Crystal structures and cellular automata

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Cellular automata are used as dynamic topological models of crystal structures based upon frameworks consisting of fundamental building blocks. Structure is considered as an automaton that works in accord with a prescribed program. Cellular automata models are constructed for metal sulfide frameworks in minerals and compounds of the pentlandite–djerfisherite–bartonite series, for zeolite ACO and compounds with pharmacosiderite structure, leucophosphite, phosphovanadylite etc.

1. Introduction

The theory of crystal growth is well elaborated in its thermodynamic and kinetic aspects. However, the process of the growth of crystal structures in the crystal-chemical sense is poorly understood, *i.e.* how complex structures grow in terms of atoms, atomic clusters, molecules *etc.* On one hand, the crystal-chemical theory of crystal growth should be based upon direct observations of events happening on the surface of a crystal with necessary resolution at the atomic and molecular scales. On the other hand, such a theory must satisfy all present crystal-chemical knowledge acquired during the last 90 years. In this regard, construction of theoretical crystal-chemical models of the growth of complicated structures might be relevant for a future experiment-based crystal-chemical theory of crystal growth.

The aim of this paper is to point out that the theory of automata may be used as a crystal-chemical model of construction of complicated structures step by step. Within this theory, the structure is thought of as a machine that works in accord with a prescribed program. In this regard, it can be compared to a computer that performs a certain sequence of a finite number of operations divided into single steps. A structure grows in three-dimensional space and has an active surface and a program working at this surface. The question is whether it is possible to outline general crystal-chemical rules for this program and to compare it with similar rules for chemically or structurally related crystals.

As a first model for a crystal-chemical model of growing structures based upon automata, the theory of cellular automata may be used. Cellular automata are discrete deterministic dynamical systems first introduced by von Neumann (1951) as models for self-reproductive biological systems. A version of a two-dimensional cellular automaton is known as a 'Life game', invented by the mathematician John Conway. Application of cellular automata to modeling physical laws was considered in detail by Toffoli & Margolus (1987). Of recent interest to cellular automata is Stephen Wolfram's book *A New Kind of Science* (Wolfram, 2002), where he points out that cellular automata can be considered as universal models for physical, biological, sociological and other systems [for critical comments, see Krantz (2002) and Gray (2003)]. A comprehensive account of the theory of cellular automata may be found in Ilachinski (2001). We note that cellular automata have been applied in crystallography for modeling the growth of snowflakes (Wolfram, 2002) and the growth of dendritic crystals in general (Kessler *et al.*, 1990), and for modeling microstructures (Gandin & Rappaz, 1997) *etc.* As far as we know, cellular automata have never been used in crystal chemistry.

In this paper, we concentrate mostly on inorganic crystal structures and, in particular, those that can be considered as composed from finite atomic clusters also known as fundamental building blocks (FBBs). The FBB concept is similar to the concept of secondary building units (SBU) and is widely used for describing complex structural architectures observed in phosphates, sulfates, borates, silicates, sulfides, oxides *etc.* (Banfield & Veblen, 1992; Hawthorne, 1994; Burns *et al.*, 1995; Férey, 2000; Cahill & Parise, 2000). The FBB concept is especially convenient for cellular automata modeling since the growth of a structure can be thought of as consisting of single steps corresponding to an addition of a new FBB to the already existing piece of structure.

2. Cellular automata: a brief introduction

A simple example of a cellular automaton is shown in Fig. 1(*a*). It consists of a line of square cells. Each cell takes on one of two possible states: black (1) or white (0). Each horizontal line of cells corresponds to a single step in time, *t*. At each step in time, each cell updates its current state according to a transition rule taking into account the states of cells in its neighborhood. The transition rule for the automaton shown in Fig. 1(*a*) is depicted in Fig. 1(*b*). This rule makes a cell white whenever both of its immediate neighbors were white on the step before. The initial condition (*t* = 0) is one black cell. The result of the work of this automaton is a periodic checker-board-like pattern of black and white cells.

