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METASTRUCTURES AND NONTETRAHEDRAL ZEOLITE-LIKE FRAMEWORKS

by

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Abstract

Certain complex compounds can be described as metastructures based on the topology of three-dimensional Wells-nets homeomorphic to the nets of simple crystal structure-types such as diamond, rutile, halite, NbO or ReO_3. The larger the magnification of the metastructures relative to their basic nets, the greater the chance that these frameworks have zeolitic properties. Particular emphasis is placed on the pharmacosiderite type structure.

1. Introduction

I would like to illustrate two separate, but in some instances related points. One is the concept of metastructures based on the decoration of simple three-dimensional nets by ever more complex chemical entities (atoms or clusters of atoms). The second is the fact, that the larger the magnification of the metastructures becomes, the better the chance that these compounds have zeolitic properties. In the most narrow definition zeolites are microporous aluminosilicates with tetrahedral coordination of oxygen atoms around aluminum and silicon. However, as has been recognized a long time ago, nontetrahedral and nonsilicate compounds can have zeolitic properties as well (ZEMANN, 1947, 1991, 1993).

Systematizing and classifying the crystal structures of minerals and inorganic compounds is becoming more and more difficult as increasingly complex structures are being described. Even the visualization of these structures is often not simple. Thus it helps to pay attention to the ways in which they are represented.

A compact way to represent a crystal structure is to state its cell constants, space group symmetry and the positional coordinates of all symmetrically independent atoms in the unit cell. Unfortunately it is very difficult to visualize such presentation. Except for special cases it is even more difficult to recognize relationships among various structures described that way. Therefore, from the very beginning crystal structures were represented conceptually and graphically by making use of a variety of approaches. BRAGG (1920) understood crystal structures as packings of atomic spheres.

Pauling emphasized the packing of coordination polyhedra formed by anions around the cations. This means that one can visualize simultaneously a whole group of atoms that are close to each other. As an example Fig. 1 shows the crystal structure of high cristobalite represented as a collection of spheres and as connected tetrahedra.

Three ways to represent the structure of high cristobalite

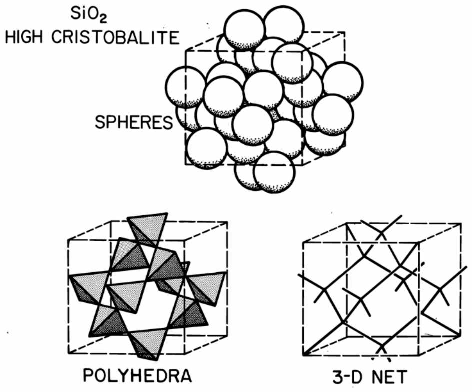

Fig. 1
The crystal structure of high cristobalite represented as spheres, as polyhedra and as a Wells-net (after BAUR, 1977).

Wells proposed in a series of papers an alternate view (WELLS, 1954 to 1976; summarized in WELLS, 1977). He saw crystal structures as 3-dimensional nets of bonds between the individual atoms. These atoms are located at the nodes or vertices of the 3-dimensional nets, while the bonds between the atoms are the links between the nodes. I shall call these nets Wells-nets. This approach proved particularly fruitful for describing and classifying the crystal structures of zeolites. The nets of zeolite frameworks are three-dimensional and have tetrahedrally four-connected vertices. Their classification is based on the topological properties of their underlying nets (BAERLOCHER et al., 2001; SMITH, 2000). Currently 139 distinct zeolitic tetrahedral frameworks are known.

One can generalize this method and use it to classify nontetrahedral frameworks as well. The nodes of the nets are then seen to be occupied by stereochemically significant groupings of atoms, while the edges represent the links between these clusters. The topology of the arrangement relates to whole groups, not just to individual atoms on the vertices of the nets. This was pointed out by SCHINDLER et al. (1999) in a review of these so-called metastructures, which can be viewed as simple frameworks decorated at their nodes by large or small clusters. Both the vertices and the links in the metastructures can consist either of individual atoms or of groups of atoms.

