4\}$); these vertices are equivalent as their permutation does not change the topology of the graph. The same is true for vertices 2 and 5 which belong to the class C_2 . The third class, C_3 , consists of the vertex 1, which has no equivalent vertex in the graph. The probability of a vertex from certain class to be chosen randomly is equal to $2/5$ for C_1 and C_2 , and $1/5$ for C_3 : $p_1 = p_2 = 0.4$ and $p_3 = 0.2$. According to Rashevsky (1955) and Trucco

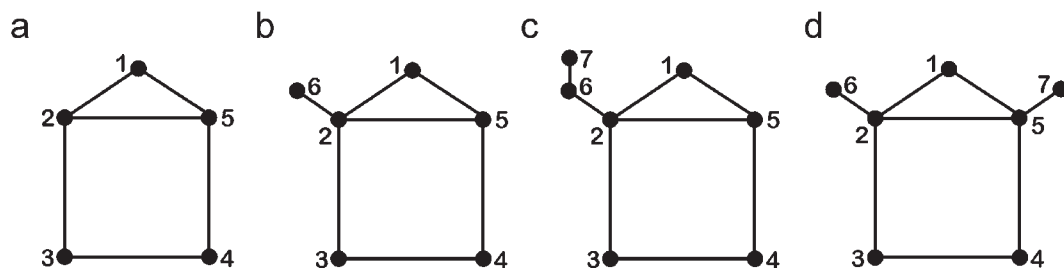


FIG. 1. Graphs of different complexity. See text for details.

(1956), the structural information content, I_G , of a graph, G , is defined as

$$I_G = -\sum_{i=1}^k p_i \log_2 p_i \text{ (bits/vertex)} \quad (8)$$

where p_i is the probability of occurrence of the vertex of the i th class and k is the number of different classes.

The information content of the graph shown in Fig. 1a is

$$I_G = -[0.2 \log_2(0.2) + 0.4 \log_2(0.4) + 0.4 \log_2(0.4)] = 1.53 \text{ bits/vertex.}$$

Its total information content, $I_{G,\text{total}}$, is equal to the product of I_G and the number of vertices, i.e. $5 \times 1.53 = 7.65$ bits.

The graphs shown in Fig. 1b,c,d illustrate the evolution of structural information content along the topological modifications of the initial graph shown in Fig. 1a. Addition of an additional vertex, (6), and an additional edge (2-6) to the vertex 2 (Fig. 1b) results in a dramatic increase in I_G , from 1.53 to 2.62 bits/vertex (the total information content increases from 7.65 to 15.72 bits, i.e. more than twice!). The reason for such an increase in information is that addition of vertex 6 and edge 2-6 destroys the symmetry of the original graph; now all the vertices of the graph are inequivalent. Addition of vertex 7 and edge 6-7 (Fig. 1c) results in a slight increase in I_G , from 2.62 to 2.80 bits/vertex ($I_{G,\text{total}}$ changes from 15.72 to 19.60 bits). However, addition of vertex 7 and edge 5-7 to the graph shown in Fig. 1b restores the symmetry of the original graph (Fig. 1d), and the information content drops from 2.62 to 1.96 bits/vertex. The total information content changes from 15.72 to 13.72 bits, i.e. the information content of the graph with 6 vertices shown in Fig. 1b is higher than that for the graph with 7 vertices shown in Fig. 1d.

The seminal work by Rashevsky (1955) was followed by extensive work summarized by Dehmer and Mowshowitz (2011). The informa-

tion content of a graph has been considered as a measure of its complexity: the more information the graph contains, the more complex it is. A number of different and complicated information-based complexity measures have been developed for complex graphs and networks of different nature and origin (Bonchev and Rouvray, 2005). Application of the Shannon formula to quantitative evaluation of the complexity of crystal structures was first done by Krivovichev (2012a).

Crystal structure as a message

From the topological point of view, a crystal structure can be mapped onto an infinite 3-dimensional graph (network) with the vertex set representing atoms and the edge set representing bonds. It is assumed that one bond links two atoms. Within this particular mapping procedure, a crystal-structure network is simple, i.e. it contains no loops or multiple edges, and is 3-periodic, i.e. there are three linearly independent translation vectors that map the graph into itself. Owing to its periodic character, the network of atoms and bonds in a crystal can be described using a finite graph that contains translationally non-equivalent vertices and edges only. From a mathematical point of view, transition from a 3-periodic net to its finite graph corresponds to the operation of projection, where all translationally equivalent vertices of the network project onto one vertex of the finite graph. This graph is called a *quotient graph* of a 3-periodic net (Chung *et al.*, 1984; Klee, 2004).

Figure 2a shows a simple 2-periodic graph consisting of black and white vertices. Its quotient graph (Fig. 2b) is quite simple, having 3-connected black and 2- and 4-connected white vertices. Figure 3a shows the structure of lopezite, $\text{K}_2\text{Cr}_2\text{O}_7$, a rare soluble secondary mineral discovered by Bandy (1937) in vugs in massive

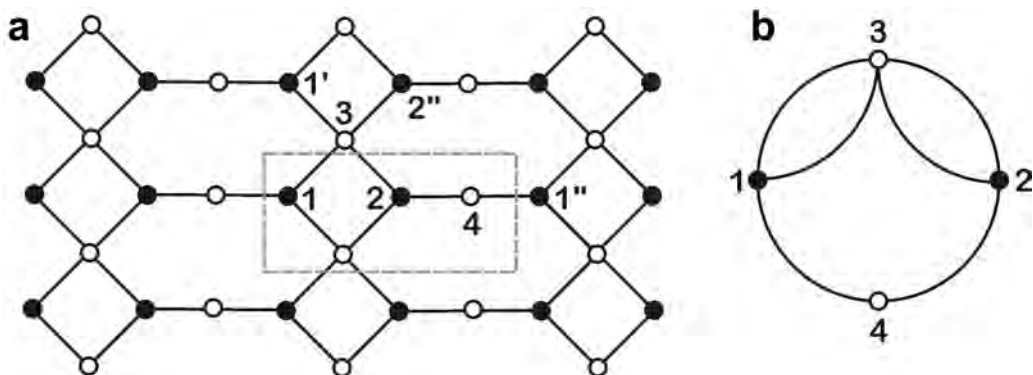


FIG. 2. (a) Two-dimensional periodic network and (b) its quotient graph.

nitrate rocks in Tarapaca mine, Chile. The quotient graph of the structure is shown in Fig. 3b, and one can easily observe its complexity.

As the quotient graph completely represents crystal-structure topology, its complexity has a direct correspondence to the complexity of the whole structure. Application of the Rashevsky formula (equation 8) requires equivalence criteria to be defined for the graph vertices. Krivovichev (2012a) suggested subdividing the vertices of a quotient graph into equivalence classes according to the Wyckoff sites that corresponding atoms occupy in the crystal structure. The important condition is that the multiplicity of a site should be related to the *reduced* (i.e. primitive) unit cell.

The following formula is proposed to calculate the *structural information content* of a crystal structure:

$$I_G = -\sum_{i=1}^k p_i \log_2 p_i \text{ (bits/atom)} \quad (9)$$

where k is the number of crystallographic orbits and p_i is the probability of occurrence of the atom of the i th crystallographic orbit, that is:

$$p_i = m_i/v \quad (10)$$

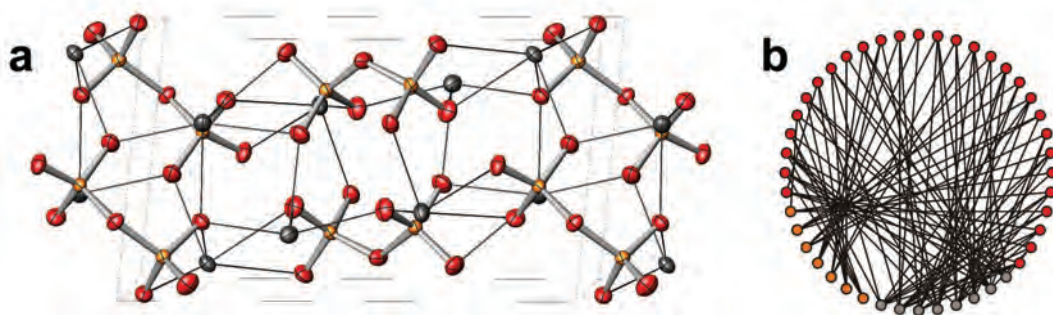
where m_i is the multiplicity of the crystallographic orbit relative to the reduced unit cell, and v is the number of atoms in the reduced unit cell (= number of vertices in the quotient graph).

For instance, the structure of lopezite (Fig. 3a) is triclinic, space group $P\bar{1}$ (Weakley *et al.*, 2004). All atoms in the structure occupy $2i$ Wyckoff sites: there are four K, four Cr, and fourteen O sites, which correspond to the total number of 22 equivalence classes. The total number of atoms in the reduced unit cell (which in this case coincides with the crystallographic unit cell) is 44. Atoms from each equivalence class have the same probability of occurrence equal to $2/44 = 0.0455$. The structural information content for lopezite is

$$I_G = -22 \times (2/44) \log_2 2/44 = 4.459 \text{ bits/atom.}$$

The total information content is determined by the formula:

$$I_{G,\text{total}} = v \times I_G \text{ (bits/unit cell)} \quad (11)$$

FIG. 3. (a) The crystal structure of lopezite, $K_2Cr_2O_7$, and (b) its quotient graph.

For lopezite, $I_{G,total} = 44 \times 4.459 = 196.196$ bits per unit cell (bits/u.c.).

The maximal structural information content $I_{G,max}$ for a graph G with v vertices occurs, where all vertices are non-equivalent according to the automorphism group of G (which is defined as a group of permutations of the graph vertices and edges that do not change one-to-one correspondence between them). It can be calculated according to the following formula:

$$I_{G,max} = \log_2 v \text{ (bits/vertex)} \quad (12)$$

In order for I_G to be independent of v , we may define the normalized structural information content, $I_{G,norm}$, as:

$$I_{G,norm} = I_G / I_{G,max} = -[\sum_{i=1}^k p_i \log_2 p_i] / \log_2 v \quad (13)$$

For the structure of lopezite, $I_{G,max} = \log_2 44 = 5.459$ bits/atom and $I_{G,norm} = 4.459 / 5.459 = 0.817$.

The approach described above considers structure as a message consisting of atoms; the complexity of the structure is determined by its information content calculated through the direct application of the modified Shannon formula. The I_G and $I_{G,norm}$ parameters are sensitive to the symmetry of the structure and thus describe its combinatorial complexity, whereas $I_{G,total}$ combines both symmetry and size of the structure, and therefore combines combinatorial and symbolic complexities in the context discussed by Steurer (2011).

Information density

The information-based complexity measures allow us to introduce the concept of *information density*, which can be defined as a number of bits of information per cubic ångström:

$$\rho_{inf} = I_{G,total} / V \text{ (bits/Å}^3\text{)} \quad (14)$$

where V is a unit-cell volume.

For lopezite, $\rho_{inf} = 0.270$ bits/Å³. For another modification of K₂Cr₂O₇ (Krivovichev *et al.*, 2000), $\rho_{inf} = 0.156$ bits/Å³, which indicates its lower complexity compared to lopezite. It is important to note that information density should be calculated using the volume of the reduced unit cell.

For two structures with similar unit cells but different symmetry, information density will be higher for the structure with lower symmetry (and higher complexity). For instance, cation ordering within the same unit cell would lead to the formation of superstructure with higher informa-

tion density than that of the original structure. This shows that unit-cell volume alone cannot be considered as a measure of structural complexity, since it reflects only symbolic complexity of the system and is not sensitive to its combinatorial complexity.

Information density can also be used as a measure of complexity for crystal structures of similar composition. The fact that complexity is a function of both information content and unit-cell volume makes it dependent upon the size of atoms and ions that constitute the respective crystal, as well as upon temperature and pressure. Suanite, Mg₂B₂O₅ (Guo *et al.*, 1995), and natrosilite, Na₂Si₂O₅ (Pant, 1968), have the same total structural information content (114.117 bits/u.c.), but their information densities are drastically different (0.333 and 0.242 bits/Å³, respectively), which is an obvious consequence of the different ionic radii of the Mg²⁺ and Na⁺ ions, on one hand, and of the B³⁺ and Si⁴⁺ ions, on the other.

Information content of crystals

As the total information content of the crystal structure, $I_{G,total}$, is defined per unit cell, it is possible to calculate a total information amount of particular crystals. For instance, a 1-mole crystal of α -quartz, P322₁, $Z = 3$, contains $\sim 2.00738 \times 10^{23}$ unit cells calculated as the Avogadro number, 6.02214×10^{23} (Mohr *et al.*, 2008), divided by $Z = 3$. The total information content of the crystal structure of α -quartz is $I_{G,total} = 8.265$ bits/u.c. Therefore, the total information content of the 1-mole crystal is equal to $\sim 16.59100 \times 10^{23}$ bits. This means that, similar to mass, entropy, volume, etc. information is an *extensive* property as opposed to *intensive* properties such as temperature and pressure. The approach suggested here allows us to calculate the information amount of any finite aggregate of crystals, e.g. paragenetic associations or particular rocks.

Structural vs. topological complexity

Nepheline, Na₃K(AlSiO₄)₄, and kalsilite, KAlSiO₄, are two important feldspathoid minerals with structures based on a three-dimensional framework of high-tridymite type, stuffed with alkali-metal cations. The topological information content of the framework of tetrahedra (which corresponds to its modification of highest symmetry) is very low (17.510 bits/u.c.).

However, Al–Si ordering, stuffing the framework with Na^+ and K^+ ions, and its distortions due to tilting of tetrahedra, lead to a significant increase in information content. Nepheline with space group $P6_3$ (Foreman and Peacor, 1970) has $I_{G,\text{total}} = 193.134$ bits/u.c., whereas kalsilite 1H (Dollase and Freeborn, 1977) and kalsilite 1T (Cellai *et al.*, 1997) have 45.510 and 29.793 bits/u.c., respectively. Trikalsilite (Bonaccorsi *et al.*, 1988) and panunzite (a natural analogue of tetrakalsilite; Merlino *et al.*, 1985), are modifications of kalsilite, where combination of atomic ordering and complex distortions results in a dramatic increase of the $I_{G,\text{total}}$ value to 562.942 and 1182.496 bits/u.c., respectively. The structural complexity defined by equations 9, 11 and 13 may be higher than the topological complexity, which makes the latter more important in the study of the structural topology of minerals. In addition, information-based parameters of structural complexity are dependent on correct crystal-structure determination, whereas topological information content is a measure of topological complexity only. The latter can be seen as a complexity of crystal structure network defined in terms of vertices with different topological functions. The concept of topological complexity can better be explained in terms of topological structure and the complexity of structural units considered as networks of atoms and bonds.

Topological complexity of structural units

The information-based complexity measures described above can be applied to the topological complexity of structural units of any size and dimensionality (Krivovichev, 2012b). In order to do this, one has to identify topologically distinct atoms and to find out their relative quantities within the cluster (if the unit is zero-dimensional) or translationally independent part of the structural unit.

Let us consider the finite clusters of tetrahedra shown in Fig. 4a–d. We denote atoms at the centres of tetrahedra as X and those at corners of tetrahedra as M. As the clusters shown in Fig. 4a–d are finite, their quotient graphs are topologically identical to the clusters themselves. A single tetrahedron XM_4 (Fig. 4a) contains vertices of two types, X and M, in the ratio of X:M = 1:4 ($v = 5$). Therefore, the probability of occurrence of different types of vertices can be written as follows:

$$\begin{aligned} \text{X:} & \quad m_1 = 1; p_1 = 0.2 \\ \text{M:} & \quad m_2 = 4; p_2 = 0.8 \end{aligned}$$

According to equation 9, the topological information content of a single tetrahedron is:

$$I_G = - [0.2 \times \log_2(0.2) + 0.8 \times \log_2(0.8)] = \log_2 5 - 1.6 = 0.722 \text{ bits/atom}$$

The normalized topological information content is:

$$I_{G,\text{norm}} = 0.722/\log_2 5 = 0.316$$

and the total information content is:

$$I_{\text{vd}} = 5 \times 0.722 = 3.610 \text{ bits}$$

A dimer of two edge-sharing tetrahedra (Fig. 4b) is obviously more complex than a single tetrahedron, as its M vertices now belong to two distinct topological types: M_1 and M_2 . In turn, a finite cluster of three *trans*-edge-sharing tetrahedra is even more complex, as its atoms correspond to four topologically different types: X_1 , X_2 , M_1 and M_2 (Fig. 4c). It is obvious that complexity increases with increasing number n of edge-sharing tetrahedra (= multiplicity of a structural unit) (Fig. 4d). The general formula of finite clusters of *trans*-edge-sharing tetrahedra is $[\text{X}_n\text{M}_{2n+2}]$. Some simple geometrical considerations provide the following general equations for the topological information content:

(1) n is odd ($n = 2m + 1$, where m is a positive integer or zero):

$$I_G = \log_2[3n + 2] - (5n + 3)/(3n + 2) \quad (15)$$

$$I_{G,\text{norm}} = 1 - (5n + 3)/((3n + 2)\log_2[3n + 2]) \quad (16)$$

$$I_{G,\text{total}} = (3n + 2)\log_2[3n + 2] - (5n + 3) \quad (17)$$

(2) n is even ($n = 2m$, where m is a positive integer):

$$I_G = \log_2[3n + 2] - (5n + 2)/(3n + 2) \quad (18)$$

$$I_{G,\text{norm}} = 1 - (5n + 2)/((3n + 2)\log_2[3n + 2]) \quad (19)$$

$$I_{G,\text{total}} = (3n + 2)\log_2[3n + 2] - (5n + 2) \quad (20)$$

Thus, under topological conditions of linkage of tetrahedra *via* sharing of their *trans*-edges, the I_G , $I_{G,\text{norm}}$ and $I_{G,\text{total}}$ parameters are the functions of n .

Figure 4f–i shows multiple chains formed by successive linkage of the single $[\text{X}_2\text{M}_4]$ chain of *trans*-edge-sharing tetrahedra (Fig. 4f). Multiple chains of *trans*-edge-sharing tetrahedra (Fig. 4f–i) have the general formula $[\text{X}_{2n}\text{M}_{2(n+1)}]$, where n is a chain multiplicity, i.e. the number of single chains in the multiple chain. Chains with n up to 6 are known (see below).

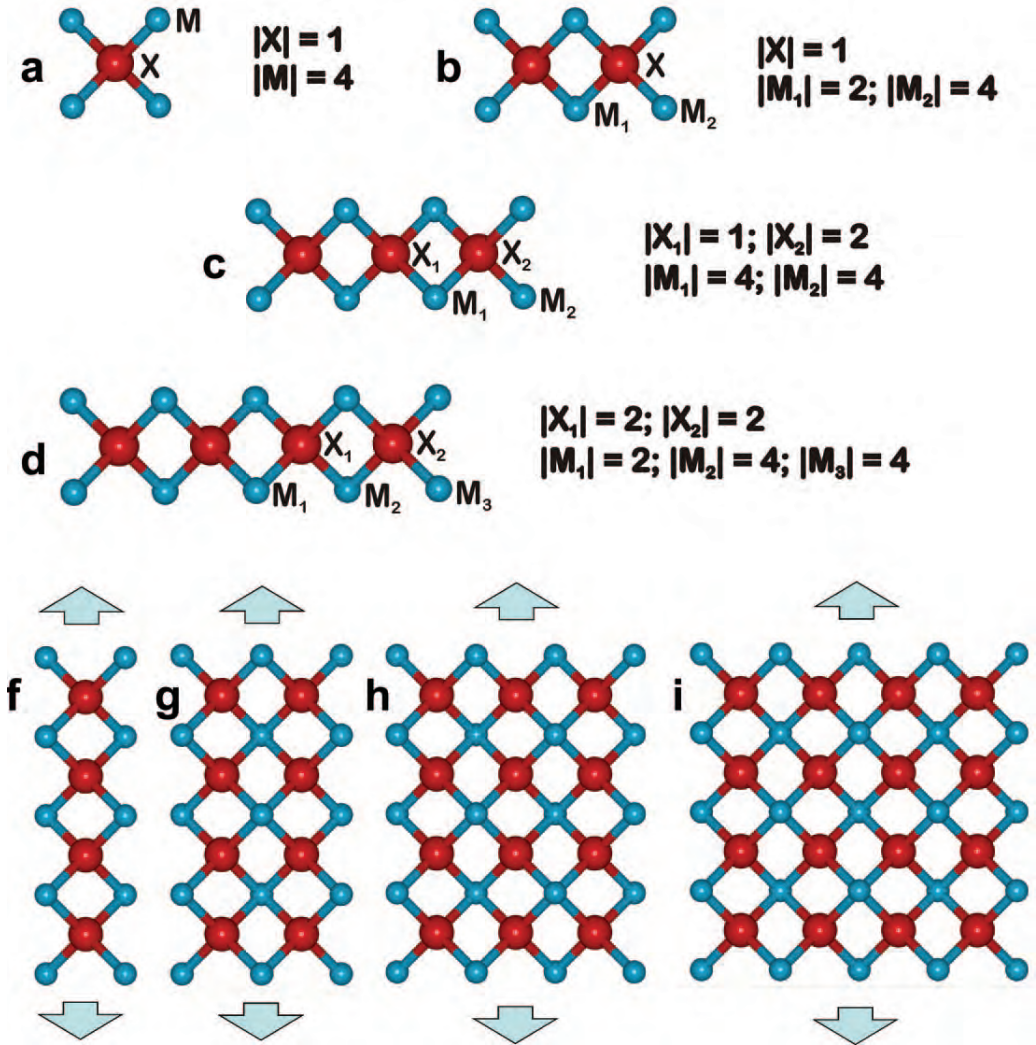


FIG. 4. (a) Single tetrahedron, (b–d) finite clusters of edge-sharing tetrahedra and (f–i) infinite chains of edge-sharing tetrahedra.