Table 1
Crystallographic data for metal sulfide minerals based upon M_8S_{14} clusters.

Mineral	Formula	Framework	Space group	a (Å)	c (Å)	Reference
Pentlandite	$(Fe,Ni)_9S_8$	$[(Fe,Ni)_8S_8]$	$Fm\bar{3}m$	10.038 (1)	–	(a)
Cobalt pentlandite	Co_9S_8	$[Co_8S_8]$	$Fm\bar{3}m$	9.923 (1)	–	(b)
Argentopentlandite	$(Fe,Ni)_8AgS_8$	$[(Fe,Ni)_8S_8]$	$Fm\bar{3}m$	10.044 (3)	–	(c)
Djerfisherite	$K_6Na(Fe,Cu)_{24}S_{26}Cl$	$[(Fe,Cu)_{24}S_{26}]$	$Pm\bar{3}m$	10.465 (1)	–	(d)
Owensite	$(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$	$[(Cu,Fe,Ni)_{24}S_{26}]$	$Pm\bar{3}m$	10.349 (1)	–	(e)
Thalfenisite	$Tl_6(Fe,Ni,Cu)_{25}S_{26}Cl$	$[(Fe,Ni,Cu)_{24}S_{26}]$	$Pm\bar{3}m$	10.29	–	(f)
Bartonite	$K_6Fe_{24}S_{26}(S,Cl)$	$[Fe_{24}S_{26}]$	$I4/mmm$	10.424 (1)	20.626 (1)	(g)
Chlorbartonite	$K_6Fe_{24}S_{26}(Cl,S)$	$[Fe_{24}S_{26}]$	$I4/mmm$	10.3810 (8)	20.614 (2)	(h)

References: (a) Rajamani & Prewitt (1973); (b) Rajamani & Prewitt (1975); (c) Hall & Stewart (1973); (d) Dmitrieva & Ilyukhin (1975); (e) Szymański (1995); (f) Rudashevskii et al. (1977); (g) Evans & Clark (1981); (h) Yakovenchuk et al. (2003).

In general, a cellular automaton consists of an *n*-dimensional *lattice* of cells that take one of a finite number of possible states. The dynamics of the automaton is defined by local interactions of each cell with cells in its local neighborhood. At each step in time, each cell updates its state according to a *transition rule* (Ilachinski, 2001).

Wolfram (2002) classified cellular automata into four basic classes according to their behavior: (1) all initial conditions lead to the same uniform final state; (2) the final state is a periodic or nested pattern; (3) the behavior is more complicated than in classes 1 and 2 and is in many respects random, although some small-scale structures are present at all steps; (4) the behavior is very complicated and involves a complex mixture of order and randomness. Since crystal structures are periodic, in the following we shall use only cellular automata of class 2.

One important class of cellular automata is mobile automata described by Wolfram (2002). They are similar to the usual cellular automata but differ from them in that they have active cells and rules that specify how active cells should move from one step to the next. An example of a mobile automaton is shown in Fig. 2. Active cells in this automaton are marked by a black circle. Transition rules that are sufficient to describe the evolution of this automaton from a single grey cell are defined in Fig. 2(b). The result of the work of the mobile automaton is shown in Fig. 2(a). It is a pattern of white and gray cells with cross-shaped aggregates of five white cells each.

In the following section, we shall apply the theory of cellular automata to describe structures based upon frameworks of cubic clusters.

3. Cellular automata and structures based upon cubic clusters

3.1. Cubic clusters in structures of metal sulfides and oxysalts

Fig. 3(a) shows an M_8S_{14} cluster that occurs in a number of transition-metal sulfides (M = Fe, Cu, Ni, Co). The cluster consists of eight M atoms tetrahedrally coordinated by four S atoms. The MS_4 tetrahedra share edges to form the cubic M_8S_{14} cluster shown in Fig. 3(b). The M_8S_{14} clusters were found as separate entities in several metal–organic compounds (Christou et al., 1982, 1985) and as FBBs of complex frameworks in a number of metal sulfides of the pentlandite–djer-

fisherite–bartonite series (Table 1). In fact, the M_8S_{14} cluster shown in Fig. 3(a) represents a unit-cell content of the structure of fluorite, CaF_2, if the latter is described as a framework of FCa_4 tetrahedra (Belov, 1979; Long & Holm, 1994; Krivovichev, 1999a,b). The cluster is also known as a *stella octangula*, or 'a star with eight rays' (O'Keeffe & Hyde, 1996; Krivovichev & Filatov, 1999).