What follows is a small selection meant to illustrate a wide field. More examples are presented by SCHINDLER et al. (1999), but even they offer just a sample from the available multitude of frameworks.

2. Diamond, cristobalite and faujasite are based on the same three-dimensional Wells-net

We start with a simple example, in which we are dealing mainly with tetrahedral environments at the nodes. The net for high cristobalite shows us the bonds between the silicon atoms situated at the tetrahedral vertices to the oxygen atoms that are located halfway between the silicon atoms (Fig. 1, Table 1). One can see how useful this presentation is, because the three-dimensional net of high cristobalite (PEACOR, 1973) is immediately recognized as the net of the diamond crystal structure (BRAGG, 1913) when we imagine replacing the Si–O–Si part of the cristobalite structure by C–C in diamond (the silicon atoms are replaced by the carbon atoms, the centers of the C–C bonds assume the positions of the oxygen atoms).

Both structures are based on the same three-dimensional net. This is not obvious when we inspect the representation of these structures using spheres (Fig. 1). Actually one could put it another way and say that the cristobalite structure is just elemental silicon with oxygen atoms inserted in between. Any link between vertices can also be taken as a 2-connected node: [Si] is connected by a bond in cubic silicon, but by [O] in high cristobalite. The square brackets serve to identify atoms or groups of atoms as occupants of nodes in a net. The black and white coloring in Table 1 is used to distinguish the 4-connected node [Si] from the 2-connected node [O] of cristobalite.

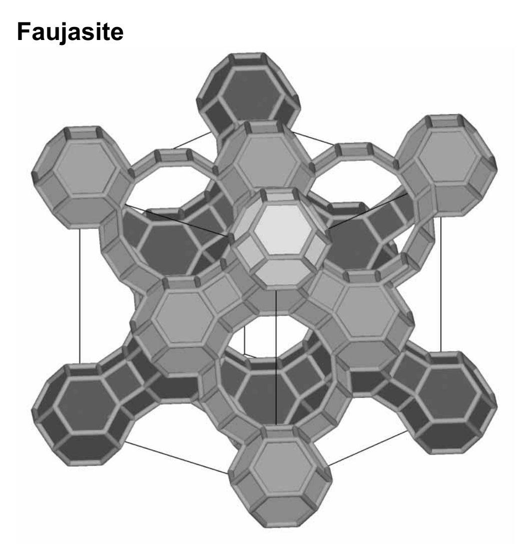

Fig. 2

Diagram of faujasite, the $[Si_{0.3}Al_{0.7})_{24}O_{36}O_{24/2}]$ *groups are located at the tetrahedral nodes of the diamond net (after BAUR & FISCHER, 2002).*