Topological information content and its normalized version are the same for chains with odd and even n values and can be calculated according to the following equations:

$$I_G = \log_2[2n + 1] - 2n/(2n + 1) \quad (21)$$

$$I_{G,norm} = [\log_2[2n + 1] - 2n/(2n + 1)] / (1 + \log_2[2n + 1]) \quad (22)$$

$$I_{G,total} = 2(2n + 1) \log_2[2n + 1] - 4n \quad (23).$$

The same kind of calculation can be done for silicate anions, where the occurrence of multiple structural units is quite frequent (Liebau, 1985).

For finite chains of corner-sharing tetrahedra, $[\text{Si}_n\text{O}_{3n+1}]$, complexity increases with increasing multiplicity n (Fig. 5a–d). It does not take much effort to detect that information-content measures are different for the finite chains with odd and even values of n .

(1) n is odd ($n = 2m + 1$, where m is a positive integer or zero):

$$I_G = \log_2[4n + 1] - (6n + 3.510)/(4n + 1) \quad (24)$$

$$I_{G,norm} = 1 - (6n + 3.510) / ((4n + 1) \log_2[4n + 1]) \quad (25)$$

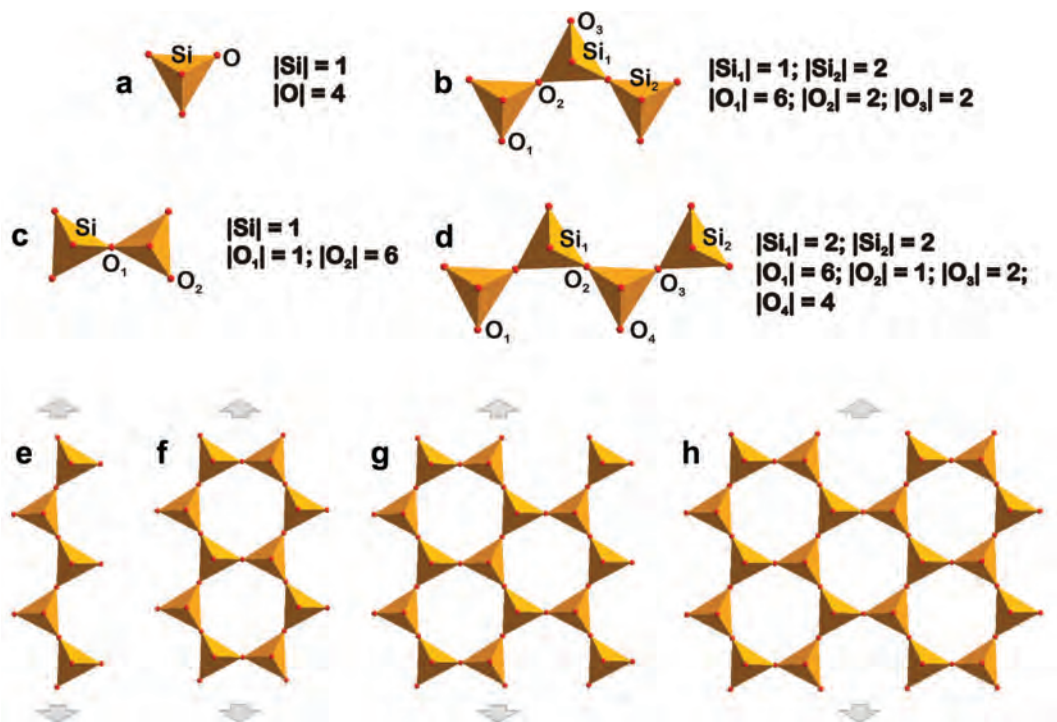


FIG. 5. Structural units based upon corner-sharing tetrahedra. See text for details

$$I_{G,\text{total}} = (4n + 1)\log_2[4n + 1] - (6n + 3.510) \quad (26)$$

(2) n is even ($n = 2m$, where m is a positive integer):

$$I_G = \log_2[4n + 1] - (6n + 5.510)/(4n + 1) \quad (27)$$

$$I_{G,\text{norm}} = 1 - (6n + 5.510)/((4n + 1)\log_2[4n + 1]) \quad (28)$$

$$I_{G,\text{total}} = (4n + 1)\log_2[4n + 1] - (6n + 5.510) \quad (29)$$

A similar approach can be used for *zweier* multiple-chain silicate anions, $[\text{Si}_{2n}\text{O}_{5n+1}]$, present in chain biopyriboles such as pyroxenes ($n = 1$), amphiboles ($n = 2$), chesterite and jimthompsonite ($n = 3$) (Fig. 5*f–i*). The information-based topological-complexity measures for these one-dimensional structural units can be calculated according to the following equations (for the sake of uniformity, a single chain is treated in the same manner as multiple chains, though its topological symmetry is obviously higher).

(1) n is odd ($n = 2m + 1$, where m is a positive integer or zero):

$$I_G = \log_2[7n + 1] - (9n + 1)/(7n + 1) \quad (30)$$

$$I_{G,\text{norm}} = 1 - (9n + 1)/((7n + 1)\log_2[7n + 1]) \quad (31)$$

$$I_{G,\text{total}} = (7n + 1)\log_2[7n + 1] - (9n + 1) \quad (32)$$

(2) n is even ($n = 2m$, where m is a positive integer):

$$I_G = \log_2[7n + 1] - 9n/(7n + 1) \quad (33)$$

$$I_{G,\text{norm}} = 1 - 9n/((7n + 1)\log_2[7n + 1]) \quad (34)$$

$$I_{G,\text{total}} = (7n + 1)\log_2[7n + 1] - 9n \quad (35)$$

Figure 6 shows information-based complexity measures I_G and $I_{G,\text{total}}$ vs. n expressed according to equations 15–35. As can be seen, the topological-information content increases with increasing multiplicity of the structural units. However, for units with edge-sharing tetrahedra, the rate of the increase is not as large as that for units with corner-sharing tetrahedra. This correlates with the occurrence of multiple chains in minerals and inorganic compounds. Multiple chains of *trans*-edge-sharing tetrahedra of the kinds shown in Fig. 4*f–i* are known in minerals for $n = 1$ [e.g. $[\text{O}_2\text{Pb}_4]^{4+}$ chains in lanarkite, $\text{Pb}_2\text{O}(\text{SO}_4)$ (Sahl, 1970), phenicochroite, $\text{Pb}_2\text{O}(\text{CrO}_4)$ (Williams *et al.*, 1970), philolite, $[\text{Pb}_{12}\text{O}_6]\text{Mn}(\text{Mg}, \text{Mn})_2(\text{Mn}, \text{Mg})_4(\text{SO}_4)(\text{CO}_3)_4$

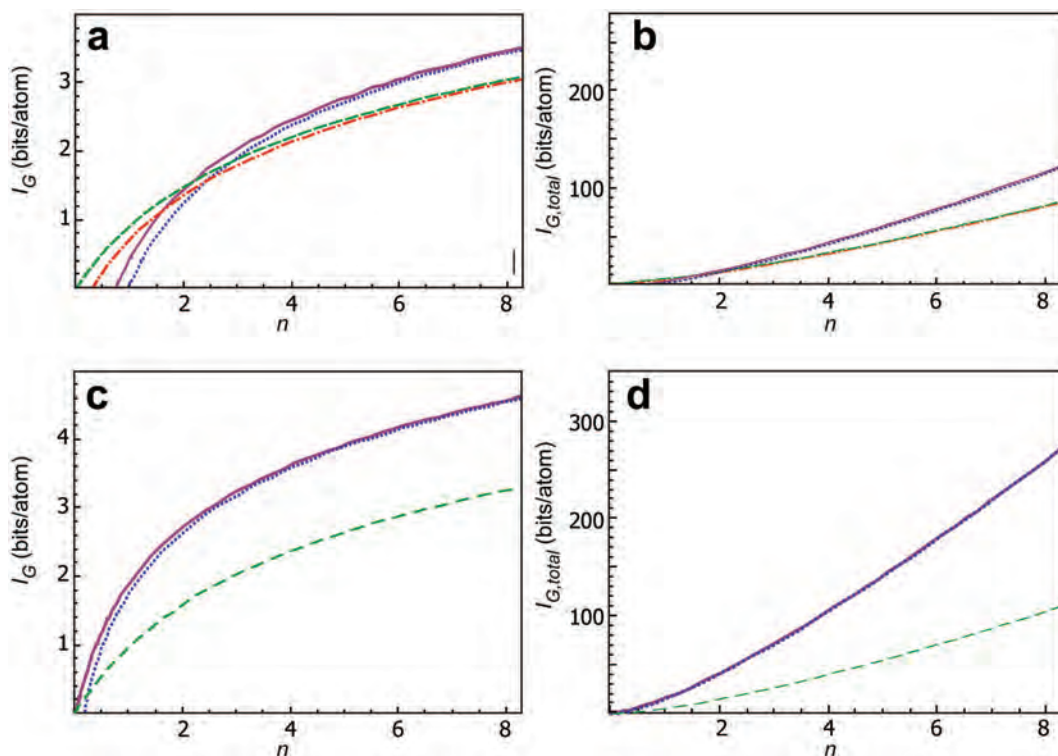


FIG. 6. Structural information content (I_G) and total structural information content ($I_{G,total}$) vs. multiplicity (n) for structural units based on linked tetrahedra (Figs 4 and 5): (a, b) for finite clusters of tetrahedra (green and red lines: finite clusters of edge-sharing tetrahedra with odd and even n , respectively; purple and blue lines: finite clusters of corner-sharing tetrahedra with odd and even n , respectively); (c, d) for infinite chains of tetrahedra (green line: chains of edge-sharing tetrahedra; purple and blue lines: for chains of corner-sharing tetrahedra with odd and even n , respectively). See text for details.

$\text{Cl}_4(\text{OH})_{12}$ (Moore *et al.*, 2000), etc.; $[\text{O}_2\text{Cu}_4]^{4+}$ chains in piypite, $\text{K}_4\text{Cu}_4\text{O}_2(\text{SO}_4)_4[\text{Cu}_{0.5}\text{Cl}]$ (Effenberger and Zemmann, 1984), klyuchevskite, $\text{K}_3\text{Cu}_3(\text{Fe,Al})\text{O}_2(\text{SO}_4)_4$ (Gorskaya *et al.*, 1992), coparsite, $\text{Cu}_4\text{O}_2((\text{As,V})\text{O}_4)\text{Cl}$ (Starova *et al.*, 1998), etc.], $n = 2$ ($[\text{O}_2\text{Pb}_3]^{2+}$ chains in mendipite, $\text{Pb}_3\text{O}_2\text{Cl}_2$ (Pasero and Vacchiano, 2000; Krivovichev and Burns, 2001), damaraite, $\text{Pb}_3\text{O}_2(\text{OH})\text{Cl}$ (Keller *et al.*, 2001; Krivovichev and Burns, 2001), chloroxiphite, $\text{Pb}_3\text{CuO}_2(\text{OH})_2\text{Cl}_2$ (Siidra *et al.*, 2008b), rickturnerite, $\text{Pb}_7\text{O}_4[\text{Mg}(\text{OH})_4](\text{OH})\text{Cl}_3$ (Rumsey *et al.*, 2012), etc.; $[\text{Fe}_2\text{S}_3]^+$ chains in rasvumite, KFe_2S_3 (Mitchell *et al.*, 2004) and pautovite, CsFe_2S_3 (Pekov *et al.*, 2005), etc.). Multiple chains with $n > 3$ are unknown in minerals, but have been described in synthetic compounds (Colmont *et al.*, 2006; Huvé *et al.*, 2006). The total topological information content of the ‘maximal’ known

chain, $[\text{X}_{12}\text{M}_{14}]$, is equal to 74.586 bits per repeat unit.

In contrast, for multiple silicate chains, minerals are known only for $n \leq 3$. The triple chain in the structures of jimthompsonite, $\text{Mg}_5(\text{Si}_6\text{O}_{16})(\text{OH})_2$, and chesterite, $\text{Mg}_{17}(\text{Si}_{20}\text{O}_{54})(\text{OH})_6$ (Veblen and Burnham, 1978), has $I_{G,total} = 89.107$ bits per repeat unit, comparable to the value for the $[\text{X}_{12}\text{M}_{14}]$ chain of edge-sharing tetrahedra. It may be suggested that, in the world of inorganic and mineral crystalline compounds, there is a certain limit on the amount of information that can be contained by a single crystal structure in the form of a structural unit.

Complexity of structural units necessarily correlates with the complexity of the crystal structure that accommodates it. This can be followed by the sequence of chain biopyriboles with the increasing multiplicity of silicate chains, n :

$n = 1$: enstatite, MgSiO_3
 (*Pbca* (Sasaki *et al.*, 1982), $I_{G,\text{total}} = 265.754$ bits/u.c.);
 $n = 2$: anthophyllite, $\text{Mg}_7(\text{Si}_8\text{O}_{22})(\text{OH})_2$
 (*Pnma* (Welch *et al.*, 2011),
 $I_{G,\text{total}} = 715.508$ bits/u.c.);
 $n = 3$: jimthompsonite, $\text{Mg}_5(\text{Si}_6\text{O}_{16})(\text{OH})_2$
 (*Pbca* (Veblen and Burnham, 1978),
 $I_{G,\text{total}} = 1127.052$ bits/u.c.).

There is another conclusion that can be derived from Fig. 6, which may seem somewhat surprising: units based on edge-sharing tetrahedra are *simpler* than those based upon corner-sharing tetrahedra. If a structural topology in compounds with complexes of tetrahedra were dictated by the complexity alone, edge linkage of tetrahedra would dominate in inorganic compounds. However, the situation is exactly the opposite, owing to the considerable electrostatic repulsion forces associated with sharing edges of tetrahedra centred by high-valent cations (Si^{4+} , P^{5+} , S^{6+} , etc.). It should be noted that, for both cation- and anion-centred units of tetrahedra with central ions having an absolute charge 3 or 2 (e.g. Fe^{3+} , O^{2-} and N^{3-} -centred tetrahedral units), the repulsion forces reduce and edge linkage dominates structural organization, due to its lower information content (Bergerhoff and Paeslack, 1968; Krivovichev *et al.*, 1998; Magarill *et al.*, 2000; Schleid and Lissner, 2008; Siidra *et al.*, 2008a).

Methods

Information-based complexity measures for crystal structures of minerals were calculated using *TOPOS* software (Blatov *et al.*, 2000) with the function 'Information Measures' implemented by Prof. V.A. Blatov at the request of

the author. The parameters were calculated according to the formulae (9), (11) and (13) as defined above. At present, all atom sites with different sets of coordinates, irrespective of their occupancies, were included in the computation procedure. Thus, a structure with low-occupied disordered positions has greater complexity than a similar structure with completely ordered atom sites. At the same time, if one site is occupied by two or more elements simultaneously, it is treated as a single site, regardless of its mixed occupancy.

A total of 19531 structure reports on minerals was extracted from the *Inorganic Crystal Structure Database* (ICSD, version 2011-2) and analysed using *TOPOS*. From these, 3949 entries were selected according to the following criteria: (1) for the same mineral, the most recent and most complete structure refinement was chosen for final calculations (e.g. a structure report with determined H atoms was preferred over the report with no H atoms); (2) if the same mineral was refined in different space groups, the entries for each space group were used. The values of the structural information parameters for 3949 entries on mineral crystal structures can be found in Table S1 deposited as Supporting Information with the Principal Editor of *Mineralogical Magazine* and available at http://www.minersoc.org/pages/e_journals/dep_mat_mm.html

Figure 7 shows the total structural information content of minerals ($I_{G,\text{total}}$) vs. the information content per atom (I_G) and the number of atoms in the reduced unit cell (v). The graphs show that neither the symmetry-sensitive I_G , nor the size-sensitive v parameters can be used as single complexity measures, whereas the combined $I_{G,\text{total}}$ value is sensitive to both size and symmetry.

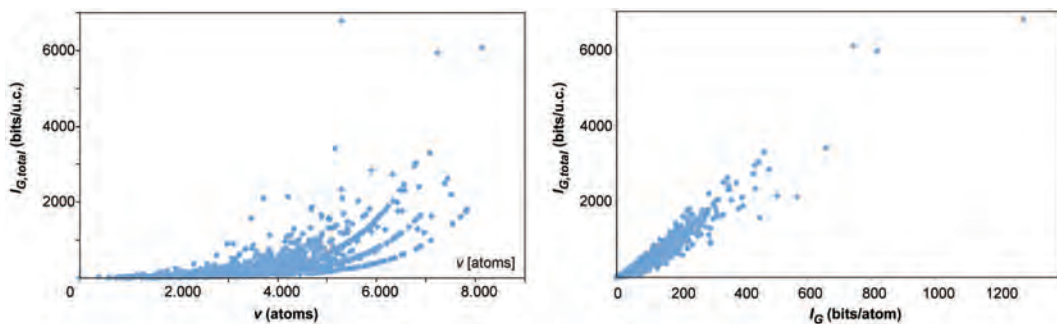


FIG. 7. The total structural information content of minerals ($I_{G,\text{total}}$) plotted against the number of atoms in the reduced unit cell (v ; above) and the information content per atom (I_G ; below).

Average information content and classification of minerals according to their complexity

Statistical analysis of the data compiled in Table S1 allows us to calculate the average information content for mineral structures as 228(6) bits/u.c. per structure and 3.23(2) bits per atom. A classification scheme for minerals according to their structural information content or complexity is presented in Table 1. Minerals can be subdivided into five categories: [1] very simple, [2] simple, [3] intermediate, [4] complex, and [5] very complex. Most of the rock-forming minerals fall into the first three categories. However, several exceptions are known. For instance, vesuvianite, a common mineral in skarns, is regarded as very complex. The structural complexity of vesuvianite is a consequence of its modularity: its structure is built from one-dimensional modules from the structure of grossular (Warren and Modell, 1931). Channels between the modules are occupied by a range of cations and anions, which results in a rather complex crystal-chemical behaviour (Allen and Burnham, 1992; Groat *et al.*, 1992*a,b*, 1993, 1994*a,b*; Gnos and Armbruster, 2006).

Which minerals are the most complex and information-rich?