In order to describe topologies of metal sulfide frameworks based upon M_8S_{14} clusters, we represent one cluster as a cube (Fig. 3c) and linkage of two adjacent clusters (Fig. 3d) as a
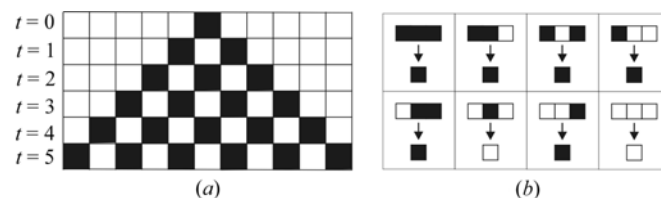

Figure 1
Cellular automaton (a) with transition rule (b) that makes a cell white whenever both of its immediate neighbors were white on the step before.
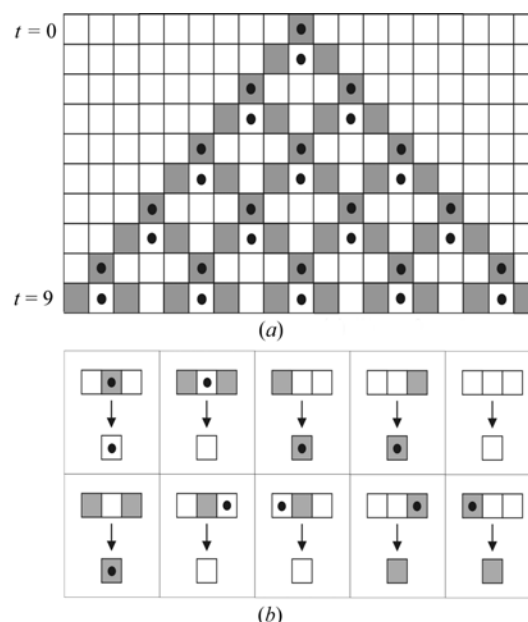

Figure 2
Mobile automaton (a) with active cells marked by black circles and its transition rule (b).

linkage of two cubes *via* a common edge (Fig. 3*e*). Using this approach, frameworks in compounds of the pentlandite–djerfisherite–bartonite series can be described as arrangements of layers consisting of cubes (Fig. 4).

In the pentlandite structure type, layers are composed from cubes arranged in a checker-board fashion (Fig. 4*a*). Two adjacent layers are shifted relative to each other by one cube.

The structure of djerfisherite and related compounds are based upon layers of two types: one identical to the layers in pentlandite and another one that consists of isolated cubes only (Fig. 4*b*). The layers alternate and two layers of the same type are translationally equivalent.

The metal sulfide framework in the structure of bartonite contains the same types of layers as observed in djerfisherite. The layers of different types alternate, however, their stacking sequence is different. Whereas the pentlandite-like layers are in translationally equivalent positions, the layers of isolated cubes are in two positions shifted relative to each other by one cube (Fig. 4*c*).