Compound	Group at black vertices	Group at white vertices	Magnification
Diamond-type:			
Diamond, C	[C]	same as black	1
High cristobalite, SiO_2	[Si]	[O]	2.0
Faujasite, $(Na_2,Ca,Mg)_{29}$ $[Al_{58}Si_{134}O_{384}]\ .\ 240H_2O$	$[Si_{0.3}Al_{0.7})_{24}O_{36}O_{24/2}]$	same as black	6.9
Rutile-type:			
Rutile, TiO_2	[Ti]	[O]	1
$[Cd\{Cd(CN)_3\}_2]\ .\ (C_3H_4N_2)_2\ .$ p-$C_6H_4(CH_3)_2$	[Cd]	[Cd(CN)3]	2.9
Halite-type:			
Halite, NaCl	[Na]	[Cl]	1
Pyrite, FeS_2	[Fe]	$[S_2]$	1.0
SiP_2O_7	$[SiO_{6/2}]$	$[OP_2O_{6/2}]$	1.3
Zunyite, $[Si_5Al_{13}O_{20}(OH)_{14}F_4Cl]$	$[AlO_4Al_{12}O_{12/2}(OH)_{14}F_4]$	$[SiO_4Si_4O_{12/2}]$	2.5
Zeolite A, $Na_{12}[Al_{12}Si_{12}O_{48}]\ .\ 27H_2O$	$[Al_{12}Si_{12}O_{36}O_{24/2}]$	same as black	4.4
NbO-type:			
NbO	[Nb]	[O]	1
Sodalite, $Na_6[Al_6Si_6O_{24}].\ 2NaCl$	$[Si_2Al_2O_4O_{8/2}]$	same as black	2.1
$[Cu_6(CO_3)_{12}]\ K_4(C(NH_2)_3)_8\ .\ 8H_2O$	$[Cu_4(CO_3)_4(CO_3)_{8/2}]$	same as black	3.4
FVP-1, $Na_v[((V^{4+}{}_{4-w}V^{5+}{}_{1+w})\ O_9)$ $(PO_4)_2]\ .\ (PO_4)_x\ .\ (OH)_y\ .\ zH_2O$	$[V_5O_9(PO_4)_{4/2}]$	same as black	3.8
ReO_3-type:			
ReO_3	[Re]	[O]	1
Boracite, $Mg_3[B_4O(BO_4)_3]Cl$	$[OB_4]$	$[BO_4]$	1.6
$K_3[Zn_4O(AsO_4)_3]\ .\ 4H_2O$	$[OZn_4]$	$[AsO_4]$	2.1
Pharmacosiderite, $K[Fe_4\,(OH)_4$ $(AsO_4)_3]\ .\ 6\text{-}8H_2O$	$[Fe_4(OH)_4]$	$[AsO_4]$	2.1

Table 1

Survey of metastructures, their groups at the black and white vertices, and the approximate magnification factor compared with the original structure type (after SCHINDLER et al., 1999).

What helps us to tell the cristobalite-type net apart from other tetrahedral nets is the topology of the arrangement of its nodes. In the cristobalite net there exist only 6-rings of tetrahedral vertices. When we have a look at the quartz-type net we find that it contains both 6-rings and 8-rings of tetrahedral nodes. Viewing the underlying nets of bonds in crystal structures is a way to recognize their topology and to distinguish them from frameworks possessing different topologies. Frameworks with the same topologies can still crystallize with very different symmetries. Identifying the underlying framework topology helps to establish the relationships between symmetrically different but similar crystal structures.

In principle we can imagine substituting for the carbon atom in the diamond-type net any larger and more complex unit. That is the way one views the structure of the zeolite faujasite when seen as a diamond-type arrangement of cuboctahedral $[Si_{0.3}Al_{0.7})_{24}O_{36}O_{24/2}]$ units (BAUR, 1964; Fig. 2). One carbon atom in diamond is replaced by 72 silicon, aluminum and oxygen atoms in faujasite (Table 1). The twelve oxygen atoms given in the chemical formula as 24/2 correspond to those shared between two cuboctahedral units within the double six-rings (hexagonal prisms), therefore, only one half of them is counted as belonging to each neighboring cuboctahderon. The unit cell length of faujasite is almost seven times the cell length of diamond. We can call this the magnification factor of the more complex structure over the basic structure. Consequently the small pores of diamond become in faujasite so large that they can admit not only water molecules and exchangeable cations, but also small organic molecules. This facilitates the interesting catalytic properties of faujasite-type materials. Half of the volume of faujasite is pore space.

The hierarchical progression as exemplified above by showing the topological similarities of the frameworks of diamond or silicon, cristobalite and faujasite leads us to ever more complex metastructures based on the same type of net. Cristobalite and faujasite are metastructures of silicon and diamond (Table 1).