General notes

Table 2 provides a list of the twenty most complex minerals known so far. All of them, except the oxyhydroxide vandendriesschieite, are oxysalts, i.e. contain TO_4 anions ($\text{T} = \text{Si}, \text{Al}, \text{S}, \text{P}, \text{As}, \text{B}$) either polymerized (silicates and aluminosilicates) or isolated (phosphates, arsenates, sulfates). It is worth noting that Table 2 does not include information-rich superstructures of simpler structure types reported in the ICSD, such as cannizzarite, $\text{Pb}_{46}\text{Bi}_{54}\text{S}_{127}$ (Matzat, 1979), djurleite, $\text{Cu}_{31}\text{S}_{16}$ (Evans, 1979), and the superstructure of wuestite, $\text{Fe}_{0.856}\text{O}$ (Andersson and Sleines, 1977). We also did not include the structure of bijvoetite, $\text{Y}((\text{UO}_2)_2\text{O}(\text{OH}(\text{CO}_3)_2)(\text{H}_2\text{O})_6$ (Li *et al.*, 2000), as it is a variation of the phosphuranylite topology (Burns, 2005), or biachellaite, $\text{Na}_{52}\text{Ca}_{36}\text{K}_{21}(\text{SO}_4)_{26}(\text{Si}_{90}\text{Al}_{90}\text{O}_{360})\text{Cl}_3(\text{H}_2\text{O})_6$ (Rastsvetaeva and Chukanov, 2008), the structure of which we were not able to confirm by independent investigation (there is also a tendency of the first author of the cited publication to lower the real symmetry of crystal structures). According to the data of Baur and Tillmanns (1964), the structure of natrophosphate,

TABLE 1. Classification of minerals according to their complexity.

Category	Total information content (bits/u.c.)	Approximate number of mineral species	Examples
Very simple	0–20	600	diamond, copper, halite, galena, uraninite, fluorite, quartz, corundum, ringwoodite, calcite, dolomite, zircon, goethite, lepidocrocite
Simple	20–100	1100	alunite, jarosite, nepheline, kieserite, szomolnokite, kaolinite, olivine-group minerals, diopside, orthoclase, albite, biotite 1 <i>M</i>
Intermediate	100–500	1800	enstatite, epidote, biotite 2 <i>M</i> ₁ , leucite, apatite, natrolite, talc 2 <i>M</i> , pyrope, grossular, beryl, muscovite 2 <i>M</i> ₁ , staurolite, actinolite, holmquistite, coesite, tourmaline, analcime, boracite
Complex	500–1000	300	eudialyte, steenstrupine, coquimbite, sapphirine, alum, cymrite, aluminite
Very complex	>1000	100	vesuvianite, paulingite, bouazzerite, ashcroftine-(Y), bementite, antigorite

TABLE 2. Twenty structurally most complex minerals (based on data published up to 2012) and their information-based complexity parameters.

Mineral name	Chemical formula	Space group	H at.*	dis.**	ν	I_G (bits/atom)	$I_{G,total}$ (bits/u.c.)	$I_{G,norm}$	Ref.
Paulingite	$K_6Ca_{16}(Al_{38}Si_{130}O_{336})(H_2O)_{113}$	$Im\bar{3}m$	no	yes	1278	5.295	6766.998	0.513	1
Fantappieite	$(Na_{82.5}Ca_{33}K_{16.5})(Al_{99}Si_{99}O_{396})(SO_4)_{33}(H_2O)_6$	$P\bar{3}$	no	yes	821	7.245	5948.330	0.748	2
Sacrofanite	$Na_{61}K_{19}Ca_{32}(Si_{84}Al_{84}O_{336})(SO_4)_{26}Cl_2F_6 \cdot 2H_2O$	$P\bar{6}2c$	no	yes	834	6.376	5317.353	0.657	3
Mendeleevite-(Ce)	$Cs_{12}(\square, K)_6(REE, Ca, \square)_{30}(Si_{70}O_{175})(H_2O, OH, F)_{35}$		no	yes	658	5.165	3398.878	0.552	4
Bouazzerite	$Bi_6(Mg, Co)_{11}Fe_{14}(AsO_4)_{18}O_{12}(OH)_4(H_2O)_{86}$	$P2_1/n$	no	no	446	6.805	3035.201	0.773	5
Megacyclite	$Na_{16}K_2(Si_{18}O_{36}(OH)_{18})(H_2O)_{38}$	$P2_1/c$	yes	no	436	6.768	2950.928	0.772	6
Vandendriesscheite	$Pb_{1.5}((UO_2)_{10}O_6(OH)_{11})(H_2O)_{11}$	$Pbca$	no	yes	480	5.907	2835.307	0.663	7
Giuseppettite	$Na_{42}K_{16}Ca_6(Si_{48}Al_{48}O_{192})(SO_4)_{10}Cl_2(H_2O)_5$	$P31c$	no	yes	430	6.333	2723.097	0.724	8
Stilpnomelane***	$KFe_8(AlSi_{11}O_{28})(OH)_8(H_2O)_2$	$P\bar{1}$	n.a.	no	336	7.392	2483.819	0.881	9
Stavelotite-(La)	$La_3Mn_3Cu(Fe_7Mn_{19})(Si_2O_7)_6O_{30}$	$P3_1$	n.a.	no	351	6.870	2411.498	0.813	10
Rogermitchellite	$Na_{12}(Sr, Na)_{24}Ba_4Zr_{26}Si_{78}(B, Si)_{12}O_{246}(OH)_{24}(H_2O)_{18}$	$P\bar{3}c$	no	yes	438	5.298	2320.653	0.604	11
Parsettensite***	$K_{7.5}Mn_{49}(Si_{64.5}Al_{7.5}O_{168})(OH)_{50}$	$C2/m$	no	yes	351	6.581	2309.820	0.778	9
Apjohnite	$MnAl_2(SO_4)_4(H_2O)_{22}$	$P2_1/c$	yes	no	356	6.476	2305.361	0.764	12
Tounkite	$Na_{31}Ca_{16}K(Si_{36}Al_{36}O_{144})(SO_4)_{10}Cl_8$	$P3$	yes	no	324	6.946	2250.397	0.833	13
Antigorite M	$Mg_{2.823}(Si_2O_5)(OH)_{3.639}$	$P1m1$	yes	no	291	7.518	2187.799	0.919	14
Tschoertnerite	$Ca_4Ca_3Cu_3(Si_{12}Al_{12}O_{48})(OH)_8(H_2O)_{20}$	$Fm\bar{3}m$	no	yes	505	4.222	2132.228	0.470	15
Farneseite	$Na_{46}Ca_{10}(Al_{42}Si_{42}O_{168})(SO_4)_{12}(H_2O)_6$	$P6_3/m$	no	yes	394	5.315	2094.012	0.616	16
Kircherite	$Na_{90}Ca_{36}K_{18}(Al_{108}Si_{108}O_{432})(SO_4)_{36}(H_2O)_6$	$R32$	no	yes	341	6.019	2052.539	0.715	17
Bannisterite	$KMn_{10}(Si_{15}AlO_{38})(OH)_8(H_2O)_6$	$A2/a$	no	yes	320	6.347	2031.017	0.763	18
Mutinaite	$NaCa(Al_3Si_{21}O_{48})(H_2O)_{15}$	$Pnma$	no	yes	360	5.625	2025.067	0.662	19

* H atoms determined (yes/no; part. = partially);

** dis. = presence of disorder (positions with low occupancy) (yes/no);

*** theoretical model.

References: (1) Gordon *et al.*, 1966; (2) Cámara *et al.*, 2010; (3) Bonaccorsi *et al.*, 2012; (4) Sokolova *et al.*, 2011; (5) Brugger *et al.*, 2007; (6) Yamnova *et al.*, 1992; (7) Burns, 1997; (8) Bonaccorsi, 2004; (9) Guggenheim and Eggleton, 1994; (10) Bernhardt *et al.*, 2005; (11) McDonald and Chao, 2010; (12) Menchetti and Sabelli, 1976; (13) Rozenberg *et al.*, 2004; (14) Capitani and Mellini, 2004; (15) Effenberger *et al.*, 1998; (16) Cámara *et al.*, 2005; (17) Cámara *et al.*, 2012; (18) Heaney *et al.*, 1992; (19) Vezzali *et al.*, 1997.

$\text{Na}_7\text{F}(\text{PO}_4)_2(\text{H}_2\text{O})_{19}$, should be regarded as very complex (2109.177 bits). The refinement of the structure by Genkina and Khomyakov (1992) on a natural crystal provided a more reasonable structure model in terms of the F positions, but, without the H atoms determined, their model registers only 888.586 bits/u.c. and falls into the category of complex structures (Table 1).

According to their crystal chemistry, the twenty structures listed in Table 2 can be subdivided into zeolites and complex feldspathoids, misfit layered silicates, minerals with nanoscale clusters and tubules, complex sulfates (apjohnite), and complex modular structures. Below, we provide a brief description of the structures to outline the basic features that are responsible for their high complexity.

Zeolites and complex feldspathoids

The most complex mineral known to date is the zeolite paulingite, $\text{K}_6\text{Ca}_{16}(\text{Al}_{38}\text{Si}_{130}\text{O}_{336})(\text{H}_2\text{O})_{113}$ (Gordon *et al.*, 1966), which registers 6766.998 bits/u.c. Its structure (Fig. 8a,b) is a complex aluminosilicate framework of three different types of secondary building units (Fig. 8c) linked into two interpenetrating **pcu** (primitive cubic) nets (Fig. 8d,e) connected by additional T nodes. The problem of complexity of paulingite was pointed out by Mackay and Klinowski (1986), and there are different approaches to decipher reasons for the mineral to be so complex (Shevchenko and Krivovichev, 2008; Blatov and Ilyushin, 2011; Ilyushin and Blatov, 2011). From the genetic point of view, the most reasonable explanation of zeolite complexity is in the crystal-growth mechanism of zeolites from prenucleation nanoclusters already existing in the crystallization media (de Moor *et al.*, 1999; Depla *et al.*, 2011, and references therein). It is of interest that, among zeolites, the paulingite framework (that has the symbolic notation PAU in the Atlas of Zeolite Structure Types (Baerlocher *et al.*, 2007)), is the second in its topological complexity (4763.456 bits/u.c.) after the framework SFV reported for the synthetic zeolite SSZ-57 by Baerlocher *et al.* (2011) (19557.629 bits/u.c.) (see Krivovichev, 2013 for details).

Sacrofanite, fantappiëite, giuseppettite, tounkite, kircherite, and farneseite are members of the sodalite-cancrinite supergroup (modular series) and will be considered in a separate section below.

Tschoertnerite, $\text{Ca}_4(\text{K}, \text{Ca}, \text{Sr}, \text{Ba})_3\text{Cu}_3(\text{Si}_{12}\text{Al}_{12}\text{O}_{48})(\text{OH})_8(\text{H}_2\text{O})_{20}$ (Effenberger *et al.*,

1998), is a complex Cu-containing zeolite from the Eifel Quaternary volcanic region (Germany). Its structure (Fig. 9a) is remarkable in that it contains five topologically different polyhedral secondary building units (Fig. 9b) that form a tiling of three-dimensional space without gaps and overlaps (Fig. 9c). The high complexity of tschoertnerite is probably the result of incorporation of Cu^{2+} cations, along with alkali metal and alkaline-earth elements, into framework cavities. The topological information content of the corresponding tetrahedral framework (TSC) is 888.469 bits, which is much lower than the structural information content (2132.228 bits). This shows that the complexity of the mineral is the result of combination of both framework topological complexity and the complexity of the extraframework content.

Misfit layered silicates

This group includes hydrated phyllosilicates with modulated structures induced by the misfit between tetrahedral and octahedral sheets (Guggenheim and Eggleton, 1988): stilpnomelane, parsettensite (Guggenheim and Eggleton, 1994), antigorite (polysome with $n = 17$: Capitani and Mellini, 2004), and bannisterite (Heaney *et al.*, 1992). The high structural-information content of these structures (Table 2) is due to the complexity of the tetrahedral sheets with islands of inverted tetrahedra (Fig. 10). The sheets are also remarkable in the topological diversity of the rings of tetrahedra: five-, six- and eight-membered rings in stilpnomelane (Fig. 10b), four-, five-, six- and twelve-membered rings in parsettensite (Fig. 10d), four-, six- and eight-membered rings in antigorite (Fig. 10f), and five-, six- and seven-membered rings in bannisterite (Fig. 10h). It should be noted that the structures of stilpnomelane and parsettensite have not been determined directly, and their structure models stored in the ICSD were obtained by a combination of electron diffraction and theoretical modeling. In general, misfit between structural elements is an important complexity-generating mechanism, as exemplified by the Fe, Mg and Mn layered silicates described above and by other hydrated phyllosilicates such as shafarovskite, $\text{K}_2\text{Na}_3(\text{Mn}, \text{Fe}, \text{Na})_4[\text{Si}_9(\text{O}, \text{OH})_{27}](\text{OH})_2 \cdot n\text{H}_2\text{O}$ ($n \sim 2.33$) (1602.588 bits/u.c.) (Krivovichev *et al.*, 2004a) and armbrusterite, $\text{K}_5\text{Na}_6\text{Mn}^{3+}\text{Mn}^{2+}_4[\text{Si}_9\text{O}_{22}]_4(\text{OH})_{10} \cdot 4\text{H}_2\text{O}$ (972.191 bits/u.c.) (Yakovenchuk *et al.*, 2007).

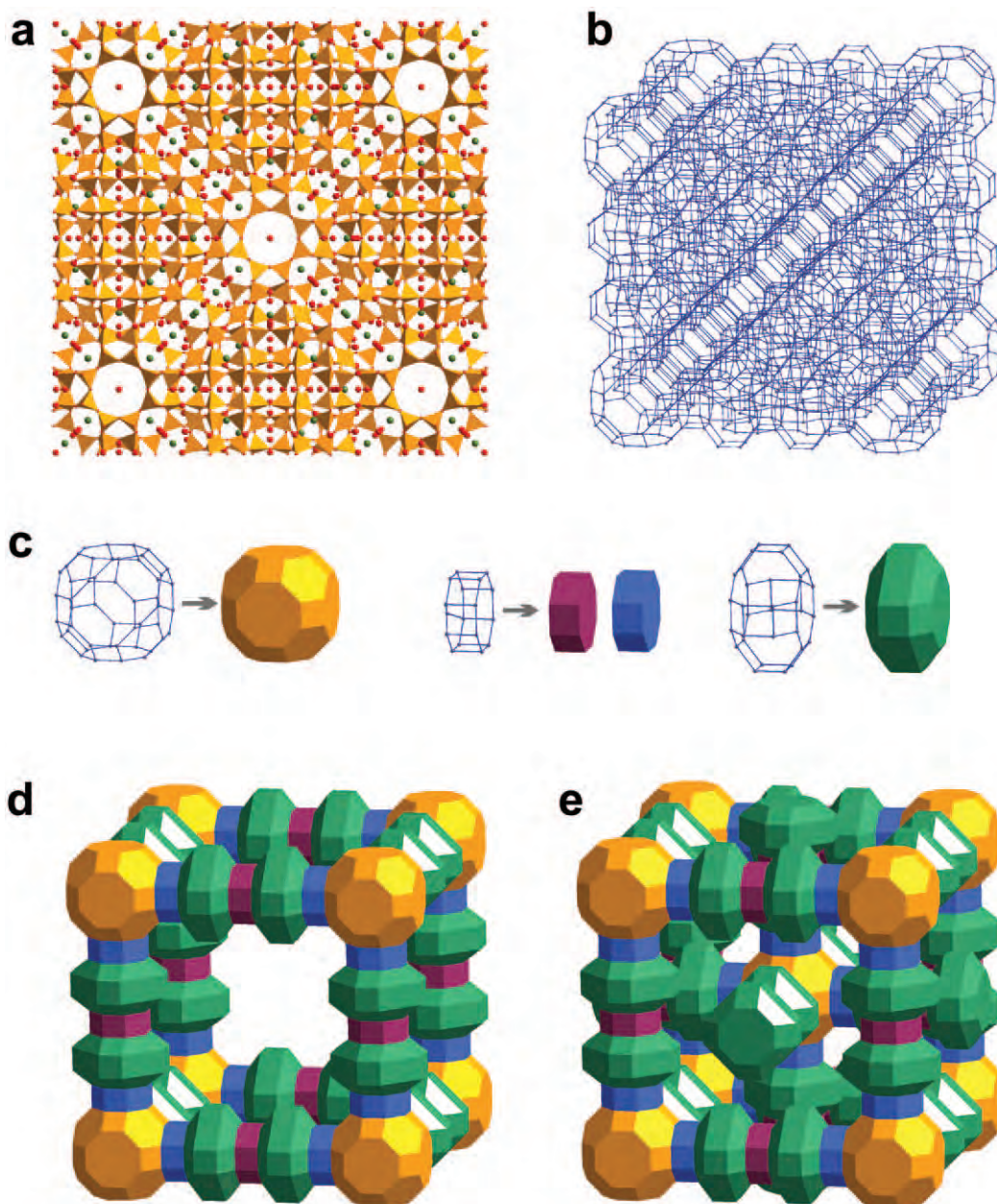


FIG. 8. (a) The structure of paulingite viewed along the *a* axis and (b) the nodal representation of tetrahedral framework. The framework can be considered as consisting of cages (c) that share edges to form a three-dimensional framework (d). Two frameworks interpenetrate and are linked by additional nodes (not shown) to form a complete paulingite topology (e).

Minerals with nanoscale clusters and tubules

Self-assembly of many-atomic nanoscale clusters and tubules into 3-periodic arrays results in a high

information content of the resulting crystal structures. The structure of bouazzerite, $\text{Bi}_6(\text{Mg},\text{Co})_{11}\text{Fe}_{14}(\text{AsO}_4)_{18}\text{O}_{12}(\text{OH})_4(\text{H}_2\text{O})_{86}$, a

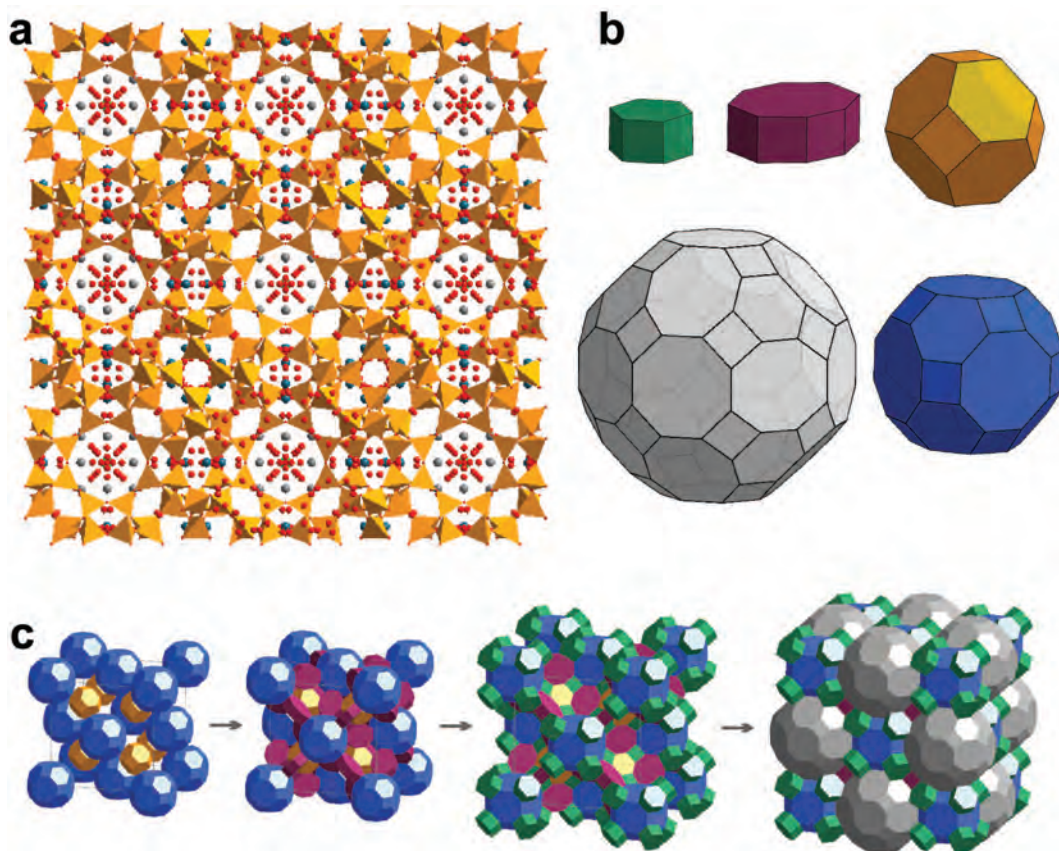


FIG. 9. The structure of tschoertnerite viewed along (a) the c axis, (b) its polyhedral cages and (c) linkage of cages in topological structure of the tetrahedral framework.

rare mineral from the weathering zone of the Bou Azzer As-Co-Ni-Cr-Ag-Au deposit (Brugger *et al.*, 2007), is based on $[\text{Bi}_3\text{Fe}_7\text{O}_6(\text{OH})_2(\text{AsO}_4)_9]^{11-}$ anionic nanoclusters (Fig. 11a). The core of the nanocluster consists of seven Fe^{3+} cations, one of which is in trigonal prismatic coordination, whereas six others are in octahedral coordination. The core is surrounded by nine arsenate tetrahedra and three Bi^{3+} cations. The nanoclusters are about 1.3 nm in diameter and are linked together by chains of $\text{Mg}(\text{H}_2\text{O})_6$ octahedra. Though the clusters are rather symmetric (their point symmetry is $P\bar{6}2m$), this symmetry is not conserved in the crystal structure, which appears to be very complex (3035.201 bits/u.c.). The presence in the structure of heavy Bi^{3+} cations did not allow resolution of the positions of the H atoms, which means that the structural information would be even greater.