Fig. 4(*d*) shows construction of a framework topologically related to those shown in Figs. 4(*a*), (*b*), (*c*). This framework contains only layers of isolated cubes; each cube shares four corners with cubes from the layer below and four corners with cubes from the layer above. A framework of this type has not been observed in metal sulfides. It can be found in the structure of $[(C_2H_{10}N_2)_4(H_2O)_2][Co_{7.12}Al_{0.88}P_8O_{32}]$ (ACO zeolite topology; Feng *et al.*, 1997) with a tetrahedral framework consisting of the $T_4P_4O_{20}$ cubic clusters (T = Co, Al) of eight corner-sharing TO_4 tetrahedra (Fig. 5*a*). The same topology is also known for the pentahedral–tetrahedral framework in the structure of $(C_2H_{10}N_2)_2[Fe_4O(PO_4)_4](H_2O)$ (de Bord *et al.*, 1994) based upon $[Fe_4O(PO_4)_4]^{2-}$ FBBs (Fig. 5*b*) and the octahedral–tetrahedral framework in leucophosphite, $K_2[Fe_4(OH)_2(H_2O)_2(PO_4)_4](H_2O)_2$ (Moore, 1972; Dick & Zeiske, 1997), and related compounds, consisting of 'butterfly'-shaped FBBs shown in Fig. 5(*c*). We note that the framework of cubes shown in Fig. 4(*d*) corresponds to the **bcu** regular net described by Delgado Friedrichs *et al.* (2003) (see §4 for more details).
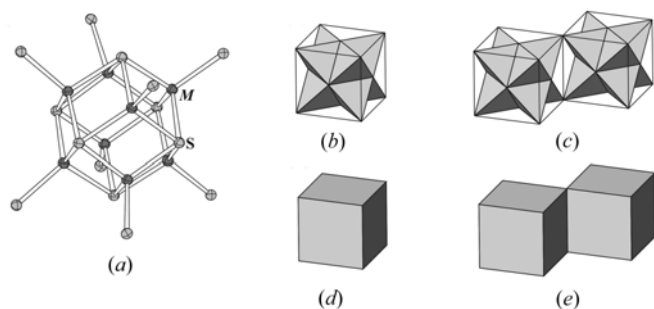
3.2. Cellular automata and frameworks of cubes

The three-dimensional frameworks of cubes shown in Fig. 4 can be obtained as a product of evolution of two-dimensional cellular automata. In contrast to the patterns shown in Figs. 1 and 2, these frameworks should be constructed by successive addition of layers of cells that are updated at each step in time according to a transition rule.

The cellular automata corresponding to the framework shown in Fig. 4 and configurations resulting after 12 steps in their evolution are depicted in Fig. 6. The automata are based upon cubic lattices of either black or white (empty) cubes. The initial condition for all automata is a single black cell.

The cellular automaton for the pentlandite framework is very simple (Fig. 6*a*). Its transition rule states that, if the cell is black, all its immediate (non-diagonal) neighbors in the next layer are black. The cellular automaton corresponding to the framework shown in Fig. 4(*d*) is also simple (Fig. 6*d*). It has the following transition rule: if the cell is black, all its diagonal neighbors in the next layer are black.
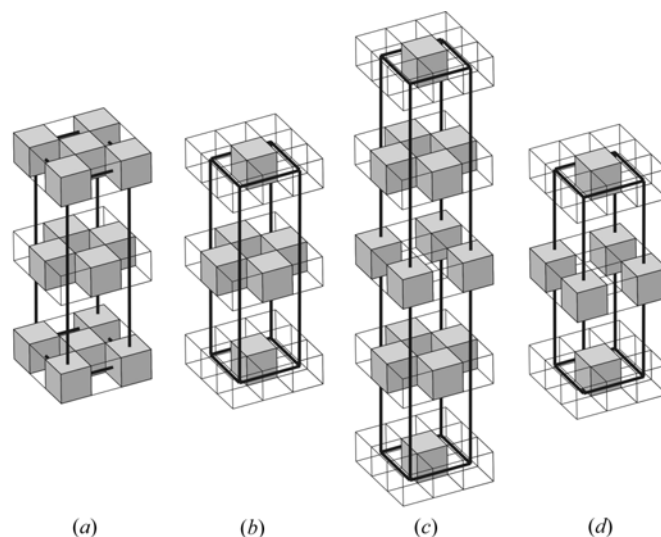
Figure 4
(*a*) Pentlandite, (*b*) djerfisherite, (*c*) bartonite and (*d*) zeolite ACO frameworks separated into layers of cubes that symbolize cubic FBBs and expanded in the direction perpendicular to the layers (see text for details).
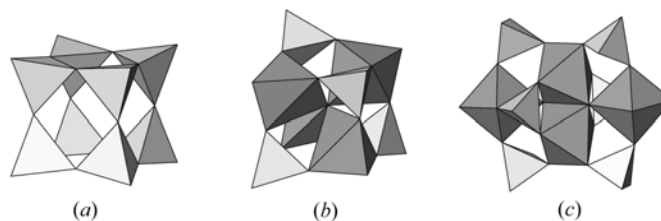
Figure 3
The M_8S_{14} cluster (M = Fe, Cu, Ni, Co) that occurs in transition-metal sulfides of the pentlandite–djerfisherite–bartonite series (*a*) and its representation as a group of eight MS_4 tetrahedra (*b*) and as a cube (*d*). Linkage of two clusters (*c*) can be represented as linkage of two cubes *via* an edge (*e*).