2. A metastructure of the rutile type

The rutile-type crystal structure is one of the basic AB_2 structure types (BAUR, 1956). The titanium atoms in TiO_2 are surrounded in a distorted octahedral coordination by six oxygen atoms, each oxygen atom is surrounded in an approximately trigonal coordination by three titanium atoms. Recently a number of metastructures of the rutile-type have been synthesized. One of them has the composition $(Cd\{Cd(CN)_3(C_3H_4N_2)\}_2).p\text{-}C_6H_4(CH_3)_2$ (KIM & IWAMOTO, 1997). This looks forbidding and far removed from the TiO_2 composition of rutile itself. Actually when we rewrite it as $[Cd^o\{Cd^t(CN)_3\}_2].(C_3H_4N_2)_2.p\text{-}C_6H_4(CH_3)_2$ it becomes clear what the framework is (in square brackets) and what the pore-filling is. The first cadmium atom, Cd^o, is octahedrally six-coordinated by the nitrogen atoms of the cyano groups. The second cadmium atom, Cd^t, is coordinated by three carbon atoms of the cyano group. The arrangement of $[Cd^o\{Cd^t(CN)_3\}_2]$ corresponds to the topology of the rutile-type (Fig. 3). The symmetry is lowered from tetragonal to monoclinic. Both, the Ti and the O-positions of rutile are occupied here by Cd atoms. In order to distinguish the two different kinds of nodes it is useful to label them separately, thus, one Cd-atom is said to reside at the black vertex, the other at the white vertex (Table 1). The 1H-imidazole (1,3-diazole) group of $(C_3H_4N_2)_2$ composition, and the *p*-xylene ($p\text{-}C_6H_4(CH_3)_2$) group are not part of the framework. However, a nitrogen atom of the 1H-imidazole complements the approximately trigonal coordination of the second cadmium atom Cd^t to a tetrahedral environment.

What is apparently needed to crystallize these complex rutile-type frameworks are octahedrally 6-connected centers together with approximately trigonal 3-connected centers in a ratio of 1:2, which can occupy the appropriate nodes of the rutile topology (BATTEN et al. 1998). It is likely that additional complex representatives of the rutile-type net will be discovered in the future.

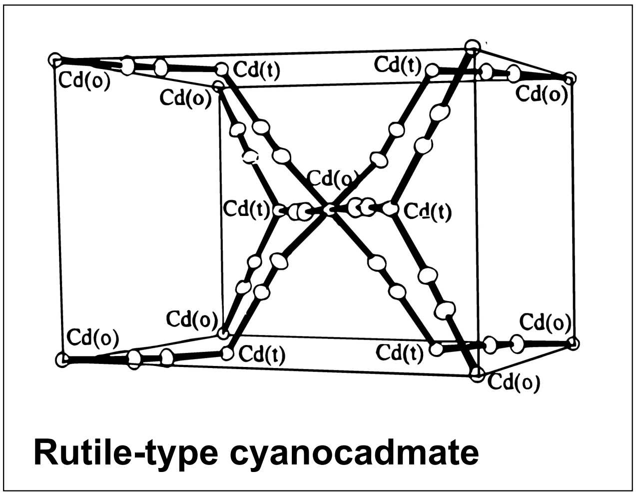

Fig. 3
Rutile-type $[Cd\{Cd(CN)_3\}_2]$*-framework of* $[Cd\{Cd(CN)_3\}_2].(C_3H_4N_2)_2].p\text{-}C_6H_4(CH_3)_2$*. The pore-filling 1H-imidazole and p-xylene molecules are not shown (after KIM & IWAMOTO, 1979).*

3. Metastructures of the halite or NaCl-type

The crystal structure of NaCl, halite, is one of the simplest AB structures and one of the first to be determined (BRAGG, 1914) by X-ray diffraction. Halite crystallizes in space group $Fm\bar{3}m$ with Na and Cl located in Wyckoff sites 4(a) and 4(b). The simplest way to describe it is to say that it is a three-dimensional checkerboard pattern with six white particles surrounding octahedrally one black particle and *vice versa*. When we look at it Wells' way we say it is a three-dimensional six-connected net with two different vertices, each of which is coordinated by six vertices of the other kind. Looking at it strictly topologically there is of course only one kind of node. Chemically we distinguish them by coloring the six-connected vertices occupied either by [Na] or by [Cl] (Table 1).