The structure of megacyclite, $\text{Na}_{16}\text{K}_2(\text{Si}_{18}\text{O}_{36}(\text{OH})_{18})(\text{H}_2\text{O})_{38}$ (Yamnova *et al.*, 1992), contains eighteen-membered silicate rings, $[\text{Si}_{18}\text{O}_{36}(\text{OH})_{18}]^{18-}$, the largest known ring in minerals (Fig. 11b). The longest diameter of the ring is 2.3 nm, which makes the term ‘nano-ring’ acceptable for its description. It is hard to imagine that crystallization of megacyclite was not due to the presence of the nanorings in an initial hydrothermal solution. Yamnova *et al.* (1992) were able to determine positions of 46 symmetry-independent H atoms, which make a considerable contribution to the information content of the structure.

The structure of charoite, $(\text{K},\text{Sr},\text{Mn},\text{Ba})_{15.5}(\text{Ca},\text{Na})_{32}[\text{Si}_6\text{O}_{11}(\text{O},\text{OH})_6]_2[\text{Si}_{12}\text{O}_{18}(\text{O},\text{OH})_{12}]_2[\text{Si}_{17}\text{O}_{25}(\text{O},\text{OH})_{18}]_2(\text{OH},\text{F})_4(\text{H}_2\text{O})_3$ (Rozhdestvenskaya *et al.*, 2009, 2010, 2011), though not included in the list of the

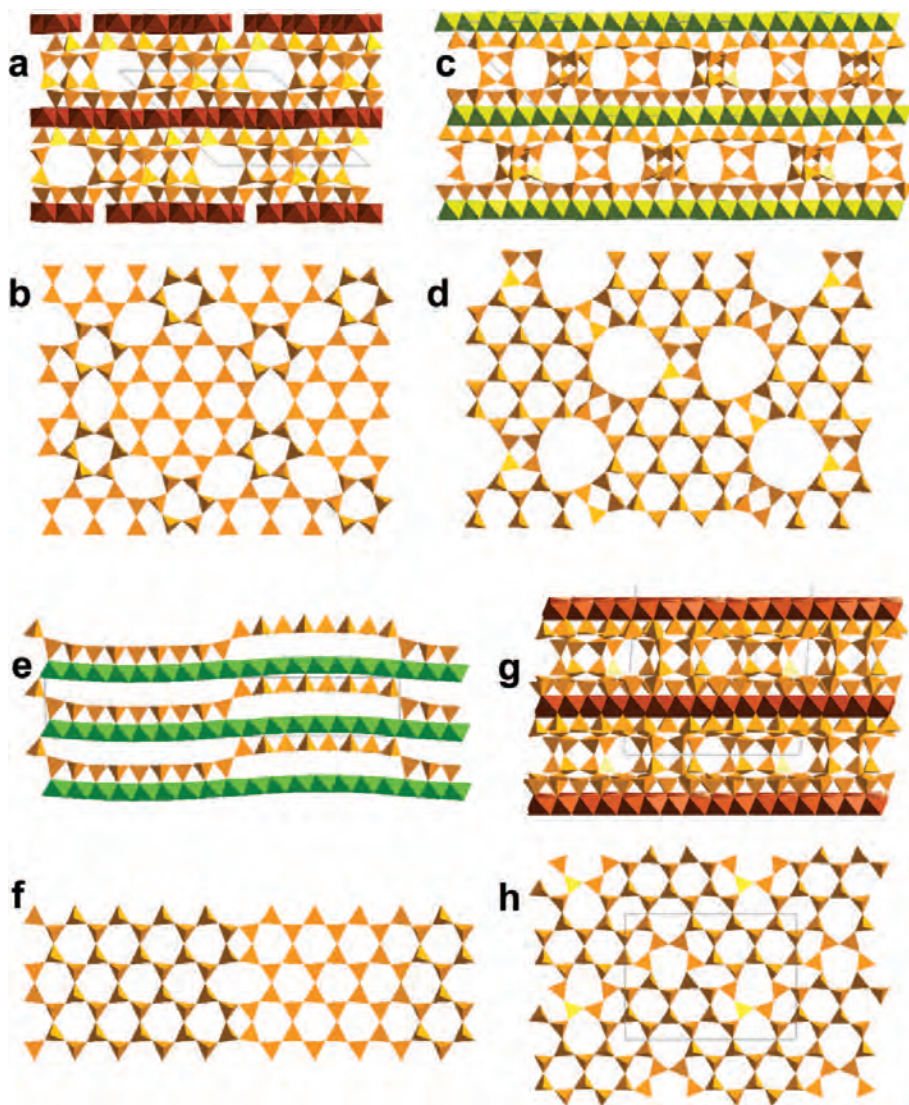


FIG. 10. Misfit layered silicates with very complex structures: octahedral-tetrahedral frameworks in (a) stilpnomelane, (c) parsettensite, (e) antigorite ($m = 17$ polysome) and (g) bannisterite; projections of their tetrahedral sheets are shown in (b, d, f, h), respectively.

twenty most complex structures, is remarkable in many respects. This is the only mineral and inorganic compound known that contains three different silicate anions (Fig. 11c). The largest shown in Fig. 11d can be described as a nanoscale tubular unit delineated with four-, six- and eight-membered silicate rings. The high complexity and nanoscale features of the structure of charoite made its determination rather problematic. It was the application of modern sophisticated techni-

ques such as an automated electron tomography (Kolb *et al.*, 2007, 2008) that allowed its complete structure solution. In its only known world locality, the Murun alkaline massif in Siberia, charoite occurs in large amounts (many tonnes), despite its high structural complexity.

Another example of a complex structure of one-dimensional nanoscale units is yuksporite, $(\text{Sr}, \text{Ba})_2 \text{K}_2 (\text{Ca}, \text{Na})_{14} (\square, \text{Mn}, \text{Fe}) \{(\text{Ti}, \text{Nb})_4 (\text{O}, \text{OH})_4 [\text{Si}_6\text{O}_{17}]_2 [\text{Si}_2\text{O}_7]_3\} (\text{H}_2\text{O}, \text{OH})_3$

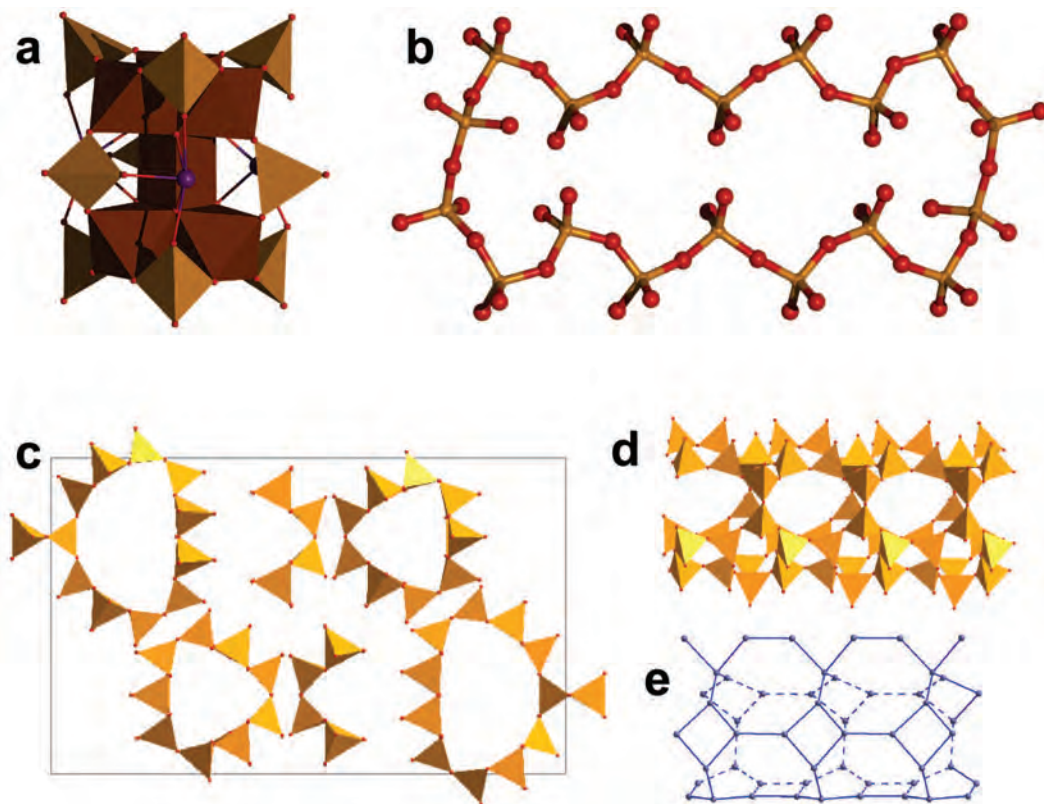


FIG. 11. Nanoscale units in minerals with very complex structures: (a) Bi-ferriarsenate nanoclusters in bouazzerite; (b) 18-membered silicate ring in megacyclite; (c) silicate nanotubules in charoite projected parallel to the tube extension; (d, e) structure of largest silicate nanotubule in charoite and its nodal representation

(Krivovichev *et al.*, 2004b), a very complex (1291.899 bits/u.c.) mineral from Khibiny (Kola peninsula, Russia; Fersman, 1923) and Murun (Konev *et al.*, 1985) alkaline complexes. The structure of yuksporite is based upon titanosilicate nano-rods, $\{(\text{Ti}, \text{Nb})_4(\text{O}, \text{OH})_4[\text{Si}_6\text{O}_{17}]_2[\text{Si}_2\text{O}_7]_3\}$, with an elliptical cross-section of $\sim 1.6 \times 1.9 \text{ nm}^2$. The nano-rods are packed together according to the packing mode of ellipses (Krivovichev *et al.*, 2004b). More information about tubular chains in natural and synthetic silicates can be found in the recent review by Rozhdestvenskaya and Krivovichev (2011).

The structure of mendeleevite-(Ce), $\text{Cs}_6\text{Ce}_{22}\text{Ca}_6(\text{Si}_{70}\text{O}_{175})(\text{OH}, \text{F})_{14}(\text{H}_2\text{O})_{21}$ (Sokolova *et al.*, 2011), is remarkable in its combination of nanoscale clusters and three-dimensional zeolite-like framework. The full

description of its crystal structure has been reported by Sokolova *et al.* (2011) and here we provide only some details about its complex organization. The primitive cubic unit cell (Fig. 12a) of the crystal structure of mendeleevite-(Ce) is centred by an unprecedented $[\text{Si}_{36}\text{O}_{90}]^{36-}$ nanocage (Fig. 12b–d) occupied by two Cs^+ cations and one H_2O molecule. The silicate cage is hosted inside the complex tetrahedral framework, $[\text{Si}_{26}\text{O}_{65}]^{26-}$, that can be described as consisting of two polyhedral units shown in Fig. 12e,f. The identification of these units allows us to recognize the framework as a severely interrupted and modified version of the framework described by Corma *et al.* (2002) in the germanatosilicate zeolite ITQ-21. Mendeleevite-(Ce) is unique in that it is composed from both a complex interrupted zeolite framework and nanoscale silicate clusters.

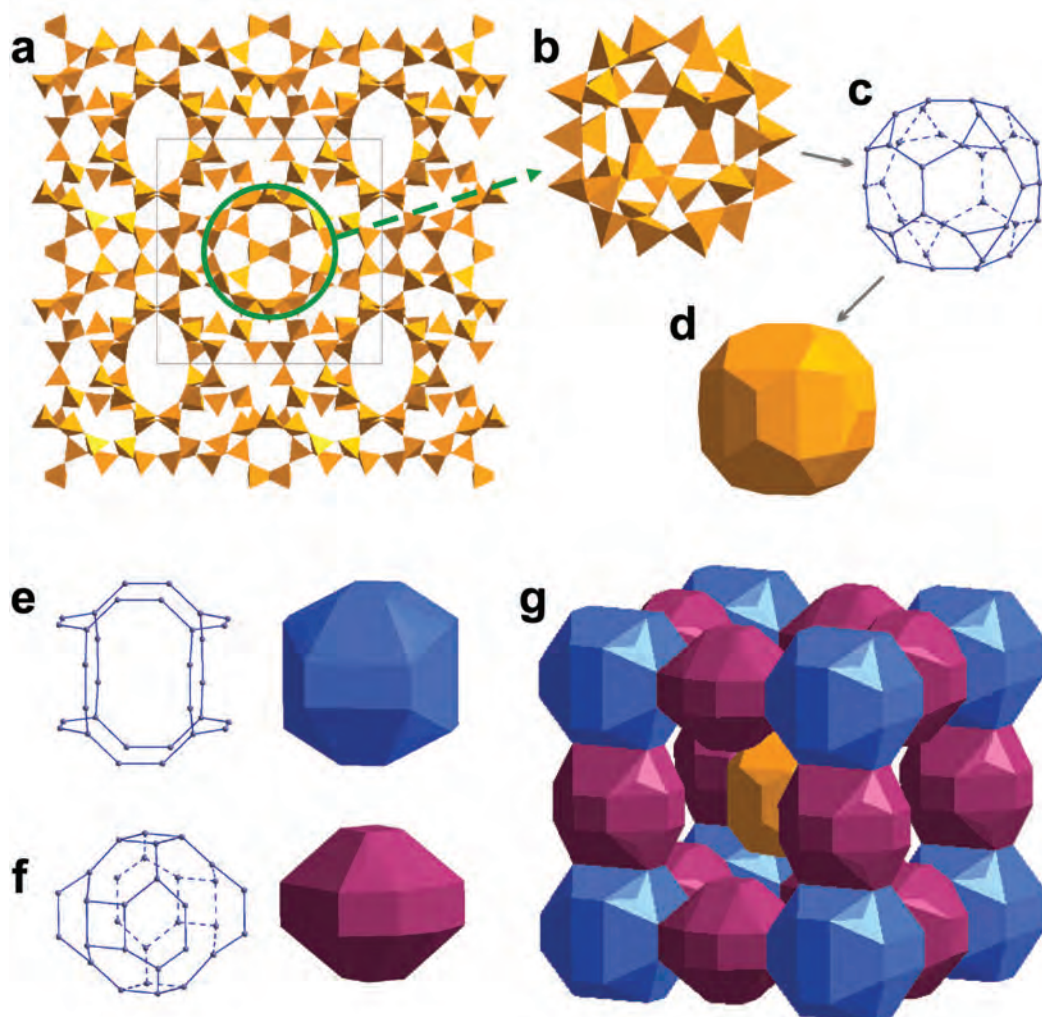


FIG. 12. (a) Tetrahedral substructure in mendelevite-(Ce), (b) central spherical cage, (c) its topology and (d) polyhedral representation; (e, f) topology of polyhedral cages that form three-dimensional silicate framework and (g) representation of the structure as a combination of polyhedral cages of different kinds.

Complex modular structures

The modular approach to the description of complex crystal structures is both elegant and efficient for the description of complex structural topologies (see above). Also, it shows one of the most common mechanisms of generating diversity and complexity: simple things are combined together in various ratios and combinations. What is considered as an eclectic in art and architecture, is considered as a modular structure in crystal chemistry. In fact, many of the structures described

above can be considered as based on modules derived from simpler structures (e.g. the sodalite cage present in tschoertnerite can be considered as a fragment of the sodalite framework).

Complexity has been considered by Burns (2011) as an 'intrinsic' property of hexavalent uranium minerals, and the inclusion of vanderiesscheite in the list of the twenty most complex minerals confirms this definition. Through application of the anion-topology approach, Burns (1999b) showed that uranyl-oxyhydroxide sheets in these minerals have a modular structure, i.e. they can be

regarded as combinations of slabs of topologically simpler sheets. For instance, the vandendriesscheite sheet (Burns, 1997) can be constructed by combination of modules extracted from the structures of fourmarierite and protasite, whereas the sheet in wölsendorfite (1919.819 bits/u.c.; Burns, 1999a) is based upon alternating protasite and β - U_3O_8 modules.

McDonald and Chao (2010) described the structure of rogermitchellite, $\text{Na}_{12}(\text{Sr},\text{Na})_{24}\text{Ba}_4\text{Zr}_{26}\text{Si}_{78}(\text{B},\text{Si})_{12}\text{O}_{246}(\text{OH})_{24}\cdot 18(\text{H}_2\text{O})$, as a hybrid of the benitoite and wadeite structures. Indeed, the zirconoborosilicate octahedral-tetrahedral framework in rogermitchellite (Fig. 13a) can be clearly separated into hexagonal-prismatic benitoite modules (Fig. 13b) and trigonal-prismatic wadeite modules (Fig. 13c,d). The structure of rogermitchellite was solved by McDonald and Chao (2010) in the space group $P\bar{3}c$ and has a high information content of 2320.653 bits/u.c. However, the octahedral-tetrahedral framework itself has a higher symmetry and can be described in the space group $P6_3/mcm$. Nevertheless, it is also very complex: its topological information content is 1919.731 bits/u.c. Loading the framework with Na^+ , Sr^{2+} , Na^{2+} cations and H_2O molecules generates an additional 400 bits of information per unit cell due to framework distortion and the new extraframework sites.

Stavelotite-(La), $\text{La}_3\text{Mn}_3\text{Cu}(\text{Fe}_7\text{Mn}_{19})(\text{Si}_2\text{O}_7)_6\text{O}_{30}$ (Bernhardt *et al.*, 2005), is a complex La-Mn sorosilicate with structure based

on four different types of layers. Bernhardt *et al.* (2005) pointed out that three of the four layers occur in lāngbanite, $(\text{Mn}^{2+},\text{Ca})_4(\text{Mn}^{3+},\text{Fe}^{3+})_9\text{Sb}(\text{SiO}_4)_2\text{O}_{16}$ (Moore *et al.*, 1991), whereas the fourth one is a glaserite layer (Hawthorne *et al.*, 2000). In turn, from the three lāngbanite layers, one also occurs in pyrochlore and minerals of the alunite supergroup, and two others are observed in mitridatite. Thus the high complexity of the structure of stavelotite-(La) is a consequence of its complex modular construction. However, Bernhardt *et al.* (2005) noted a strong rhombohedral pseudosymmetry in stavelotite-(La), which means that its topological information content is probably much lower than its structural information content.

Apjohnite, $\text{MnAl}_2(\text{SO}_4)_4(\text{H}_2\text{O})_{22}$ (Menchetti and Sabelli, 1976), is a unique structure that does not fall into any of the groups considered above. Its high information content is due to (1) the presence of 44 well defined H positions associated with H_2O molecules, and (2) the presence in the structure (Fig. 14a) of four different structural units linked together by hydrogen bonding only: $[\text{Mn}(\text{SO}_4)(\text{H}_2\text{O})_5]^0$ finite clusters (Fig. 14b), isolated $(\text{SO}_4)^{2-}$ groups (Fig. 14c), isolated $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ octahedra (Fig. 14d), and separate H_2O groups not bonded to any cations. This unique combination of structural features and complete ordering of all atom positions accounts for the high information content of 2305.361 bits per unit cell.