Figure 5
FBBs forming frameworks with topology shown in Fig. 4(*d*): (*a*) $T_4P_4O_{20}$ cubic clusters (T = Co, Al) of eight corner-sharing TO_4 tetrahedra in the zeolite ACO, (*b*) pentahedral–tetrahedral cluster $[Fe_4O(PO_4)_4]^{2-}$ in the structure of $(C_2H_{10}N_2)_2[Fe_4O(PO_4)_4](H_2O)$ and (*c*) $[Fe_4(OH)_2(H_2O)_2(PO_4)_4]$ 'butterfly'-shaped cluster in the structure of leucophosphite.

Construction of the djerfisherite and bartonite frameworks (Fig. 4a, b, respectively) requires mobile automata (Figs. 6b, c, respectively). The transition rules for these automata are similar. In both cases, if a white cell is active, it is black and active in the next layer. The rules for a black active cell differ. In both automata, it is white in the next step and its immediate neighbors are black. However, the djerfisherite automaton (Fig. 6b) generates five active white cells, whereas the chlor-bartonite automaton generates only four (Fig. 6c). The difference in the transition rules results in different framework topologies.

3.3. Transition rules of cellular automata and chemical requirements

The metal sulfide frameworks shown in Figs. 4(a), (b), (c) can be generated by the successive addition of cubic Fe_8S_{14} clusters using different transition rules. What controls these rules, at least in chemically related systems such as metal sulfides based upon M_8S_{14} clusters? A partial answer to this question may be derived from the chemical composition of respective compounds. The metal sulfide framework in pentlandite-group minerals contains relatively small cubic cavities occupied by transition-metal atoms M in octahedral coordinations (Fig. 7a). Both djerfisherite and bartonite frameworks contain large cavities occupied by the octahedral A_6X moieties (A = K, Tl, Pb, Ba; X = S, Cl) (Figs. 7b and c). In addition to the large cavities, there are additional small cubic cavities in djerfisherite (as in pentlandite) occupied by Na (or by another relatively small cation such as Li or Mg). In the chlorbartonite framework, only large cavities are present. Thus, the presence of potassium favors 'modification' of the transition rules of a cellular automaton in order to accommodate K_6X complexes in the framework cavities.

