ORIGINAL RESEARCH



Structural complexity and crystallization: the Ostwald sequence of phases in the $Cu_2(OH)_3Cl$ system (botallackite-atacamite-clinoatacamite)

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Abstract Analysis of the evolution of structural complexity of the Cu₂(OH)₃Cl polymorphs along the botallackite-atacamite-clinoatacamite Ostwald cascade of phases from the viewpoint of Shannon information-based complexity parameters shows that structural information increases during the transition from less stable to more stable phases. Among the three polymorphs, botallackite is the simplest, atacamite is intermediate, and clinoatacamite is the most complex. This agrees well with the Goldsmith's simplexity rule and shows that complexity is a physically important parameter that characterizes crystallization in complex chemical systems. Consideration of the crystal structures of the Cu₂(OH)₃Cl polymorphs in terms of their Cu–Cl arrays shows that transformation between the phases involves breaking and formation of chemical bonds and therefore has a reconstructive character.

Keywords Structural complexity · Crystallization · Atacamite · Botallackite · Clinoatacamite · Crystal structure · Mineral · Ostwald step rule · Metastability

Dedicated to A.L. Mackay on the occassion of his 90th birthday.

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Introduction

Structural complexity is one of the most interesting and rather unexplored themes in modern crystallography. Mackay [1-5] is one of the few researchers who emphasized the desirability of jointly investigating the concept of complexity and the mechanisms of formation of complex crystal structures. Recently, complexity of crystals has received a renewed attention from the various points of view, including its role in the interpretation of energy landscapes in solids [6], mathematical description of complex alloys [7], and analysis of disordered materials [8]. In a series of recent papers, Krivovichev [9–12] suggested estimation of structural complexity of crystals in terms of their Shannon information contents per atom and per unit cell and showed that the latter represents a negative contribution to the configurational entropy of crystalline solids [13].

In 1956, Goldsmith [14] pointed out that structural complexity or 'simplexity' is one of the important factors that govern crystallization of minerals under far-fromequilibrium conditions. The Goldsmith's simplexity principle states that metastable structurally simple polymorphs are kinetically favored over their stable, but structurally more complex counterparts. The most striking application of this rule is the interpretation of structural complexity of metastable phases that occur in the Ostwald cascades of phases. We remind that the Ostwald step rule is a conjecture that a crystallizing system first forms a sequence of metastable phases before forming the stable phase [15]. There are different interpretations of this rule that take into account structures of precursors in solutions and melts, competition between surface energy and polymorphism, etc. Goldsmith [14] observed that metastable polymorphs that crystallize according to the Ostwald rule are usually

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less complex than the final stable product in the sequence. For instance, disordered dolomite (or high-magnesium calcite) (Ca,Mg)CO₃ that has Ca and Mg disordered over the same cation site forms metastably before dolomite, CaMg(CO₃)₂, that has a fully ordered distribution of Ca and Mg in its crystal structure. Morse and Casey [16] provided many other similar examples, and quantitative verification of the Goldsmith's principle was considered in detail by Krivovichev [11]. The aim of the present study is to examine the validity of the Goldsmith's principle for the Cu₂(OH)₃Cl system that contains three polymorphs, botallackite, atacamite and clinoatacamite.

Atacamite is an orthorhombic polymorph of Cu₂(OH)₃₋ Cl (sometimes referred to as a β -Cu₂(OH)₃Cl), which has been known since the eighteenth century. Its crystal structure was first solved by Brasseur and Toussaint [17] and later refined by Wells [18] and Parise and Hyde [19]. The latter authors pointed out the similarity of the Cu cationic array in atacamite to those in spinel and pyrochlore, and this similarity was later supported by the magnetic measurements [20]. Botallackite, α -Cu₂(OH)₃Cl, was first described by Church [21] and structurally characterized by Voronova and Vainstein [22] and Hawthorne [23]. Clinoatacamite, a γ -polymorph, was discovered by Jambor et al. [24], and its crystal structure was reported by Grice et al. [25]. It is noteworthy that two other polymorphs of Cu₂(OH)₃Cl, paratacamite and anatacamite, have been reported in the literature [26, 27]. However, it was shown that paratacamite is Zn-stabilized [26], and anatacamite [27] was discredited as a separate mineral species in 2015 by the International Mineralogical Association [28].

All three known Cu₂(OH)₃Cl polymorphs have been the subject of extensive studies due to their interesting magnetic properties [20, 29, 30], their occurrence in patinas forming on the surface of bronze artifacts [31-33] and their general mineralogical and geochemical importance [34-37]. Their relative stabilities and thermodynamic properties were investigated by several authors (see [38] and references therein). Pollard et al. [38] prepared synthetic analogues of botallackite, atacamite and 'paratacamite' and studied their crystallization and postcrystallization transformations. Note that the crystalline solid identified by Pollard et al. [38] as paratacamite was in fact clinoatacamite, which was not established as a mineral species in 1989, when the work of Pollard et al. [38] was done. These authors found out that botallackite, the rarest of the naturally occurring trimorphs, is a key intermediate and crystallizes first under most conditions. Its subsequent recrystallization leads to the formation of atacamite or clinoatacamite, or of the latter from the former, depending upon the precise nature of the reaction medium. The crystallization sequence indicated that clinoatacamite is the thermodynamically stable phase at ambient temperatures. Thus, the crystallization in the $Cu_2(OH)_3Cl$ system follows Ostwald step rule and corresponds to the sequence of phases botallackite–atacamite–clinoatacamite. Below, we analyze this sequence from the viewpoint of information-based complexity parameters [9–13] and show that the system exactly obeys the Goldsmith's simplexity principle. We also provide structural description of the three phases in order to clarify the differences in their structural architecture in more details.