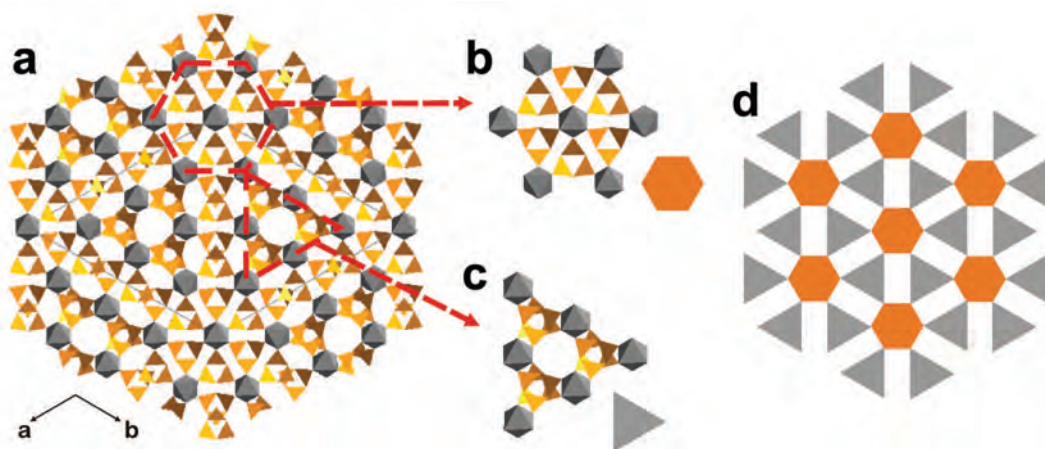


FIG. 13. (a) Octahedral-tetrahedral framework in the structure of rogermitchellite and its construction from two types of modules excised from the structures of (b) wadeite and (c) benitoite; (d) scheme showing mutual arrangement of modules in the structure.

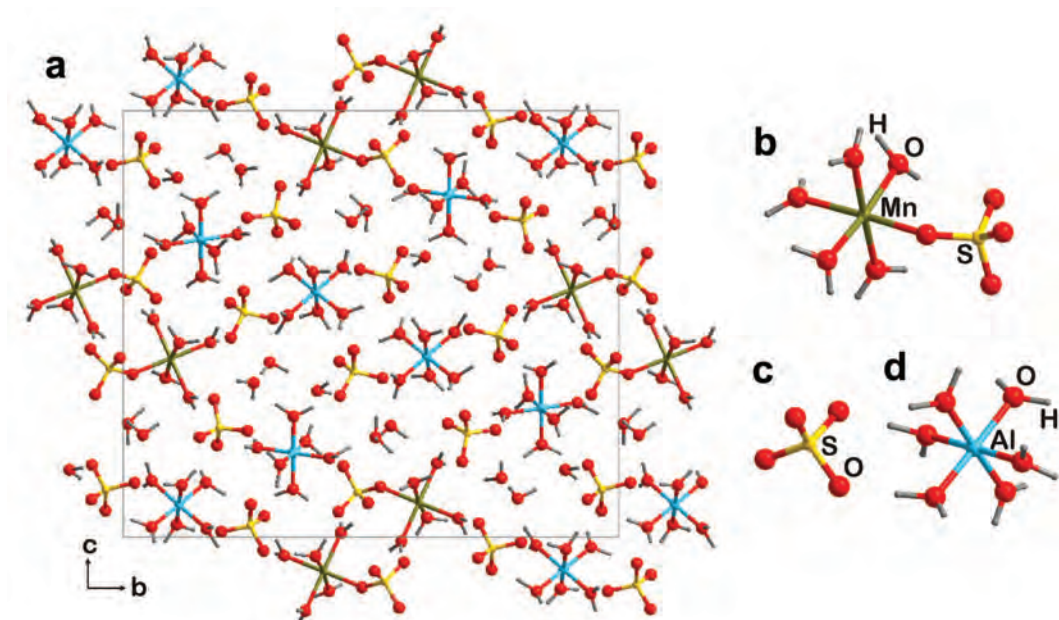


FIG. 14. (a) The crystal structure of apjohnite and its constituents: (b) the $\text{Mn}(\text{H}_2\text{O})_5(\text{SO}_4)$ cluster, (c) isolated SO_4 tetrahedron and (d) isolated $\text{Al}(\text{H}_2\text{O})_6$ octahedron.

Evolution of complexity in modular series

The cancrinite–sodalite supergroup consists of feldspathoids with an Al:Si ratio of 1:1 (Bonaccorsi and Merlino, 2005), which are not considered as zeolites (Coombs *et al.*, 1998). However, the topologies of their tetrahedral frameworks are included in the structure database of zeolite framework types of the International Zeolite Association (IZA). In this database, every zeolite framework topology has a three-letter symbol (e.g. the SOD symbol is used for the sodalite framework).

The structures of the cancrinite–sodalite supergroup minerals are based on layers of six-membered rings of tetrahedra. Each ring is linked to three rings in the preceding layer and to three rings in the succeeding layer (Bonaccorsi and Merlino, 2005). By analogy with closest sphere packings, rings in a layer may have three different positions indicated by the letters A, B and C. If rings in the layer are in the A positions, rings in the next layer should be either in B or C positions. Thus, each framework can be described as a sequence of symbols that describe positions of 6-membered rings of tetrahedra in the successive construction of its unit cell. The simplest frameworks are the 2-layer cancrinite

framework (CAN) with the AB sequence, and the 3-layer sodalite framework (SOD) with the ABC sequence. The maximal number of layers within a unit cell observed for the framework of the supergroup so far is 36, found in kircherite (Cámara *et al.*, 2012).

Considering a single layer of 6-membered rings as a module, the cancrinite–sodalite supergroup can be described as a modular series with structures controlled by the successive arrangement of two-dimensional modules. Table 3 provides a list of minerals of the supergroup that correspond to unique tetrahedral framework types (the full list of minerals of the supergroup can be found in Bonaccorsi and Merlino (2005) and current mineralogical literature), structural information contents of the representative structures, and topological information contents of the respective zeolite framework types stored in the IZA database (Baerlocher *et al.*, 2007). The latter values were calculated using Crystallographic Information Files (CIFs) that correspond to the highest symmetry of a framework with tetrahedrally coordinated T atoms treated without Al–Si ordering. For the minerals with unassigned framework codes (kircherite, sacrofanite, fantappieite), data from original publications were checked for higher symmetries

TABLE 3. Structural vs. topological information content for framework aluminosilicates of the cancrinite-sodalite supergroup.

<i>n</i>	Mineral name	Chemical formula	Layer sequence	Total structural information content (bits/u.c.)	Ref.	IZA code	Total topological information content (bits/u.c.)
2	cancrinite	$\text{Na}_2(\text{Ca}, \text{Na})_6(\text{CO}_3)(\text{H}_2\text{O})_2 [\text{Si}_6\text{Al}_6\text{O}_{24}]$	AB	135.510	1	CAN	69.059
3	sodalite	$\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$	ABC	87.025	2	SOD	16.529
4	bystrite	$\text{Ca}(\text{Na}, \text{K})_7[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_3\text{H}_2\text{O}$	ABAC	426.431	3	LOS	174.117
6	liottite	$\text{Na}_{10}\text{K}_6\text{Ca}_8[\text{Si}_{18}\text{Al}_{18}\text{O}_{72}] (\text{SO}_4)_5\text{Cl}_{3.5}\text{F}_{0.5}$	ABABAC	830.066	4	LIO	402.352
8	afghanite	$\text{Na}_{17}\text{K}_5\text{Ca}_{10}[\text{Si}_{24}\text{Al}_{24}\text{O}_{96}] (\text{SO}_4)_6\text{Cl}_6$	ABABACAC	1178.077	5	AFG	456.235
10	franzinite	$\text{Na}_{21}\text{K}_9\text{Ca}_{10}[\text{Si}_{30}\text{Al}_{30}\text{O}_{120}] (\text{SO}_4)_{10}(\text{H}_2\text{O})_2$	ABCABACABC	1607.279	6	FRA	775.240
12	tounkite	$\text{Na}_{31}\text{Ca}_{16}\text{K}[\text{Si}_{36}\text{Al}_{36}\text{O}_{144}] (\text{SO}_4)_{10}\text{Cl}_8$	ABABACACABAC	2250.397	7	TOL	984.704
12	marinellite	$\text{Na}_{31}\text{K}_{11}\text{Ca}_6[\text{Si}_{16}\text{Al}_6\text{O}_{24}]_6 (\text{SO}_4)_8\text{Cl}_2(\text{H}_2\text{O})_6$	ABCBCBACBCBC	1818.149	8	MAR	792.704
14	farnesite	$\text{Na}_{36}\text{K}_9\text{Ca}_8[\text{Al}_{42}\text{Si}_{42}\text{O}_{168}] (\text{SO}_4)_{11}\text{Cl}(\text{H}_2\text{O})_3$	ABCABABACBACAC	2094.012	9	FAR	974.864
16	giuseppettite	$\text{Na}_{43}\text{K}_{16}\text{Ca}_3[\text{Si}_{48}\text{Al}_{48}\text{O}_{192}] (\text{SO}_4)_{10}\text{Cl}_2(\text{H}_2\text{O})_5$	ABABABACBABABABC	2723.097	10	GIU	1164.469
28	sacrofanite	$\text{Na}_6\text{K}_{19}\text{Ca}_{32}[\text{Si}_{84}\text{Al}_{84}\text{O}_{336}] (\text{SO}_4)_{26}\text{Cl}_2\text{F}_6(\text{H}_2\text{O})_2$	ABCABACACABACBACB ACABABACABC	5317.353	11	-	2417.728
33*/11**	fantappiètte	$(\text{Na}_{82.5}\text{Ca}_{23}\text{K}_{16.5})[\text{Al}_{99}\text{Si}_{99}\text{O}_{396}] (\text{SO}_4)_{33}(\text{H}_2\text{O})_6$	ACBACABACBACBACB CACBACBACBACBACB	5948.330	12	-	2636.37*/878.790**
36*/12**	kircherite	$\text{Na}_{90}\text{Ca}_{36}\text{K}_{18}(\text{Al}_{108}\text{Si}_{108}\text{O}_{432}) (\text{SO}_4)_{36}(\text{H}_2\text{O})_6$	ACABCABCABCACBACB CABCABCABCABCACBACB	2052.539	13	-	3267.447*/1089.149**

* *R*-centering is ignored. ** *R*-centering is taken into account.

References: (1) Hassan and Grundy, 1991; (2) Loens and Schulz, 1967; (3) Pobedinskaya *et al.*, 1991; (4) Ballirano *et al.*, 1996; (5) Ballirano *et al.*, 1997; (6) Ballirano *et al.*, 2000; (7) Rozenberg *et al.*, 2004; (8) Bonaccorsi and Orlandi, 2003; (9) Cámara *et al.*, 2005; (10) Bonaccorsi, 2004; (11) Bonaccorsi *et al.*, 2012; (12) Cámara *et al.*, 2010; (13) Cámara *et al.*, 2012.

using the *PLATON* software (Speck, 2003) with all T atoms treated as Si.

Figure 15 shows the topological information content of the frameworks plotted against the number n of the layers. Here kircherite (**krh**) and fantappieite (**fnt**) are present twice, as their frameworks possess rhombohedral unit cells and can be described using two types of layer sequence. As seen in Fig. 15, increasing complexity correlates with increasing n . However, the topological information content does not depend solely on n . There are two frameworks, TOL and MAR, that have $n = 12$, but their topological information contents differ by 192 bits per unit cell. The layer sequences are ABABACACABAC and ABCBCBACBCBC, respectively, which does not provide much useful information about the difference in their complexity. The reason for the high information content of the TOL framework is in its lower topological symmetry ($P\bar{3}m1$) compared to the symmetry of the MAR framework ($P6_3/mmc$).

Another way to look at the complexity of framework construction is to describe the frameworks as arrays of secondary building (polyhedral) units. There are five different polyhedral units (cages) present in the frameworks of the supergroup (Bonaccorsi and Merlino, 2005) and they are shown in Fig. 16. The simplest CAN ($n = 2$) and SOD ($n = 3$) frameworks are based upon

can and *sod* cages, respectively) (Fig. 17). The four-layer LOS and eight-layer AFG frameworks (Fig. 17) are based on cages of two different types (*can* and *los*, and *can* and *lio*, respectively). The six-layer LIO framework (Fig. 17) consists of cages of three different types. It has a smaller number of layers compared to the eight-layer AFG framework, but its topological information content (402.352 bits/u.c.) is approaching that of AFG (456.235 bits/u.c.), which is an obvious consequence of its high complexity. Both LIO and TOL frameworks are based on the *can*, *los* and *lio* cages, but their arrangement in the latter is more complex than in the former (Fig. 17), which is reflected in their different values of n and topological information content (Table 3). The MAR and FAR frameworks contain cages of the same types (*lio*, *sod* and *can*), but again, with different arrangements (Fig. 18). The MAR framework can be considered as based on two different columns of cages, ...-lio-lio-... and ...sod-can-can-sod-can-..., whereas the FAR framework contains the columns ...sod-can-sod-lio-... and ...sod-can-can-sod-can-can-... Intuitively, the construction of the FAR framework is more complex, and this is reflected in its higher topological-information content, 974.864 bits/u.c., vs. 792.704 bits/u.c. for the MAR framework. The FRA and kircherite frameworks are also based on the same cages, but their topological

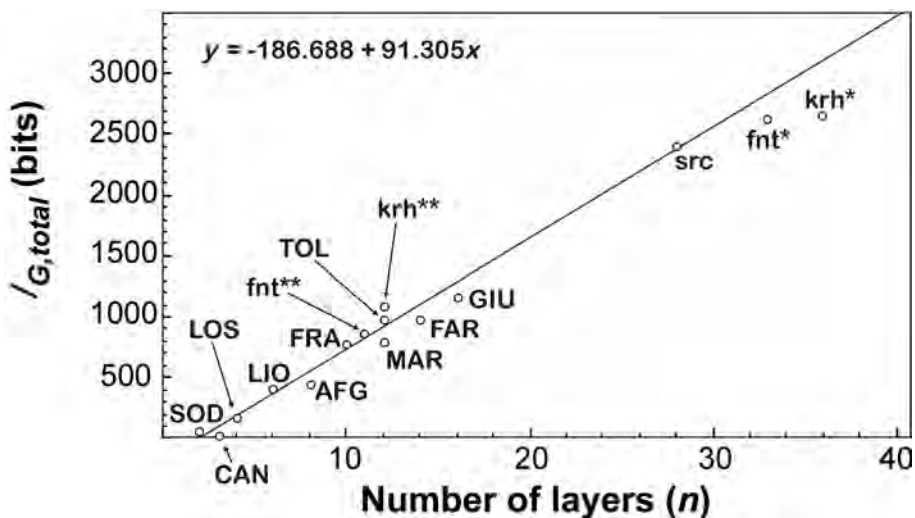


FIG. 15. Total topological information content vs. number of layers for aluminosilicate frameworks of the cancrinite–sodalite supergroup (legend: **krh*** and **krh**** = kircherite framework considered as consisting of 36 and 12 layers, respectively; **fnt*** and **fnt**** = fantappieite framework considered as consisting of 33 and 11 layers, respectively).

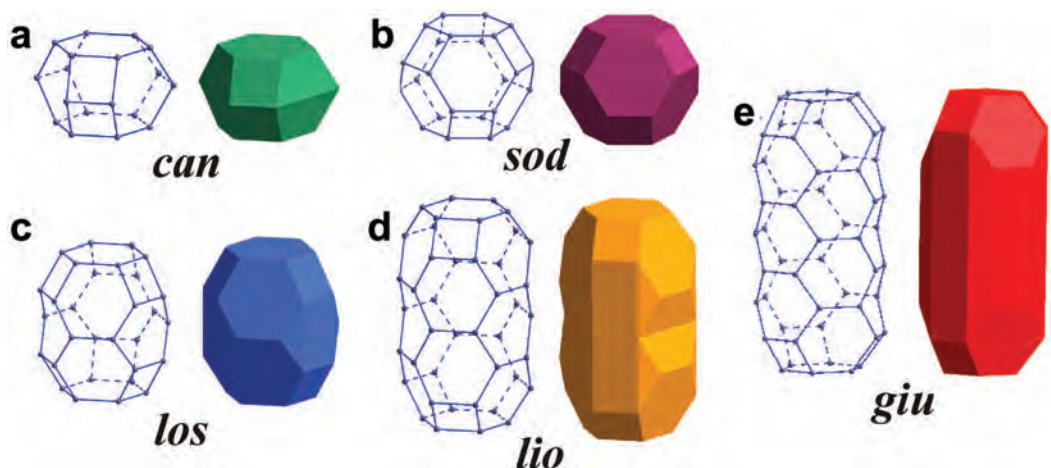


FIG. 16. Polyhedral cages present in the frameworks of the cancrinite–sodalite-supergroup minerals.

information differs by 313.909 bits per unit cell, in agreement with different arrangements of cages (Figs 17 and 18). From the viewpoint of topological information, the sacrofanite framework (Fig. 18) is the most complex in the supergroup, but the crystal structure of fantappièite registers more information, due to the combination of the Al–Si ordering and extra-framework species (Table 3). The structural information content of fantappièite is higher than the topological information content of its framework by a factor of ~ 6.5 .

The evolution of the structural and topological information in the cancrinite–sodalite supergroup

(modular series) shows that neither of the two depends solely on the size of the system (e.g. understood in terms of a number of modules). Of equal importance is the mode of combination of modules, which may have a profound impact upon the combinatorial symmetry and complexity.

Structural complexity and chemical composition

The relations between chemical composition and structural complexity is intuitively obvious: the structure of bouazzerite, $\text{Bi}_6(\text{Mg},\text{Co})_{11}\text{Fe}_{14}$

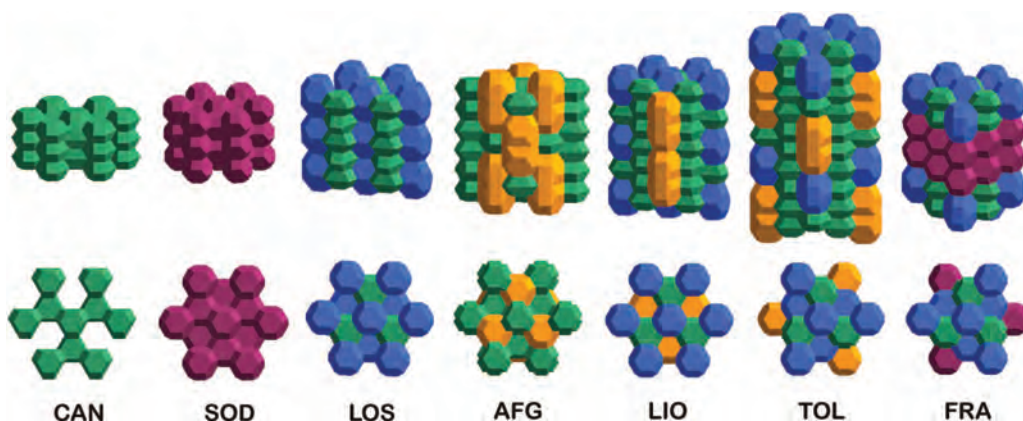


FIG. 17. Frameworks of the cancrinite–sodalite-supergroup minerals as built up from polyhedral cages: CAN, SOD, LOS, AFG, LIO, TOL and FRA frameworks.

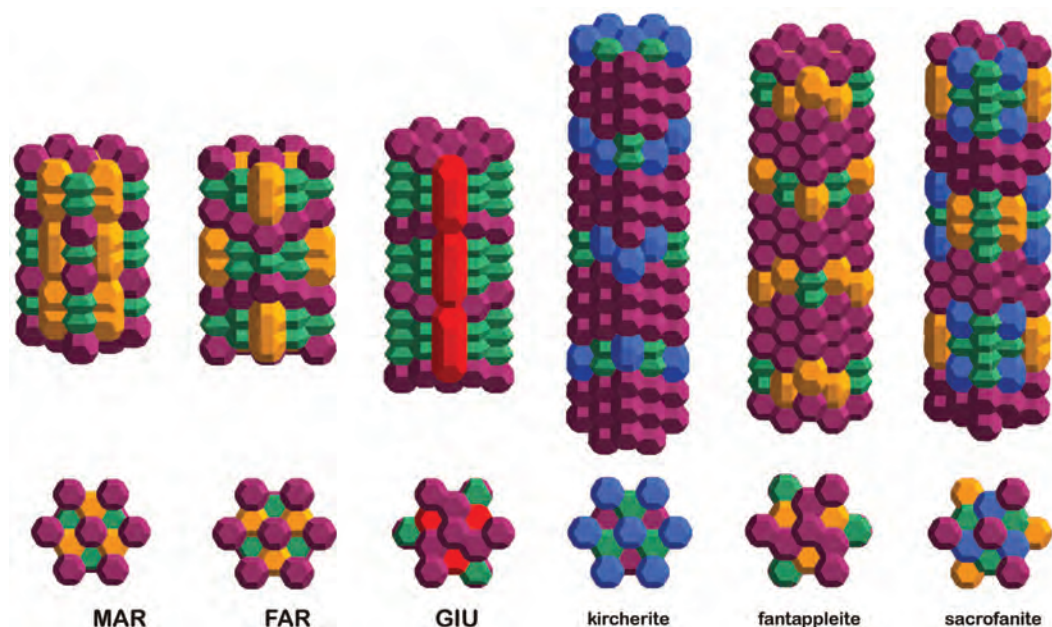


FIG. 18. Frameworks of the cancrinite–sodalite–supergroup minerals as built up from polyhedral cages: MAR, FAR, GIU frameworks and framework present in kircherite, fantappleite, and sacrofanite.