4. Cellular automata and three-dimensional nets

Studies of the topology of three-dimensional nets are relevant to the problem of construction and investigation of relation-
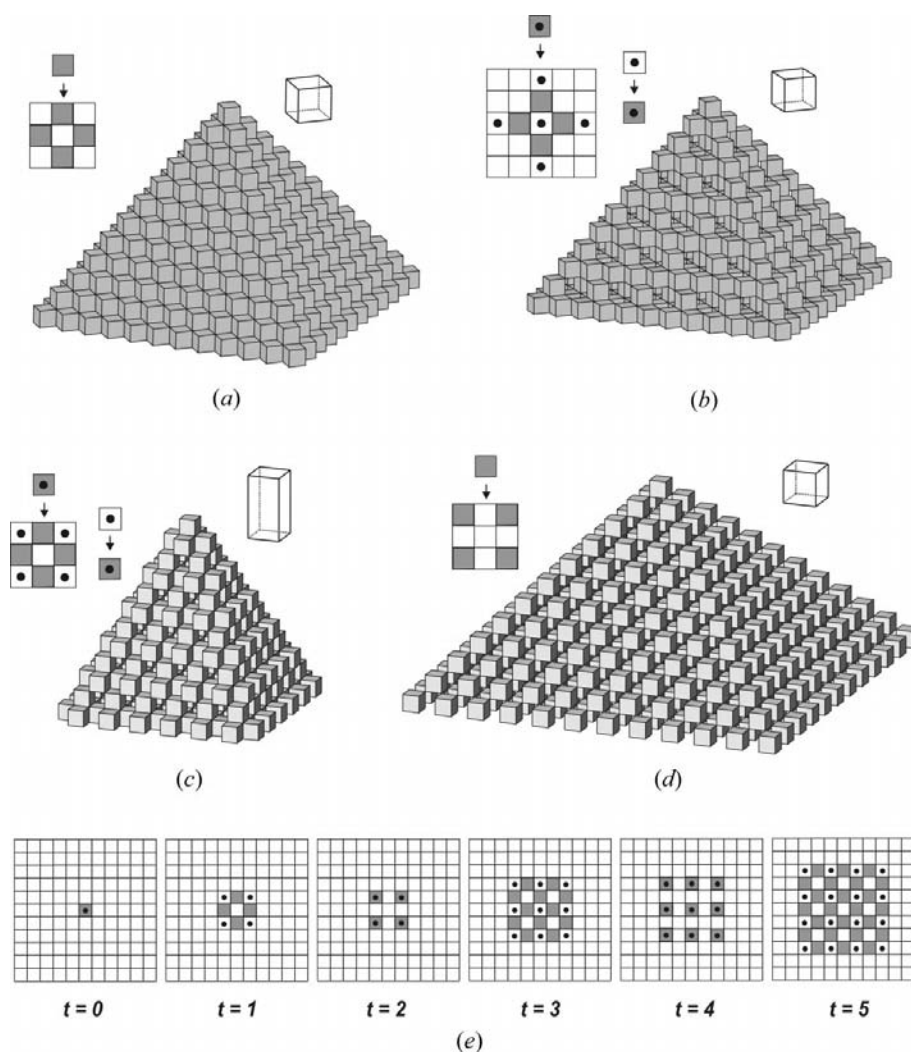

Figure 6
Cellular automata that correspond to the frameworks of cubes shown in Fig. 4: cellular automata for (a) pentlandite, (b) djerfisherite, (c) bartonite and (d) zeolite ACO. Pictures show configurations resulting after 12 steps in the evolution of the automata and their transition rules. (e) gives successive steps in the evolution of the two-dimensional automaton that results in the bartonite-type framework of cubes (c).

ships of open framework materials (O'Keeffe *et al.*, 2000). Recently, Delgado Friedrichs *et al.* (2003) described five regular three-dimensional nets (**dia**, **nbo**, **srs**, **bcu** and **pcu**). As we have shown above, the **bcu** topology (corresponding to a

body-centered cubic lattice) can be obtained by application of the cellular automaton shown in Fig. 6(*d*). Here we demonstrate that the **nbo** and **pcu** nets can also be produced using cellular automata.

The automata construction of the **nbo** and **pcu** topologies requires a change of the underlying lattice of a cellular automaton. It can be chosen as a three-dimensional net that corresponds to a primitive cubic lattice (Fig. 8*a*). The nodes of the net take on one of two states: black or white (empty). The nets are constructed by successive addition of layers of nodes that are updated at each step according to a transition rule.

The transition rule for the cellular automaton that emulates the **pcu** net is very simple. If the node is black, it and its immediate neighbors in the next layer are black (Fig. 8*b*).