Methods

In order to compare polymorphic variations in the system under study from the viewpoint of structural complexity, the latter was estimated as a Shannon information content per atom (I_G) and per unit cell $(I_{G,total})$. According to this approach developed in [9–13], the complexity of a crystal structure can be quantitatively characterized by the amount of Shannon information it contains measured in bits (binary digits) per atom (bits/atom) and per unit cell (bits/cell), respectively. The concept of Shannon information, also known as Shannon entropy, used here originates from the information theory and its application to various problems in graph theory, chemistry, biology, etc. The amount of Shannon information reflects the diversity and relative proportion of different objects, e.g., the number and relative proportion of different sites in an elementary unit cell of a crystal structure. For a crystal structure, the calculation involves the use of the following equations [9-13]:

$$I_{\rm G} = -\sum_{i=1}^{k} p_i \log 2p_i \quad ({\rm bits/atom}), \tag{1}$$

$$I_{G,\text{total}} = -\nu I_G = -\nu \sum_{i=1}^k p_i \log_2 p_i \quad (\text{bits/cell}), \tag{2}$$

where k is the number of different crystallographic orbits (independent crystallographic Wyckoff sites) in the structure and p_i is the random choice probability for an atom from the *i*th crystallographic orbit, that is:

$$p_i = m_i / v, \tag{3}$$

where m_i is a multiplicity of a crystallographic orbit (i.e., the number of atoms at a specific Wyckoff site in the reduced unit cell) and v is the total number of atoms in the reduced unit cell. The information-based structural complexity parameters for the Cu₂(OH)₃Cl polymorphs were calculated using the software package TOPOS [39] and are given in Table 1. The crystal structure data used in the calculations were taken from references [19, 23, 25] for botallackite, atacamite and clinoatacamite, respectively.

Mineral name	v (atoms)	I _G (bits/atom)	I _{G,total} (bits/cell)
Botallackite	18	2.725	49.050
Atacamite	36	2.725	98.100
Clinoatacamite	36	3.281	118.116

The calculation of structural complexity parameters can be illustrated by the example of botallackite. It crystallizes in the space group $P2_1/m$ and has two symmetrically independent Cu atoms that occupy 2e and 2d sites. There is one Cl atom in the 2e site, two O (2e and 4f) and two H (2eand 4f) atoms. In total, there are 18 atoms in the unit cell (v = 18; Z = 2) and seven crystallographic orbits. The atoms at the 2e and 2d sites have $p_i = 2/18$ (there are five such orbits), whereas atoms at the 4f site have $p_i = 4/18$ (there are two such orbits). Therefore,

 $I_{\rm G} = -[5 \times (2/18) \times \log_2(2/18) + 2 \times (4/18) \times \log_2(4/18)]$ = 2.725 bits/atom.

Since v = 18, $I_{G,total} = 49.050$ bits/cell.

Results and discussion

Structural relations between the Cu₂(OH)₃Cl polymorphs

The crystal structure of botallackite is shown in Fig. 1a. It is based on electroneutral [Cu₂(OH)₃Cl]⁰ layers consisting of edge-sharing Cu(OH)₅Cl and Cu(OH)₄Cl₂ octahedra (Fig. 1b). The layers are parallel to (100) and are linked through interlayer hydrogen O-H…Cl bonds. In order to compare the crystal structures of three Cu₂(OH)₃Cl polymorphs, the layers in the structure of botallackite can be described as arrays of Cu atoms that form a distorted 3⁶ net (Fig. 2a). The description of the crystal structures of complex crystalline solids in terms of cation arrays is helpful to understand their structural organization and to reveal similarities between different structural architectures [40, 41]. In the crystal structure of botallackite, the (OH)⁻ and Cl⁻ anions are located above or below the centers of the Cu₃ triangles, but, to simplify the comparison between different polymorphs, it is best to consider the positions of the Cl⁻ anions only. Figure 2 shows that the Cu–Cl arrays in botallackite may be split into chains of corner-sharing $ClCu_3$ triangles running parallel to the *b* axis.