$(\text{AsO}_4)_{18}\text{O}_{12}(\text{OH})_4(\text{H}_2\text{O})_{86}$, necessarily bears more information than the structure of halite, NaCl . Thus, a complex chemical formula usually means a complex crystal structure. However, the chemical complexity of a mineral does not necessarily result in high complexity of its structure. Structurally, most minerals in chondritic meteorites are either simple or very simple, yet these several dozens minerals “...contain all of the chemical complexity of terrestrial planets” (Hazen *et al.*, 2008). On the other hand, minerals with very similar chemical composition may differ significantly in their structural complexity. The chemical formulas for geminite, $\text{Cu}(\text{AsO}_3\text{OH})(\text{H}_2\text{O})$ (Cooper and Hawthorne, 1995), and pushcharovskite, $\text{Cu}(\text{AsO}_3\text{OH})(\text{H}_2\text{O})_{1.5}$ (Pushcharovsky *et al.*, 2000), differ by 0.5 H_2O molecules only, whereas their structural information contents are 269.212 and 1640.967 bits/u.c., respectively. It is obvious that the structural complexity of a mineral is not a simple function of its chemical complexity.

The incorporation of H_2O usually (but not always) results in essential complexification of a crystal structure. Table 4 provides information-based complexity measures for minerals and

inorganic compounds with the chemical compositions $\text{MgSO}_4(\text{H}_2\text{O})_n$ and $\text{Mg}_3(\text{PO}_4)_2(\text{H}_2\text{O})_m$, in structures of which the authors were able to determine positions of all H atoms. In general, increasing the number of H_2O molecules per formula unit corresponds to increasing structural complexity.

Information and energy

The relations between information and energy have been debated since Maxwell’s discussion of the second law of thermodynamics (Leff and Rex, 2003). The information-to-energy conversion had been a topic of numerous theoretical and experimental studies (Maruyama *et al.*, 2009; Toyabe *et al.*, 2010; Bérut *et al.*, 2012). One of the most relevant for the present review is Landauer’s principle (Landauer, 1961), which states that erasure of a bit of information in an environment at temperature T (expressed in degrees Kelvin) requires dissipation of energy no less than $k_B T \ln 2$, where k_B is the Boltzmann constant ($\sim 1.38065 \times 10^{-23}$ J/K (Mohr *et al.*, 2008)). As noted by Caves (1993), “...Landauer’s principle demands that information

STRUCTURAL COMPLEXITY OF MINERALS

TABLE 4. Information-based complexity parameters for the oxysalts with general formulas $\text{MgSO}_4(\text{H}_2\text{O})_n$ and $\text{Mg}_3(\text{PO}_4)_2(\text{H}_2\text{O})_n$.

<i>n</i>	Mineral name	Sp. gr.	<i>v</i>	I_G (bits/atom)	$I_{G,\text{total}}$ (bits/u.c.)	$I_{G,\text{norm}}$	Ref.
$\text{MgSO}_4(\text{H}_2\text{O})_n$							
0	—	<i>Cmcm</i>	12	1.918	23.020	0.535	1
1	Kieserite	<i>C2/c</i>	18	2.503	45.059	0.600	2
2	Sanderite*	<i>P2₁2₁2₁</i>	64	4.000	256.000	0.667	3
4	Starkeyite	<i>P2₁/n</i>	72	4.170	300.235	0.676	4
5	Pentahydrate	<i>P1</i>	42	4.440	186.477	0.823	5
6	Hexahydrate	<i>C2/c</i>	96	4.627	444.156	0.703	6
7	Epsomite	<i>P2₁2₁2₁</i>	108	4.755	513.528	0.704	7
11	Meridianiite	<i>P1</i>	65	5.038	327.454	0.837	8, 9
$\text{Mg}_3(\text{PO}_4)_2(\text{H}_2\text{O})_n$							
0	Farringtonite	<i>P2₁/n</i>	26	2.777	72.211	0.591	10
4	—	<i>Cmc2₁</i>	68	4.558	309.947	0.749	11
8	Bobbierite	<i>C2/c</i>	74	4.291	317.500	0.691	12
	Baricite**	<i>C2/m</i>	37	3.480	128.750	0.668	12
22	Cattiite 1A1	<i>P1</i>	79	5.316	419.999	0.843	13
22	Cattiite 1A2	<i>P1</i>	79	5.316	419.999	0.843	14, 15

* H positions are not determined. ** High-temperature polymorph

References: (1) Rentzeperis and Soldatos, 1958; (2) Bregeault *et al.*, 1970; (3) Ma *et al.*, 2009; (4) Baur, 1964a; (5) Baur and Rolin, 1972; (6) Zalkin *et al.*, 1964; (7) Baur, 1964b; (8) Genceli *et al.*, 2007; (9) Peterson *et al.*, 2007; (10) Nord and Kirkegaard, 1968; (11) Konshaug *et al.*, 2001; (12) Takagi *et al.*, 1986; (13) Schroeder *et al.*, 1978; (14) Catti *et al.*, 1981; (15) Britvin *et al.*, 2002.

be granted a physical status as a negative contribution to free energy”. Though there are many subtleties and nuances in this approach (Bennet, 2003), it can be said that there is an equivalence relation between energy and information as well as there is an equivalence relation between mass and energy. Whether structural information stored in a crystal is expressed in terms of equation (11) or any other formula, erasure of each bit of this information would require dissipation of a certain amount of energy into the environment. Therefore, transformations of minerals that involve changes in their structures may be viewed as processes of acquisition, loss and transmission of structural information and its conversion into energy. The appearance of a complex crystal structure requires some energy to be transformed into information. On the other hand, transition of complex structure into simple one means erasure of certain amount of structural information, which has to be converted into energy.

As information content of crystalline matter defined above is an extensive property, the Landauer’s principle allows to calculate its energy equivalent at a given temperature. For example, 1 mole of α -quartz contains 16.59100×10^{23} bits of information encoded in its structure. If Landauer’s principle is correct, erasure of this information would require the release of heat, H_{inf} , calculated as:

$$H_{\text{inf}} = [16.59100 \times 10^{23}] \times [298\text{K}] \times [1.38065 \times 10^{-23} \text{ J/K}] \times [\ln 2] = 15.88 \text{ J mol}^{-1} \text{ K}^{-1}.$$

This value is of the same order as the standard entropy for α -quartz given by Mao *et al.* (2001) as $S_{0,298} = 41.46 \text{ J mol}^{-1} \text{ K}^{-1}$. This example shows that Landauer’s principle gives reasonable estimates of the information-to-energy(entropy) relations for crystalline solids. More efforts are needed in order to further clarify these relations.

Landauer’s principle has received particular attention from computer scientists, due to its importance for establishing physical limits of

computation (Bennet, 1982). Due to the discreteness and periodic character of crystal structures, their growth can be modeled using finite-state machines and therefore, in the ultimate sense, is a computation (Mackay, 1976; Krivovichev, 2004, 2010, 2012c; Shevchenko *et al.*, 2010), if computation is understood as a process following a well defined model expressed as an algorithm or a protocol. This view is a natural part of the more general approach that considers the Universe as a computer that computes itself by running a cosmic program (Wolfram, 2002; Lloyd, 2006). Adami (2002) pointed out that “all processes can in principle be viewed as computations”. Taking a less global view, the process of crystallization is a cyclic performance of a finite-step program, which is accompanied by the exchange of information with the environment, including information encoded in composition and structure of solution, gas or melt, structures of surrounding phases (if any), their spatial orientation (important for epitaxial growth), etc. Identification of crystal growth as a computation makes the application of Landauer’s principle to the transformation of minerals quite relevant and reasonable.

Evolution of information through space and time

Structural complexity and microscale mineral evolution

The information-based complexity measures introduced in the previous sections can be used to investigate evolution of paragenetic associations of minerals in a particular geochemical environment. Figure 19 shows schematically the evolution of minerals during hydrothermal reworking of primary phosphates. Commenting on the original version of this Figure taken from Moore (1973), Hawthorne (1998) pointed out that the observed complexity of phosphate minerals in granitic pegmatites “...arises from the fact that, after consolidation, the primary phosphates stew in residual aqueous fluids. This results in a large number of oxidation and exchange reactions, generating a series of phosphate minerals of increasing structural and chemical complexity with decreasing temperature.” Figure 19 provides total information contents for the minerals occurring in granitic pegmatites, which shows that Hawthorne’s statement is correct. Hydrothermal reworking of original simple minerals (amblygonite-montebrazite; triphylite-lithiophilite) results in the appearance of a

diversity of more complex mineral species, some of which should be identified as complex or very complex (e.g. laubmannite and cacoxenite). One of the reasons for this emergent complexity is the complex chemical composition of the residual fluids, but the contribution of decreasing thermal energy should not be ignored. Low-temperature minerals are generally more complex than their high-temperature counterparts, which can be interpreted as transformation of some part of the thermal energy into information.

Figure 19 also provides an interesting observation. In the course of metasomatic reaction with no oxidation present, the triphylite-lithiophilite association is transformed into triploidite, wolfeite and griphite, which are complex mineral species. On the next stages of hydrothermal reworking, alteration of these minerals results in formation of a suite of minerals of intermediate complexity. It could be said that, in this case, information is disproportionated in the course of mineral reactions. To establish this on a solid basis, one has to evaluate relations between structural information and entropy in more depth than it is possible in this review. However, the general trend of increasing structural complexity with the decreasing temperature is obvious and requires further investigation.

Structural complexity and global mineral evolution

The topic of global mineral evolution has emerged as a new paradigm in mineralogical sciences (Hazen *et al.*, 2008, 2009, 2011, 2012). However, it is not always properly acknowledged that the concept of mineral evolution was first proposed and (to some extent) developed by Russian mineralogists in the 1970–1980s (Zhabin, 1981, 1983; Yushkin, 1982; Smirnova and Belov, 1979). To the best of our knowledge, this omission is due to the fact that most of the papers mentioned were published in Russian in local mineralogical books and journals with no translation into English. A short history of the concept of mineral evolution in Russian scientific literature is given in the Appendix.

Hazen *et al.* (2008) defined three eras and ten stages of mineral evolution in the Earth’s history. The initial era (>4.55 Ga) is dominated by the formation of minerals with a total information content that rarely exceeds 200 bits. At this stage, the appearance of species of intermediate complexity is usually associated with aqueous

HYDROTHERMAL REWORKING OF PRIMARY PHOSPHATES

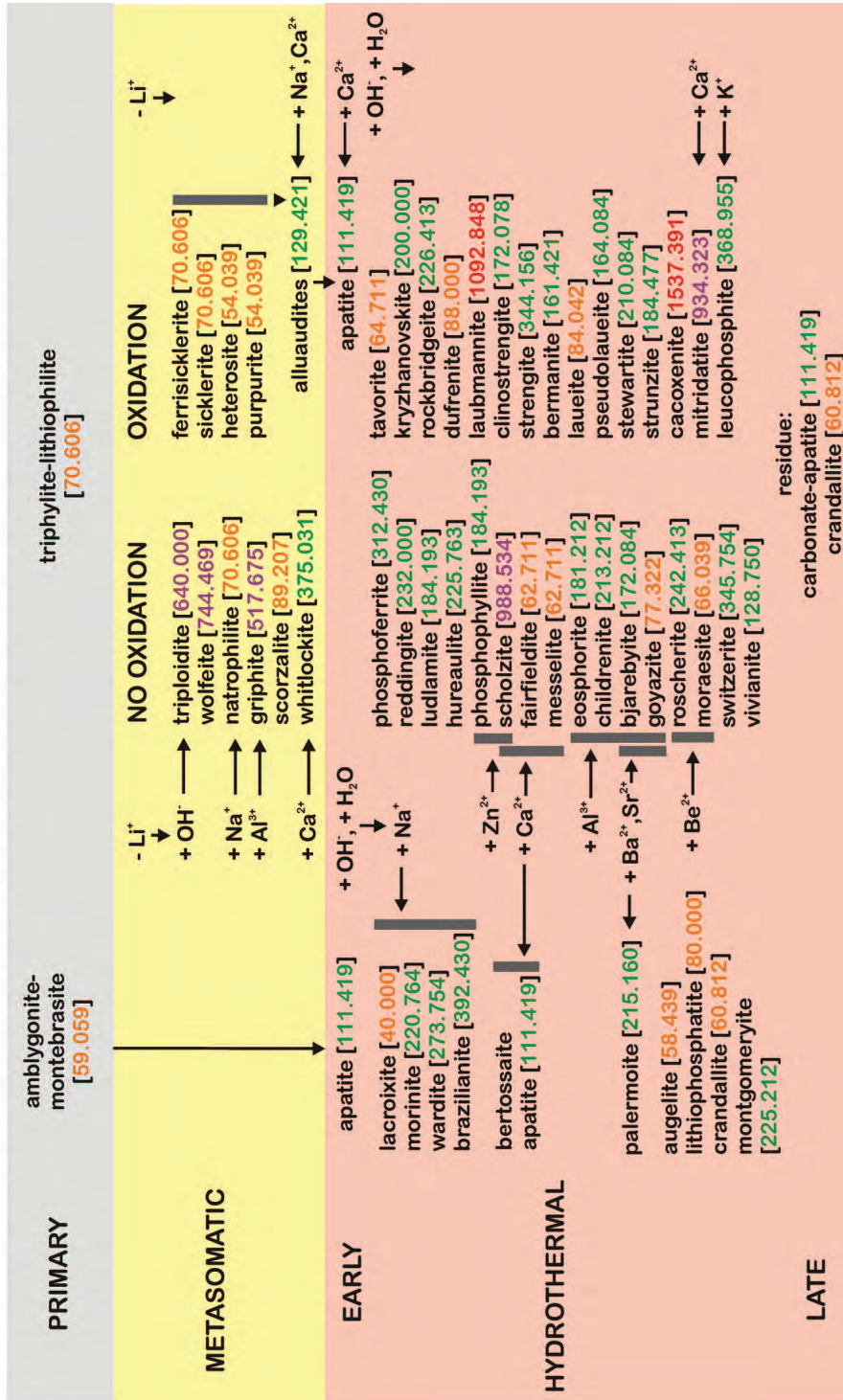


FIG. 19. Scheme of mineral transformations during hydrothermal reworking of primary phosphates (modified after Moore, 1973) with total structural information content values written in square brackets after mineral names. Colour-codes for the structure complexity: simple = orange; intermediate = green; complex = purple; very complex = red.

and thermal alteration events (formation of phyllosilicates and amphibole-supergroup minerals). The era of crust and mantle reworking (4.55 to 2.5 Ga) corresponds to the expansion of mineralogical diversity (Hazen *et al.*, 2008), but also results in the accumulation of information due to the formation of a suite of minerals with intermediate complexity such as hornblende (146.877 bits/u.c.), tourmaline-group minerals (176–207 bits/u.c.), pollucite (103.637 bits/u.c.), beryl (132.825 bits/u.c.), scapolite (135.133 bits/u.c.), staurolite (163.329 bits/u.c.), cordierite (120.175 bits/u.c.), etc. The third era of mineral evolution was identified by Hazen *et al.* (2008) as an era of bio-mediated mineralogy (2.5 Ga to present), when a diversity of new formation pathways of minerals was triggered by the activity of living organisms. This era is characterized by the appearance of minerals produced by biomineralization processes; some of these minerals are especially information-rich: vivianite $\text{Fe}_3(\text{PO}_4)_2(\text{H}_2\text{O})_8$ (128.750 bits/u.c.), struvite $\text{Mg}(\text{NH}_4)(\text{PO}_4)(\text{H}_2\text{O})_6$ (245.763 bits/u.c.), schwertmannite $\text{Fe}_{16}\text{O}_{16}(\text{OH})_{16}(\text{H}_2\text{O})_2$ (282.193 bits/u.c.), hannayite $\text{Mg}_3(\text{NH}_4)_2(\text{HPO}_4)_4(\text{H}_2\text{O})_8$ (301.775 bits/u.c.), whitlockite $\text{Ca}_{2.89}\text{Mg}_{0.11}(\text{PO}_4)_2$ (375.013 bits/u.c.), melanterite (517.528/u.c.), hazenite $\text{KNaMg}_2(\text{PO}_4)_2(\text{H}_2\text{O})_{14}$ (936.313/u.c.), bakhchisaraitsevite $\text{Na}_2(\text{Mg},\text{Fe})_5(\text{PO}_4)_4(\text{H}_2\text{O})_7$ (1128.771 bits/u.c.), etc. Extensive inorganic and bio-weathering activity during the Phanerozoic era is also responsible for the formation of very complex and information-rich minerals such as bouazzerite (Table 2; 3035.201 bits/u.c.), vandendriesscheite (Table 2; 2835.307 bits/u.c.), pertlikite $\text{K}_2(\text{Fe},\text{Mg})_2\text{Mg}_3\text{Fe}_3\text{Al}(\text{SO}_4)_{12}(\text{H}_2\text{O})_{18}$ (1865.225 bits/u.c.), richetite $(\text{Mg},\text{Fe})\text{Pb}_9((\text{UO}_2)_{18}\text{O}_{18}(\text{OH})_{12})_2(\text{H}_2\text{O})_{41}$ (1748.848 bits/u.c.), pushcharovskite $\text{Cu}(\text{AsO}_3\text{OH})(\text{H}_2\text{O})$ (1640.967 bits/u.c.), voltaite $\text{K}_2\text{Mg}_5\text{Fe}_4(\text{SO}_4)_{12}(\text{H}_2\text{O})_{18}$ (1566.017 bits/u.c.), etc. Low-temperature hydrothermal activity results in the appearance of very complex zeolites (paulingite, tschoertnerite, mutinaite) and secondary phosphates such as cacoxenite, $\text{Al}_4\text{Fe}_{21}(\text{PO}_4)_{17}\text{O}_6(\text{OH})_{12}(\text{H}_2\text{O})_{24}$ (1537.391 bits/u.c.). The general trend of mineral evolution corresponds to the accumulation of information both in terms of diversity and complexity of the mineral world. Whether this trend is related to the evolution of biological complexity (Adami *et al.*, 2000) or it is a consequence of general evolution of complexity in complex systems is an open question.

Structural complexity and mineral composition of the Earth

As mentioned above, the increase in temperature usually results in simplification of mineral structures. In contrast, the effect of pressure upon structural complexity is non-linear. With increasing pressure, structural complexity increases as well, which may be exemplified by the transformation of calcite (13.710 bits/u.c.) to aragonite (38.439 bits/u.c.) or by the transformation of olivine (70.606 bits/u.c.) to wadsleyite (78.606 bits/u.c.) in the upper mantle at a depth of ~410 km (Pushcharovsky and Pushcharovsky, 2012). Among stable SiO_2 polymorphs, coesite, which forms at pressures above 2.5 GPa and temperatures $>700^\circ\text{C}$, is the most topologically complex phase (66.039 bits/u.c.), but very high-pressure phases stishovite and seifertite are much more simple (5.510 and 11.020 bits/u.c., respectively). In general, deep geospheres are information-depleted compared to the Earth's crust, which is yet another example of the information-to-energy conversion. Pushcharovsky and Pushcharovsky (2012) pointed out that, whereas silicate minerals of the Earth's crust demonstrate remarkable structural diversity (more than 100 topologically distinct silicate anions), mantle silicates represent about 20 structure types only. The relations between temperature, pressure and structural complexity require further investigation, which should necessarily combine thermodynamic and information-based approaches.