The transition rule for the automaton for the **nbo** net is more complicated (Fig. 8*c*). Fig. 8(*d*) shows successive steps in the evolution of the two-dimensional automaton that produces the **nbo** regular net.
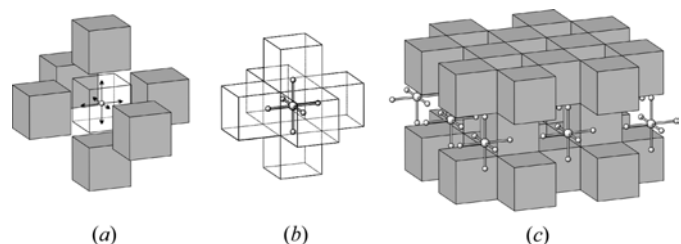

Figure 7
(*a*) Octahedrally coordinated *M* atoms in pentlandite and Na atoms in djerfisherite are in a cubic cavity that is created by six M_8S_{14} clusters (shown as cubes); (*b*) A_6X complex in djerfisherite and bartonite is at the center of a cross-like cavity consisting of seven cubes; (*c*) location of the A_6X complexes within the framework of cubic clusters in bartonite.
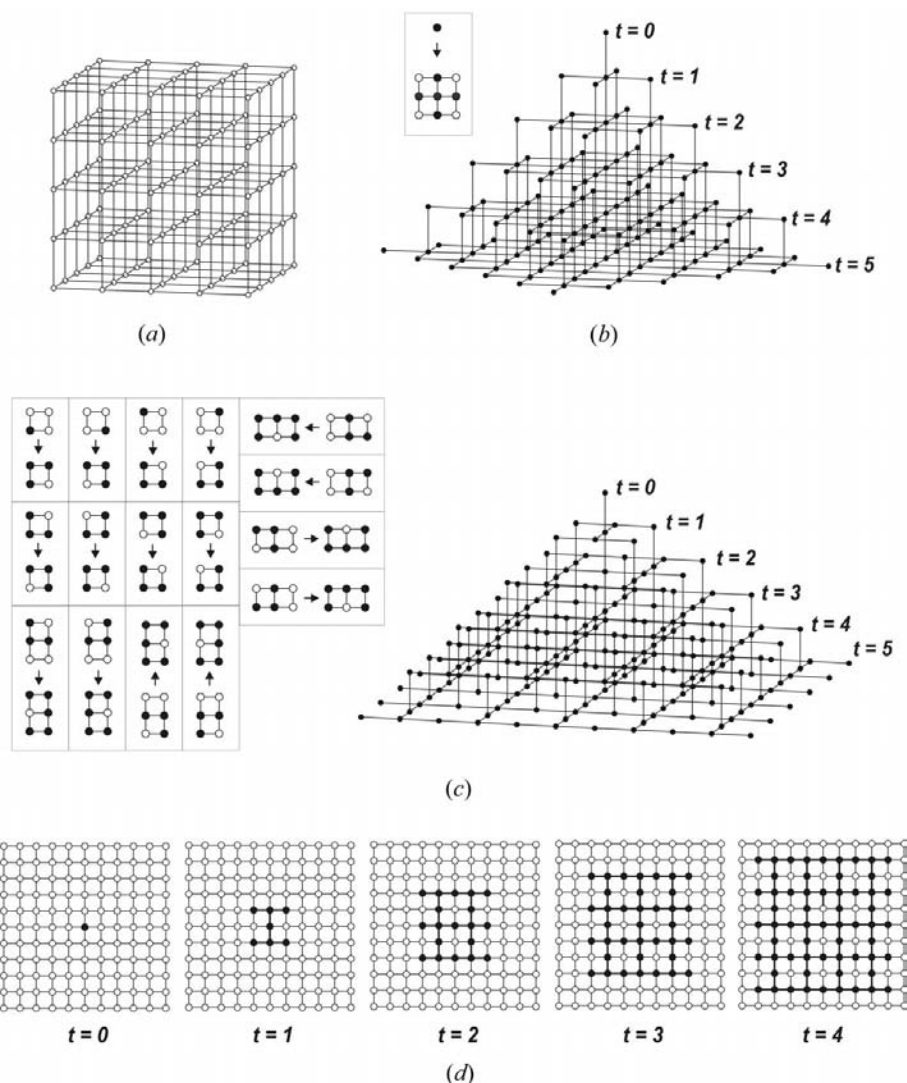