In contrast to botallackite, the crystal structures of atacamite and clinoatacamite (Fig. 3a, b) are based on three-



Fig. 1 Crystal structure of botallackite projected parallel to the *b* axis (a) and projection of the $Cu_2(OH)_3Cl$ layer parallel to the *a* axis (b)

dimensional Cu arrays of the distorted pyrochlore type (Fig. 3c, d) that define their magnetic behavior as pyrochlore antiferromagnets [20]. The pyrochlore-type Cu array corresponds to the array of the O atoms in cristobalite, SiO_2 , and can be derived from the diamond (dia) threedimensional net through its expansion. It is notable that the Cu arrays in atacamite and clinoatacamite are topologically similar to the Cu array in melanothallite, Cu_2OCl_2 [42], which forms as a result of their dehydration [43].

The difference between the crystal structures of atacamite and clinoatacamite is in the distribution of the $(OH)^{-}$ and Cl^{-} ions inside the pyrochlore-type Cu arrays



Fig. 2 Cu–Cl array in botallackite (a) and its separation into Cu–Cl one-dimensional chains (b)

that causes their distortion, which is different in the two polymorphs. Figure 3c, d shows the distribution of Cl⁻ ions inside the Cu arrays in atacamite and clinoatacamite, respectively. It is of interest that, by analogy to botallackite, both structures contain Cu₂Cl chains of cornersharing ClCu₃ triangular pyramids running parallel to the b axis. The chains in botallackite are compressed (b = 6.126 Å) compared to atacamite and clinoatacamite (b = 6.865 and 6.817 Å, respectively). In atacamite, the chains are separate from each other (Fig. 3e), whereas in clinoatacamite (Fig. 3f), they polymerize to form two-dimensional layers as shown in Fig. 4. The condensation of chains by sharing common Cu corners leaves one of the Cu atoms not bonded to Cl, and this is the position that is substituted by Zn, Mg and Ni in other atacamite group minerals [44-49].

The description of the crystal structures of the Cu_2 (OH)₃Cl polymorphs in terms of their Cu–Cl arrays shows that transition between them necessarily involves breaking and re-formation of the chemical bonds and therefore has a reconstructive character.

Structural complexity

The values of the information-based complexity parameters listed in Table 1 show that the botallackite-atacamiteclinoatacamite Ostwald cascade of phase transformations observed by Pollard et al. [38] obeys the Goldsmith's rule that the stable polymorphs are usually more complex than their metastable counterparts. On the basis of the measurements by Sharkey and Lewin [43], Pollard et al. [38] reported for clinoatacamite, atacamite and botallackite the $\Delta f G^{\circ}$ (298.2 K) values of -1341.8, -1335.1 and -1322.6 ± 3.6 kJ mol⁻¹, respectively. Figure 5 shows the plot of the $\Delta f G^{\circ}$ (298.2 K) values versus structural information amount per unit cell $(I_{G,total})$ that shows that the dependence is almost linear. Pollard et al. [38] pointed out that the most likely structural mechanism that underlies energy differences between the three phases is the formation of the strong hydrogen bonds between the (OH)⁻ groups and Cl⁻ anions, which is also expressed in the OH stretching frequencies as observed by Sharkey and Lewin [43]. This shows that in the case of the $Cu_2(OH)_3Cl$ polymorphs, increasing structural complexity provides more possibilities for the formation of more stable and energetically favored hydrogen-bonding networks.

The complexification of the Cu₂(OH)₃Cl polymorphs in the course of structural reconstructions can also be discussed from the viewpoint of general considerations of structural integrity. It is noteworthy that the first phase in the sequence, botallackite, has a layered character, whereas both atacamite and clinoatacamite possess framework structures. It is of interest that similar observations are valid for other examples of structural relations between stable and metastable phases. To cite but one prominent example, dmisteinbergite is a metastable polymorph of anorthite, CaAl₂Si₂O₈ (a calcium feldspar and one of the most common minerals in the Earth's crust), which occurs metastably during crystallization from the supercooled CaAl₂Si₂O₈ melt or from high-temperature gases [50–54]. In contrast to anorthite that contains an aluminosilicate framework, dmisteinbergite has a layered structure and its topological and algorithmic complexity is much smaller than that of anorthite [11, 55]. It seems that it is quite common that metastable simple phase has a layered character, whereas stable complex phase is framework based.

Conclusions

Analysis of the evolution of structural complexity of the $Cu_2(OH)_3Cl$ polymorphs along the botallackite–atacamite– clinoatacamite Ostwald cascade of phases from the viewpoint of Shannon information-based complexity parameters shows that structural information increases during the





Fig. 4 Two-dimensional Cu-Cl array in the crystal structure of clinoatacamite

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transition from less stable to more stable phases. This agrees well with the Goldsmith's simplexity rule and shows that complexity is a physically important parameter that

Fig. 5 Relation between $\Delta f G^{\circ}$ and $I_{G,total}$ for the Cu₂(OH)₃Cl polymorphs (*B* botallackite, *A* atacamite, *C* clinoatacamite)

characterizes crystallization in complex chemical systems and therefore should be considered during analysis of structural organization of matter, as it was frequently emphasized by Mackay [1–5] during his extremely productive and original scientific career. Acknowledgments SVK is grateful to the Russian Science Foundation (Grant 14-17-00071) for financial support of this study. FCH acknowledges support of an NSERC Discovery Grant.

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