Structural complexity and 'ease of crystallization'

General notes

The information-based complexity measures can also be used to estimate the 'ease of crystallization' from the viewpoint of the simplicity principle proposed by Goldsmith (1953) for understanding of formation of simple and complex mineral phases under both natural and laboratory conditions. In particular, Shannon information measures can be used to evaluate the complexity of metastable mineral phases crystallizing according to the Ostwald step rule (Morse and Casey, 1988; Navrotsky, 2004). The latter has been interpreted not as "an invariant rule but an observation that metastable reaction products with simpler structures form more rapidly than complicated" (Morse and Casey,

1988). One of the reasons for such behaviour is that simpler structures have smaller diameters of their critical nuclei than more complex structures, which strongly favour their formation in non-equilibrium conditions (e.g. crystallization from supercooled melts or supersaturated solutions). Below, we provide a short review of some observations of metastable appearances of minerals and discuss their structural complexities using the quantitative measures proposed above.

Silica polymorphs

Cristobalite is the most topologically simple silica polymorph with tetrahedrally coordinated Si atoms. Its total topological-information content equals 5.510 bits/u.c. (the same as that for stishovite with Si in octahedral coordination). The high simplicity of the cristobalite structure may be invoked to explain its frequent occurrence as a metastable phase in a number of geochemical environments (Darling *et al.*, 1997). Recent hydrothermal flow-through experiments of silica precipitation responsible for quartz vein formation (Okamoto *et al.*, 2010) showed the following sequence of metastable solid-phase transformations: opal-A (amorphous) → low-ordered opal-C (C = cristobalite) → high-ordered opal-C → quartz. The first structured phase has cristobalite topology, which is transformed into the more complex but stable quartz topology. Very similar transformation pathways have also been observed in silica sinters (Herdianita *et al.*, 2000) and for diagenesis processes in sediments (Morse and Casey, 1988). In the latter, the common pathway is opal-A → opal-CT → reordered opal-CT → cryptocrystalline quartz (chalcedony) → quartz. Here, CT shows the presence of both cristobalite and tridymite diffraction peaks. It is noteworthy that the tridymite topology (17.510 bits/u.c.) is more complex than those of quartz (8.265 bits/u.c.) and cristobalite (5.510 bits/u.c.). However, the formation of tridymite may be viewed as the result of topochemical twinning of the cristobalite structure. At ambient pressure, cristobalite is the most high-temperature phase and its transformation to quartz with decreasing temperature proceeds via the intermediate tridymite structure, which means that structural information increases along the pathway. It is very likely that the occurrence of tridymite as a transitional phase may be explained by purely structural reasons, i.e. a steric convenience for the reconstruction of the cristobalite topology into that of quartz.

Feldspar compositions

Svyatoslavite (Chesnokov *et al.*, 1989) and dmisteinbergite (Chesnokov *et al.*, 1990) are two metastable polymorphs of $\text{CaAl}_2\text{Si}_2\text{O}_8$, which crystallize in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system prior to the crystallization of anorthite. They were first identified by Davis and Tuttle (1952), and their stability, nucleation and growth kinetics were investigated in detail by Abe *et al.* (1991), Daniel *et al.* (1995), and Abe and Sunagawa (1995). Abe *et al.* (1991) reported that the pseudo-hexagonal (dmisteinbergite) and pseudo-orthorhombic (svyatoslavite) polymorphs nucleate prior to anorthite and grow in a supercooled $\text{CaAl}_2\text{Si}_2\text{O}_8$ melt until anorthite starts to crystallize. At that moment, these phases either dissolve or transform to anorthite. As the structure of dmisteinbergite is not precisely determined (there is information on its synthetic counterpart only: Takéuchi and Donnay, 1959; Dimitrijevic *et al.*, 1999), direct comparison of structural complexity of the metastable polymorphs and anorthite is not possible. However, the topology of the aluminosilicate frameworks is well established for all polymorphs. The dmisteinbergite structure is based on double sheets of six-membered rings of AlO_4 and SiO_4 tetrahedra and has the lowest topological information content (35.020 bits/u.c.). Both svyatoslavite and anorthite are based on three-dimensional frameworks of tetrahedra, but the svyatoslavite topology is simpler (62.039 bits/u.c.) than that of anorthite (76.211 bits/u.c.). Therefore, both metastable $\text{CaAl}_2\text{Si}_2\text{O}_8$ polymorphs are simpler than the stable anorthite structure, which explains their spontaneous crystallization from a supercooled melt. This is also an obvious explanation for their crystallization from high-temperature (up to 1200°C) gases in the coal dumps of the Chelyabinsk coal area (their holotype locality: Chesnokov *et al.*, 1989, 1990, 2008). Nestola *et al.* (2010) reported metastable formation of dmisteinbergite in a pseudotachylyte by rapid quenching of a friction melt generated by seismic slip. They suggest that “given the small grain size, ... dmisteinbergite may not be so rare, but rather that its abundance is simply underestimated... dmisteinbergite is probably more common than reported in rocks produced during large thermal impulses.”

Hwang *et al.* (2010) reported on kumdykolite, an orthorhombic (most probably pseudo-orthorhombic) polymorph of albite, $\text{NaAlSi}_3\text{O}_8$, which has very similar unit-cell parameters to svyatosla-

vite (Krivovichev *et al.*, 2012). Hwang *et al.* (2010) pointed out that kumdykolite, discovered in the Kokchetav ultrahigh-pressure massif in Kazakhstan, is a metastable phase formed at high temperature by rapid cooling in the absence of H_2O . If kumdykolite has the svyatoslavite topology (which seems likely), its formation may be explained by the higher simplicity of its structure topology compared to that of albite.

Kokchetavite, $KAlSi_3O_8$, is another mineral from Kokchetav massif (Hwang *et al.*, 2004), which probably formed metastably in the stability field of K-feldspar from infiltrated melts during retrograde exhumation. Its structure is based on double aluminosilicate sheets with the dmisteinbergite topology, which is simpler than the stable feldspar framework topology. It is of interest that kokchetavite occurs in association with cristobalite, which supports its metastable appearance as a phase that is simpler than its stable counterparts.

The dmisteinbergite double-sheet topology has also been observed in ‘hexacelsian’, $BaAl_2Si_2O_8$ (not a valid mineral species), cymrite, $BaAl_2Si_2O_8(H_2O)$, and ‘K-cymrite’, $KAl_2Si_2O_8(H_2O)$ (Fasshauer *et al.*, 1997). Both ‘hexacelsian’ and cymrite crystallize metastably well below their stability field (Graham *et al.*, 1992; Viswanathan *et al.*, 1992; Hyatt and Bansal, 1996), within the stability field of celsian. One of the reasons for their preferential crystallization may be derived from the lower complexity of their structure topologies.

Serpentine-group minerals

Antigorite is the stable phase in olivine–serpentine reactions (Evans *et al.*, 1976; Evans, 2004), but its nucleation rate is sluggish (Wunder *et al.*, 1997), which is usually explained by the high complexity of its structure. Dungan (1977) pointed out that “the role of crystal structure is manifested in the relative ease of nucleation of the various phases” and that “antigorite nucleation is hampered by its complex structure”. Indeed, the structural information content for different antigorite polysomes varies from 1277 to 2188 bits/u.c. (Uehara, 1998; Dodony *et al.*, 2002; Capitani and Mellini, 2004, 2006), which corresponds to very complex structures according to the classification proposed above (Table 1). In contrast, crystal structures of chrysotile and lizardite are much more simple (43–86 and 35–112 bits/u.c. for different polytypes, respectively (Mellini, 1982; Krstanovic and Karanovic, 1995; Gualtieri

and Artioli, 1995; Brigatti *et al.*, 1997; Guggenheim and Zhan, 1998; Zhukhlistov and Zvyagin, 1998; Falini *et al.*, 2004), and that favors their dominant (and, in the case of chrysotile, metastable (Evans, 2004)) formation in serpentinites. The structures of all serpentine-group minerals are based on sheets of silicate tetrahedra and continuous sheets of $Mg(O,OH)_6$ octahedra. The misfit between the tetrahedral and octahedral substructures results in strain, which is relaxed by rotation of tetrahedra in lizardite, formation of rolls and tubes in chrysotile, or inversion of tetrahedra in antigorite. Different numbers of inverted tetrahedra result in different polysomes, which are characterized by the number m of tetrahedra along the a repeat. For instance, the structure of antigorite shown in Fig. 10e corresponds to the $m = 17$ polysome. According to Mellini *et al.* (1987), a typical range of m values is 13–24. The structural complexity of antigorite polysomes is a function of m . For instance, the structural information contents for the $m = 16$ and $m = 17$ polysomes (Capitani and Mellini, 2004, 2006) are 1761.323 and 2187.799 bits/u.c., respectively. Wunder *et al.* (2001) investigated the pressure and temperature dependence of polysomatism and H_2O content in antigorites and found that m decreases with increasing temperature and decreasing pressure (Fig. 20). This is in agreement with the general trends of structure complexity increasing with decreasing temperature and moderately increasing pressure. Under ultrahigh pressures, the situation may be drastically different (see above).

Micas and clay minerals

It has been shown by many observations and experimental studies that the first phase that forms during initial stages of crystallization of muscovite and illite is either the $1M$ or $1M_d$ polytype ($1M_d$ has a strongly disordered structure). Velde (1965) proposed that the stable polytype of dioctahedral white mica is $2M_1$, whereas the $1M$ and $1M_d$ polytypes are metastable. Mukhamet-Galeyev *et al.* (1985) synthesized muscovite from stoichiometric-composition gels and showed that the $1M$ and $2M_1$ polytypes form at the same time. However, the crystallization rate of the $1M$ polytype is much higher (it crystallizes *more easily*) and complete crystallization of the gel occurs almost completely in the $1M$ form. After this, the $1M$ form starts to convert to the $2M_1$ form, but the conversion rate is very slow.

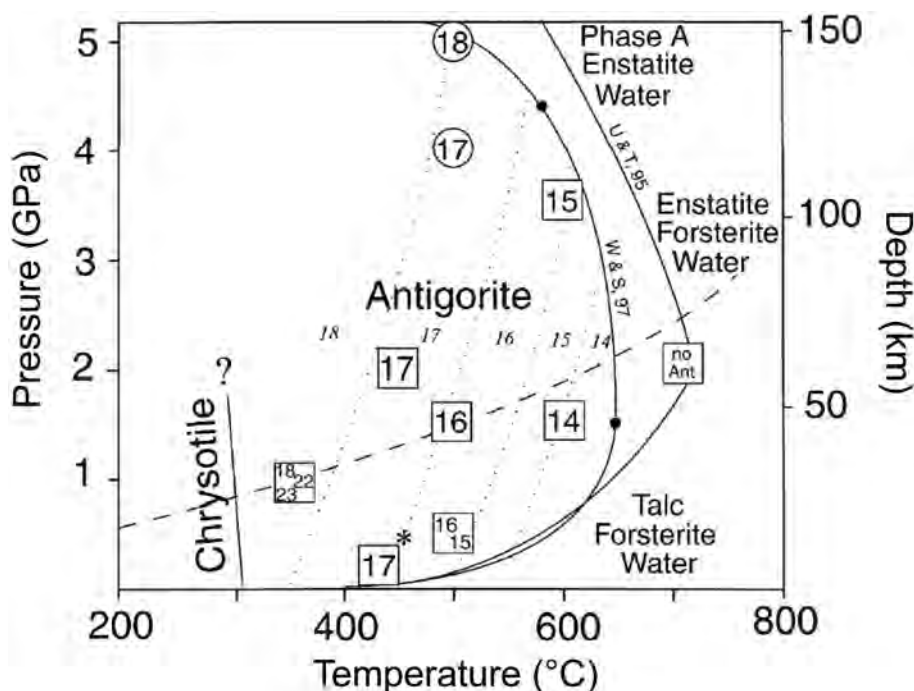


FIG. 20. P , T -dependence of antigorite polysomes with different m values (numbers given in italics). Reprinted with permission from Wunder *et al.* (2001).

According to Meunier and Velde (2004), this explains why the $1M$ polytype occurs in natural diagenetic sequences where it is a metastable form of illite. Baxter Grubb *et al.* (1991) explained the formation of the metastable $1M$ and $1M_d$ polytypes from the viewpoint of the Ostwald step rule. The relative ease of crystallization of the $1M$ polytype is in agreement with Goldsmith's simplicity principle: the structure of the $1M$ polytype is essentially simpler than that of the $2M_1$ polytype. For muscovite, their information contents are equal to 60.239 and 136.877 bits/u.c., respectively.

Metastability and structural complexity

The observations given above indicate that structural complexity may have a profound impact upon mineral reactions when kinetic factors are of importance and the system does not have enough energy to overcome the energy barrier that separates metastable simple from stable complex structures. Under non-equilibrium conditions, simpler structures may form metastably in the stability fields of more complex structures. However, metastable structures are not

always the simplest ones. For instance, zeolites and other microporous materials, many of which are complex or very complex, are generally metastable phases in the corresponding chemical systems (Navrotsky *et al.*, 2009). By rapid cooling the $Pb-O-Br-Cl$ melt with the mendipite-like composition, $Pb_3O_2(Cl,Br)_2$, Krivovichev *et al.* (2006) obtained the compound $Pb_{31}O_{22}X_{18}$ ($X = Cl, Br$), which has one of the most topologically complex tetrahedral layers known so far. Its structure is much more complex (873.264 bits) than its stable mendipite-like counterpart (70.606 bits).

Other approaches to structural complexity

Taking bonds into account

The proposed definition of structural information content according to formula (9) is based upon the information-based complexity measures of graphs initially proposed by Rashevsky (1955). A certain disadvantage of this definition is that it considers graph in terms of symmetrically distinct vertices, whereas edges are not taken into account. Figure 21 shows five different graphs, each consisting of six vertices. In all the graphs, the six vertices can

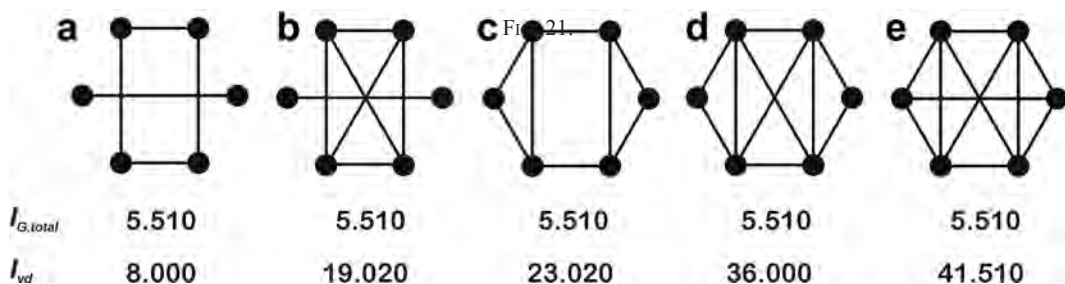


FIG. 21. Graph with six vertices that belong to two different equivalence classes. Below the graphs are written values of total structural information content ($I_{G,total}$) and vertex-degree-distribution information content (I_{vd}).

be subdivided into two equivalence classes, $\{1, 4\}$ and $\{2, 3, 5, 6\}$, according to the automorphism groups of the graphs. The topological information content is the same for all the graphs shown in Fig. 21 and is calculated according to the equation (8) as:

$$I_G = -[1/3 \log_2(1/3) + 2/3 \log_2(2/3)] = 0.918 \text{ bits/vertex.}$$

The total information content, $I_{G,total}$, is equal to $6 \times 0.918 = 5.510$ bits. Therefore, from the viewpoint of vertex equivalence, all the graphs shown in Fig. 21 have the same complexity. However, there is an intuitive feeling that the graph shown in Fig. 21e is more complex than the graph shown in Fig. 21a, obviously, because of the higher number of edges. In order to overcome the problem, one needs to formulate graph complexity measures that would take into account the complexity of the edge set of the graph.

Bonchev (2003) proposed to subdivide graph vertices into equivalence classes according to their degrees (vertex degree is the number of edges incident at a vertex). The corresponding measure of complexity is the information content of the vertex-degree distribution of the graph, I_{vd} :

$$I_{vd} = \sum_{i=1}^v a_i \log_2 a_i \text{ (bits)} \quad (36)$$

where a_i is the degree of the i th vertex and summation proceeds along all v vertices. According to this equation, graphs shown in Fig. 21 have different I_{vd} values which reflect the complexity of their edge sets.

Application of equation (36) to crystal structures means that each couple of atoms (vertices of the quotient graph) should be associated with either bonding (edge) or non-bonding (no edge) contact. This operation is not always simple and obvious. For instance, in metals and intermetallic

compounds, electrons are delocalized and there are no directed bonds that can be assigned. The same is true for large low-valent ions or cations with stereoactive lone pairs of electrons, which usually have a number of weak contacts in the coordination hemisphere opposite the strong cation-anion bonds. However, in many cases, the assignment of chemical bonds is unambiguous and the chemical bonding network can be established easily. If this is the case, calculation of the I_{vd} value is quite straightforward, as vertex degrees are equal to coordination numbers of atoms. For instance, total structural-information contents for the structures of andalusite, kyanite and sillimanite are 88.000, 128.000 and 88.000 bits, respectively, which means that andalusite and sillimanite are of the same complexity. The information contents of vertex-degree distribution are 235.575, 264.154 and 210.117 bits, respectively. The combination of the $I_{G,total}$ and I_{vd} indices indicates that the high-pressure phase, kyanite, is the most complex ($I_{G,total}/I_{vd} = 128.000/264.154$), whereas the high-temperature phase, sillimanite, is the simplest ($88.000/210.117$). Andalusite, which is the stable form at ambient conditions, is intermediate in complexity ($88.000/235.575$).

Another method to account for the bonding network in information-based complexity measures is to count bonds as quotient-graph elements along with its vertices. In this case, the total information content of a bonding network may be expressed as:

$$I_{G,total}^{bond} = -[v \sum_{i=1}^v p_i \log_2 p_i + e \sum_{j=1}^e p_j \log_2 p_j] \text{ (bits)} \quad (37)$$

where

$$\begin{aligned} p_i &= m_i/v & (\text{see equation 10}) \\ p_j &= m_j/e & (38) \end{aligned}$$

where m_i and m_j are the multiplicities of the crystallographic orbits occupied by atoms and bonds relative to the reduced unit cell, respectively, v and e are the numbers of atoms and bonds in the reduced unit cell, respectively. Crystallographic orbits of bonds can be expressed in terms of the midpoints of the edges connecting graph vertices that represent interacting atoms.

The utility of the proposed concepts can be checked on selected groups of compounds, which is one of the possible directions for further research. The assignment of bonds depends upon the structural chemistry of particular groups of compounds and the approach chosen. For instance, a weight can be assigned to bonds proportional to their bond valences.

Algorithmic complexity

The algorithmic complexity of a particular object (Kolmogorov, 1965; Chaitin, 1969, 1987) can be estimated as a length of the shortest program or algorithm that generates it. For crystals and, in particular, for minerals, this approach has fundamental importance, as crystal structures are the result of crystal-growth processes. Due to the periodic character of crystal structures, their growth can be modeled by finite-state machines such as cellular automata (Mackay, 1976; Krivovichev, 2004, 2010, 2012c; Shevchenko *et al.*, 2010). The method of evaluation of algorithmic complexity of some tetrahedral structures was outlined recently in (Krivovichev *et al.*, 2012) and will be developed in more detail elsewhere.

Concluding remarks

According to Wheeler (1990), “...all things physical are information-theoretic in origin.” The Universe is based upon information, and one of its important reservoirs is the spatial organization of matter, which is usually expressed by the term ‘structure’. Structures bear a large amount of information according to the degrees of their complexity. Complex structures store more information than simple structures. The important point is that information does not appear or dissipate without any physical effects. As was stated by Landauer (1996), ‘information is physical’, and its erasure is always associated with dissipation of energy (perhaps, in the form of entropy). Therefore, information stored in crystal structures of minerals must have an important

influence on natural processes but we are far from understanding the role of the information-to-energy conversion in geological processes. As every process can be viewed as a communication channel (Crutchfield, 2012), the mineralogical history of our planet on any scale is a story of accumulation, storage, transmission and processing of structural information.

Glossary of terms and definitions

Complexity of a system can be described from the viewpoint of its *algorithmic*, *symbolic* or *combinatorial* complexity. *Algorithmic* (or *Kolmogorov*) *complexity* is measured by the length of the program that generates the system. *Symbolic complexity* of a system is a function of its size. *Combinatorial complexity* of a system is a function of its symmetry.

Crystallographic symmetry of an atomic structure is its symmetry described by the corresponding point or space group.

Graph, $G = \{V, E\}$, is defined as a structure consisting of a set of objects $V = \{v_1, v_2, \dots\}$ called *vertices*, and a set of unordered pairs of vertices $E = \{v_i, v_j\}$, whose elements are called *edges*.