Figure 8
(*a*) The primitive cubic lattice as an underlying lattice for cellular-automata construction of the **pcu** and **nbo** nets; net configurations resulting after five steps in the evolution of the automata whose transition rules are given in the insets [(*b*), (*c*): automata that produce the **pcu** and **nbo** nets, respectively]; (*d*) successive steps in evolution of the two-dimensional automaton that results in the **nbo** regular net.

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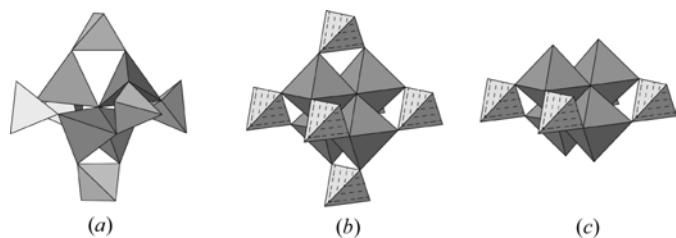
Figure 9
FBBs forming frameworks with **pcu** and **nbo** topologies: (a) $Zn_4O(XO_4)_3$ clusters in the structures of $M_3Zn_4O(XO_4)_3 \cdot n(H_2O)$ (M = Na, K, Rb; X = P, As); (b) $[(AO)_4(BO_4)_6]$ clusters from the structure of pharmacosiderite; (c) $[(AO)_4(BO_4)_4]$ clusters from the structure of phosphovanadylite.

The **pcu** and **nbo** regular nets are common in frameworks based upon FBBs. In these frameworks, FBBs correspond to the nodes of the nets and linkage of nodes symbolizes linkage of adjacent FBBs. The **pcu** net describes the topology of a tetrahedral framework based upon $Zn_4O(XO_4)_3$ clusters (Fig. 9a) in the structures of $M_3Zn_4O(XO_4)_3 \cdot n(H_2O)$ (M = Na, K, Rb; X = P, As) (Harrison *et al.*, 1996). It also corresponds to the topology of the three-dimensional linkage of octahedral–tetrahedral $[(AO)_4(BO_4)_6]$ clusters shown in Fig. 9(b) in the structures of pharmacosiderite, $Fe_4H(OH)_4(AsO_4)_3(H_2O)_5$ (Zemann, 1948; Buerger *et al.*, 1967), and its titanosilicate and germanate analogs, $HM_3(AO)_4(BO_4)_3 \cdot 4(H_2O)$ (M = K, Rb, Cs; A = Ti, Ge; B = Si, Ge) (Behrens *et al.*, 1998).

The **nbo** net describes the topology of the framework of the $[(AO)_4(BO_4)_4]$ clusters (Fig. 9c) in the structures of phosphovanadylite, $(Ba,K,Ca,Na)_x[(V,Al)_4P_2(O,OH)_{16}](H_2O)_{12}$ (Medrano *et al.*, 1998) and $[(CH_3)_4N]_{1.3}(H_3O)_{0.7}[Mo_4O_8(PO_4)_2](H_2O)_2$ (Haushalter *et al.*, 1989).

5. Concluding remarks

Here we have demonstrated how frameworks consisting of FBBs can be generated using specifically constructed cellular automata. This process can be considered as a model of growth of complex structures that involves successive addition of single clusters to the growing structure. It is noteworthy that such fundamental properties of crystals as symmetry and periodicity emerge as a result of automaton-like dynamic behavior of the structure, though they are not explicitly used in the transition rules.

Here we considered only inorganic structures. The cellular automata models can also be used for structures consisting of organic molecules. Of special interest are polymorphs of molecular compounds that differ in packing of molecules. It is very likely that different packing modes can be simulated using automata with similar lattices but different transition rules.

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