Hartley equation: $H = n \log_2 s$ (bits), where H is the amount of information that can be stored by the message consisting of n symbols that belong to s different types that occur with the same probability.

Information density of a crystal structure, ρ_{inf} , is the number of bits of information per cubic ångström: $\rho_{\text{inf}} = I_{G,\text{total}}/V$ [bits/Å³], where $I_{G,\text{total}}$ is the total structural information content, and V is the volume of the reduced unit cell.

Structural information content of a crystal structure, I_G , is defined as $I_G = -\sum_{i=1}^k p_i \log_2 p_i$ (bits/atom), where k is the number of crystallographic orbits (Wyckoff sites) in the structure, and p_i is the probability of occurrence of the atom from the i th orbit: $p_i = m_i/v$, where m_i is the multiplicity of the i th crystallographic orbit relative to the reduced unit cell and v is the number of atoms in the reduced unit cell.

Normalized structural information content, $I_{G,\text{norm}}$, is defined as $I_{G,\text{norm}} = I_G/\log_2 v$, where I_G is a structural information content, and v is the number of atoms in the reduced unit cell.

Total structural information content of a crystal structure, $I_{G,\text{total}}$, is defined as $I_{G,\text{total}} = v \times I_G$ (bits/unit cell = bits/u.c.), where I_G is a structural information content, and v is the number of atoms in the reduced unit cell.

Shannon formula: $H = -\sum_{i=1}^s p_i \log_2 p_i$ (bits/symbol), where H is the amount of information that can be stored by the message consisting of n symbols that belong to s different types that occur with different probabilities p_i .

Topological symmetry of an atomic structure is the highest crystallographic symmetry that the structure may adopt by continuous transformation that does not involve breaking of any bonds between atoms.

Quotient graph of an infinite 3-periodic network is the finite graph that is obtained by projection of all translationally equivalent vertices (edges) of the network onto one vertex (edge) of the finite graph.

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Appendix

Mineral evolution in the Russian mineralogical literature (1970–1980s)

Introduction

In January 1982, Leningrad (now St Petersburg) hosted the VIth Meeting of the All-Union Mineralogical Society, which was devoted to ‘Minerals, Rocks and Mineral Deposits in Geological History’. As was indicated in the report published after the Meeting (Popkova, 1982), its theme “...was determined by the tasks formulated for the Soviet geological science by the document ‘General Directions of Economic and Social Development of the U.S.S.R. for 1981–1985 and till 1990’, which oriented us toward investigations of structure, composition and evolution of the Earth.” The document itself was approved and ratified by the XXVIth Meeting of the Communist Party of the Soviet Union. That was the start of ‘official’ mineral-evolution studies in the U.S.S.R. However, at that time, mineral evolution was already a common topic in Soviet mineralogy, at least as indicated by talks presented at the meeting: ‘General features of geological processes’ (D.V. Rundkvist), ‘Evolutionary ideas in mineralogy and their development’ (N.P. Yushkin), ‘Evolution of mineral formation in geological history of the lithosphere’ (A.G. Zhabin), ‘Evolutionary analysis of granitoid formations’ (Yu.B. Marin), ‘Evolution of rare metal mineralization in the course of Earth’s geological history’ (A.I. Ginzburg), etc.

Among the mineral-evolution ideas expressed during the conference, some were especially noteworthy: (1) distinction between phylogenesis and ontogenesis of mineral species (D.P. Grigoriev, D.V. Rundkvist); (2) subdivision of four global periods in the evolution of inorganic matter in the Universe (D.V. Rundkvist); (3) concentration of mineral evolution processes in a narrow zone around the geoid surface [now known as a ‘critical zone’ (Brantley *et al.*, 2006)] (D.V. Rundkvist, N.P. Yushkin); (4)

punctuated character of mineral evolution and its directionality (D.V. Rundkvist, N.P. Yushkin); (5) mineralogical inheritance (N.P. Yushkin, A.P. Khomyakov, A.G. Zhabin); (6) symmetry aspects of mineral evolution (N.P. Yushkin).

Below, I provide a short description of some basic ideas on mineral evolution extracted from the Soviet/Russian mineralogical and geological literature published in 1970–80s, which is not easily available to the non-Russian reader.

Evolutionary mineralogy in the works of N.P. Yushkin

In 2008, summarizing development of mineral evolution in his previous works, N.P. Yushkin pointed out that there are

“...three basic directions in mineral evolution – ontogenesis, syngeneses and phylogenesis, which together constitute foundations of modern evolutionary mineralogy. Mineral ontogenesis is a study of genesis of individual mineral crystals and aggregates from their crystallization to complete dissolution or desintegration ... Investigations of mineral ontogenesis – ontogeny – were formulated by D.P. Grigoriev and developed by his many students and followers in different countries. Mineral phylogenesis is the genesis and development of mineral species, whereas phylogeny is the study of evolution of mineral species and their distribution over geological history. Mineral syngeneses is the genesis and development of mineral associations, whereas mineral syngeny is the study of evolution of mineral associations and features of co-evolution of individual crystals of minerals...”

The relations between mineral phylogenesis, syngeneses and ontogenesis is shown in Fig. A1. Mineral evolution is intermediate between the geochemical evolution of the Earth and the evolution of rocks and geological formations. In

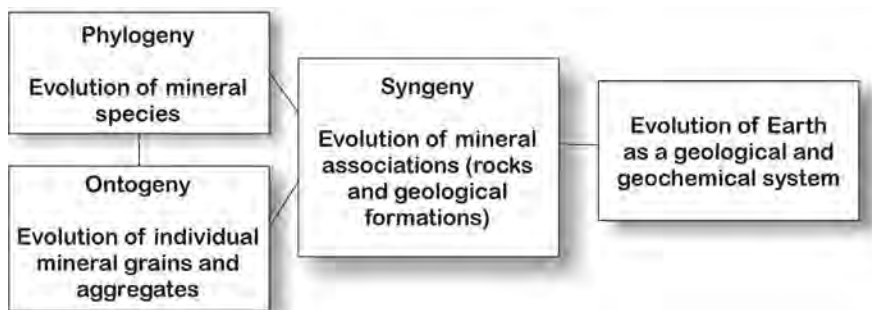


FIG. A1. Basic aspects of mineral evolution and their relation to the evolution of Earth as a geological and geochemical system (according to Yushkin, 2008).

the hierarchical scheme ‘atom (chemical element) – mineral – rock – geological formation – Earth’s core – Earth’, most research has focused on atoms (geochemical evolution), rocks and geological formations (evolution of magmatism, sedimentary rocks, mineral deposits, etc.) and Earth as a whole, whereas evolution of the mineral world was largely neglected.

Yushkin (1982) was one of the first to identify the issue of the evolution of mineral composition over geological time and studied its basic driving forces and features. In particular, he formulated a range of principles and rules that constitute the basis of evolutionary mineralogy:

- (1) the principle of directional development of the mineral world (irreversibility of mineral evolution according to the ‘arrow of time’);
- (2) the principle of paragenetic associations;
- (3) the law of increasing diversity (due to Tschermak: “... as a consequence of continuing transformation of minerals, diversity of the Earth crust’s composition is constantly increasing, which may be called a development of the mineral kingdom” (cited and translated from (Yushkin, 1982)));

- (4) the law of aggregation;

- (5) the principle of mineral transformations, etc.

Yushkin (1982) identified as an important task “...search and use in comparative-historical analysis of specific indicators, which, by characterization of complex mineralogical objects, would contain truly mineralogical information”. Yushkin (1982) subdivided these indicators into three groups: (1) concentration-dependent (which take into account volumes of mineral systems under comparison); (2) structure-dependent (which take into account features of the structural organization); (3) entropy-dependent (based upon

degree of complexity, inhomogeneity and structural diversity of minerals).

One of the concentration-dependent characteristics used by Yushkin (1982) in his mineral evolution studies was a density of atomic arrangement, P_A , initially proposed by Feklichev (1979) as:

$$P_A = (K_1V_1 + K_2V_2 + \dots + K_NV_N) \cdot Z/V_{u.c.}$$

where $V_{u.c.}$ is a unit-cell volume, Z is a number of formula units per unit cell, K_N is a number of atoms of the element N in the chemical formula, V_N is a volume of atom N in non-ionized state.

As it was shown by Feklichev (1979), for some metamorphic facies, the value of P_A decreases with the decreasing degree of metamorphism: from 0.5397 for a granulite facies through 0.4172 for amphibolite and 0.3844 for greenschist facies to 0.3175 for zeolite facies.

Similar density analysis was done by Yushkin (1982) for the minerals of the Earth, Moon and meteorites (Fig. A2).

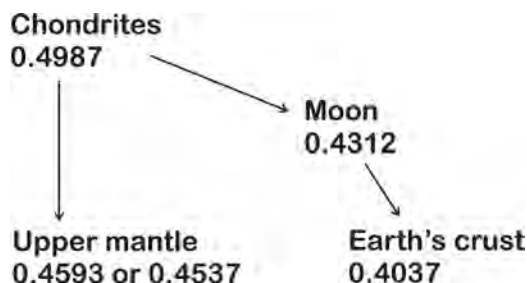


FIG. A2. Changes in the Feklichev’s density of atomic arrangement (P_A) in mineralogical matter of Earth, Moon and meteorites (modified after Yushkin, 1982).

On the basis of his studies, Yushkin (1982) made the following conclusions concerning features of mineral evolution:

(1) increasing complexity of mineralogical objects in the course of their evolution, which is expressed by the increase of their entropy;

(2) accumulation of complexity in the upper parts of the Earth crust, near the Earth's surface;

(3) decreasing of the relative energy of the evolving mineral systems, which is reflected in the decreasing of the P_A value;

(4) evolution of 'cubic' and 'cubic-orthorhombic' mineral world toward monoclinic in the external surface of the Earth; decreasing symmetry of substance contrasted by the high (or even increasing) symmetry of the Earth as a whole.

Concerning relations between mineral and biological evolution, Yushkin (1990) noted that the organic and mineral worlds "... although functionally different, developed in close interaction" (in 2008, this point, now expressed by Hazen *et al.* (2008), made a headline of some science news reports, e.g. ScienceDaily: "Mineral Kingdom Has Co-Evolved With Life, Scientists Find" (<http://www.sciencedaily.com/releases/2008/11/081113181035.htm>)).

Although some of the points raised and discussed by Yushkin (1982, 1990, 2008, etc.) may sound controversial, this was the first scientific discussion of mineral evolution, which was largely ignored by subsequent researchers in the field.

Mineral phylogeny in the works of A.G. Zhabin

In 1979, academician D.S. Korzhinskii, the famous mineralogist and petrologist and the only

Russian to receive the Roebling medal, recommended for publication in the *Doklady Akademii Nauk SSSR (Proceedings of the U.S.S.R. Academy of Sciences*, the most prestigious Soviet scientific journal at the time) the paper "Does evolution of mineral species on the Earth exist?". The author of the paper was Arkadiy G. Zhabin (1934–2007), a former student of D.P. Grigoriev, the author of the theory of mineral ontogeny. He started his paper from the definition of mineral phylogeny (as the original English translation is not available to us, I have translated all quotes from the original Russian text): "... under evolution of mineral species, we understand statistically meaningful sequence of appearances of mineral species in the course of the geological history of our planet". According to Zhabin (1979), pre-history of the Earth mineral-forming processes started with the formation of consolidated bodies in the Solar system about 5.0–4.7 billion years ago. The history itself "... may be considered from the time of consolidation of the planet and first stages of its differentiation." The first mineral species formed at the time produced a tree of mineral species that constituted about 1800–2000 in 1979.

The global sequence of mineral evolution may be presented according to the scheme shown in Fig. A3. Zhabin (1979) subdivided three eras of mineral evolution (Table A1). The following feature of mineral evolution was emphasized by Zhabin (1979) as important: "... in the course of geological time, different mineral-forming processes alternate and overlap, and correspond to different hierarchical levels of the organization of substance: evolution of the planet as a space body, evolution of the substance of the geospheres, evolution of geological formations."

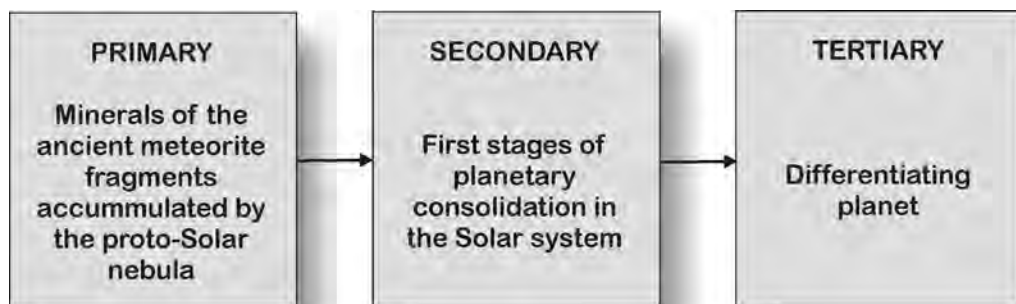


FIG. A3. Global sequence of cosmic cycles of mineral formation according to Zhabin (1979, 1983).

STRUCTURAL COMPLEXITY OF MINERALS

TABLE A1. Eras of mineral evolution according to Zhabin (1979).

Era	Number of mineral species	Dominant minerals	Features of geological processes
First (meteorite)	40–50	natural iron, kamacite, taenite, olivine, pyroxenes	consolidation of protoplanetary matter
Second (basaltic)	60–70	feldspars (with the dominance of plagioclase), pyroxenes, ilmenite, olivine, spineloids	the appearance of basaltic magmatism
Third (Earth's crust formation)	250–300	alkali feldspars, micas, quartz hypergene minerals (chlorites, serpentines, clays, hematite, pyrite, simple carbonates and halides)	differentiation, degassing of the mantle, generation of water the appearance of the oxygen atmosphere

In other words, the same physico-chemical principles of differentiation of the substance are at work at different scales in Earth system evolution. As an example, Zhabin (1979) indicated chromite mineral deposits, where the sequence of species can be described as follows: ‘...olivine – chromite – serpentine and chlorite – clay minerals, chalcedony, hematite.’ It is not difficult to see that the ontogenic cycle of chromite mineral deposits repeats general evolution of mineral species on the Earth. This was viewed as a mineralogical version of the theory of recapitulation (also known as a biogenetic law), which was expressed by Ernst Haeckel as “ontogeny recapitulates phylogeny”.

Zhabin (1979) proposed evolutionary classification of mineral species into:

(1) panchronous, which form continuously from the origin till the present days (e.g. pyroxenes, feldspars, olivine, quartz, ilmenite, apatite, zircon, spineloids, etc.);

(2) monochronous, which are characteristic for specific periods of the Earth's history (it was difficult for Zhabin to find an example, he cites only swedenborgite);

(3) polychronous, which appeared many times in the Earth's history.

Of great interest are the speculations of Zhabin (1983) about directionality of structural evolution of minerals linked to the general structural evolution of matter in the evolving Universe. In this aspect, he relied heavily on the paper by

Smirnova and Belov (1979) on the evolution of the system of structure types. These authors formulated an interesting definition of ‘crystallogenetics’ as “... a part of crystal chemistry that deals with evolution in the system of crystalline compounds, principles of their internal structure (structure types) and external forms, their structural elements (atoms and groups of atoms), structure fragments (structure parts that remain intact during transition from one structure to another), structure details (one-, two- and three-dimensional combinations of structure elements), and their dependence upon physico-chemical conditions.”

According to Smirnova and Belov (1979), during the pre-crystalline stage, “... all existing structure of the Universe originated from the chaos of differently charged fields, pre-barionic state of matter.” At the beginning of the crystalline stage, low-organized structures appear, which serve as starting points for the structural evolution. These were structures of Cu, NaCl, ZnS, and CH₄ types. This stage was followed by the stage of aromorphosis, i.e. qualitative changes of structure types. As an example of such a process, Zhabin (1983) suggests transition from structure series with high coordination numbers (e.g. 12 in close-packed metal structures) to structure series with filled octahedral interstices. Smirnova and Belov (1979) pointed out that “... at each level in the system of structure types, we observe evolution of

simplest low-organized structures with high symmetries (Cu, NaCl, ZnS) toward many-component highly-organized structure types with lower symmetries ...”

According to Zhabin (1983), mineral evolution studies are necessary to understand evolution of other planets: “... formulation and solution of the problems of mineral phylogeny of our planet will serve as a basis for creation, in the future, of evolutionary mineralogy of the Earth, which will help and provide a source of ideas and predictions for investigations of mineralogy of other planets of the Solar system.”

Mineral evolution and the problem of mineralogical inheritance

Mineral inheritance is one of the important problems in mineral evolution studies. Mechanisms of conservation and transmission of mineralogical information was a subject of study in the paper by Khomyakov and Yushkin (1981) and the brochure by Yushkin *et al.* (1984). The authors of the latter work pointed out that the problem of:

“... storage and use in new structural constructions of old primary material as a result of action of internal inheritance mechanisms ... is often underestimated or even ignored, which leads to the serious damage of mineralogical theory, especially of its prognostic methods ... In the sequence of mineral generations each subsequent generation inherits specific features of the minerals from the previous generation and this is the essence of the principle of inheritance in mineral genesis. Analysis of broad data in the field of crystal growth and genetic mineralogy shows that inheritance is a universal property of crystalline (and, in particular, mineral) systems, which to some extent is characteristic for all mineral-genetic processes.”

Yushkin *et al.* (1984) paid considerable attention to individual mineral crystals and devoted most of their work to the problems of mineral ontogeny. However, in many cases, mineralogical inheritance can be seen in the formation of a new mineral species at the expense of an old one. Of special interest is the concept of transformation mineral species introduced by A.P. Khomyakov. As an example of evolutionary sequences of mineral species, Yushkin *et al.* (1984) used the series of transformation titanite-, niobite- and zirconosilicate minerals in agpaitic nepheline syenites of the

Lovozero and Khibiny alkaline complexes. In these series, one mineral replaces the other and inherits from the latter not only basic chemical composition, but also to some extent its atomic arrangement. The examples are evolutionary series lomonosovite → murmanite → belyankinite, vuonnemite → epistolite → gerasimovskite, parakeldyshite → keldyshite → ‘hydrokeldyshite’, zirsinalite → lovozerite, kazakovite → ‘hydrokazakovite’, etc., in which each secondary mineral has a corresponding primary proto-mineral. The basic feature of the secondary minerals under consideration is that they cannot crystallize directly from solution or melt, but form as a result of alteration of the corresponding proto-phases. The concept of transformation mineral species seems to be an effective tool to establish genetic and structural relations between mineral species (Sorensen and Larsen, 2001; Khomyakov *et al.*, 2003, 2010, 2011; Yakovenchuk *et al.*, 2010, etc.).

Their discussion of the mechanisms of mineralogical inheritance Yushkin *et al.* (1984) conclude with the following passage:

“Whereas biological inheritance is based upon the principle of covariant reduplication of discrete genetic codes transmitted from one generation to the other, the principle of mineralogical inheritance may be identified as matrix-replicative. Whichever process of the mineral formation is in action, a mineral crystal grows layer-by-layer according to the structural blueprint dictated by the state of mineral-genetic media in interaction with the growing crystal. ... The crystal grows by accommodation not of single atoms, but of rather complex and structurally well defined crystalline blocks. It cannot be excluded that these micro-crystalline blocks act as elementary carriers of crystal-genetic information. ... For mineralogical processes, formation of objects from many elements is typical and therefore transmission and conservation of information is performed by the combinatorial formation of mineral series.”

Conclusions

The brief and certainly incomplete overview of mineral evolution studies given above indicates that this field of research was active in the U.S.S.R and Russia in 1970–80s, but did not receive much attention in the West due to limited access to the Russian-language scientific literature and specific Cold-War and post-Cold-War attitudes still existing on both sides of the former Iron

Curtain. The works cited above outlined general directions of mineral evolution studies, even though they were not as detailed and elaborate as in the works by Hazen *et al.* (2008, 2009, 2011, 2012). Nevertheless, many points discussed in the old Soviet literature deserve special attention. In the context of the present review on structural complexity of minerals, the most relevant is the concept of quantitative indicators of mineral evolution proposed by Yushkin (1982). The structural information content proposed in this review may be used to examine mineral evolution in strictly quantitative terms, i.e. in the amount of information that evolving mineral systems process in the course of the geological history of our planet.

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