It seems that the first person to recognize a relation of the metastructure-type was Bragg son, when he described the crystal structure of pyrite, FeS_2, and its similarity to the NaCl structure (BRAGG, 1914). The [Fe] takes the place of [Na], while $[S_2]$ replaces [Cl]. When we furthermore imagine replacing [Fe] by a coordination octahedron of oxygen around silicon $[SiO_{6/2}]$, and replacing [S2] by the diphosphate group $[OP_2O_{6/2}]$ we get the crystal structure of cubic SiP_2O_7 (TILLMANNS et al. 1973). Actually there exists a pyrite type SiP_2 and one could also say that the compound SiP_2O_7 is an SiP_2O_7 filled up with oxygen atoms. This is analogous to the case of silicon and cristobalite mentioned above. But this is another story, not to be pursued here.

The rare mineral zunyite also is a metastructure of halite. It is composed of Keggin molecule-type $[AlO_4Al_{12}O_{12/2}(OH)_{14}F_4]$ aluminate groups, with a central tetrahedrally coordinated aluminum atom, surrounded by aluminum-oxygen coordination octahedra. These Keggin molecules are arranged in a halite-type pattern together with $[SiO_4Si_4O_{12/2}]$ pentamers of silicon-oxygen coordination tetrahedra, consisting of a central SiO_4 tetrahedron connected by shared oxygen atoms to four surrounding SiO_4 groups (BAUR & OHTA, 1982). The bridging between these clusters is accomplished via the $O_{12/2}$ oxygen atoms. The magnification factor relative to halite is 2.5.

Even larger is the magnification for zeolite A, $Na_{12}[Al_{12}Si_{12}O_{48}]$. $27H_2O$ (GRAMLICH & MEIER, 1971), consequently this is a very porous substance. In this case both kinds of vertices are occupied by one type of group, a cuboctahedron of composition $[Al_{12}Si_{12}O_{36}O_{24/2}]$ (Table 1). This is the same type of cuboctahedral unit present in faujasite.

4. Metastructures derived from the NbO-type

The crystal structure of NbO can be viewed formally as a defect structure derived from NaCl by leaving vacancies in positions 0 0 0 and ${}^1/_2$ ${}^1/_2$ ${}^1/_2$, for one anion and one cation each (Fig. 4). This arrangement has space group symmetry $Pm\bar{3}m$ with Nb and O occupying the 3(c) and 3(d) sites, respectively (BOWMAN et al., 1966; WELLS, 1984, p.539). As Wells points out, the crystal structure of NbO is an example of one of the simplest three-dimensional 4-connected nets, with both, Nb and O, surrounded in square planar coordination by each other. Deriving one structure from another is a nice way to memorize both structures. However, the topology of the two Wells-nets in this case is entirely different (Table 1). The crystal structure of NbO itself is very dense. It has 40 Nb atoms per 1000 Å^3.

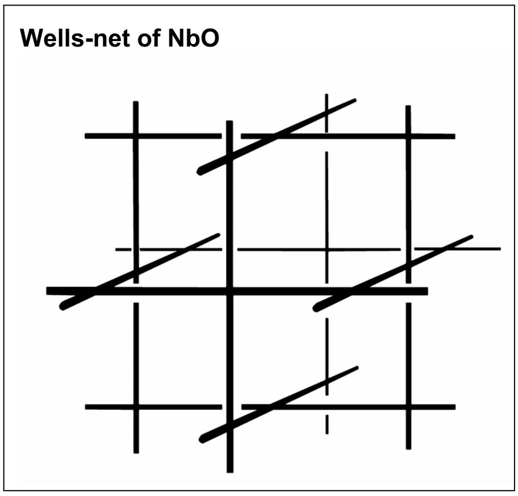

Fig. 4
The Wells-net underlying the crystal structure of NbO (after SCHINDLER et al., 1997).

The topology of the NbO-type net shows up in several other more complex structures. Two of these I wish to introduce here. In order to construct an NbO-type metastructure we need a square planar group with four external binding or connecting sites. These sites must allow a twist by 90° at the bonding juncture (Fig. 5). These conditions are fulfilled by a ring of four silicon-oxygen coordination tetrahedra: $Si_4O_4O_{8/2}$. The resulting structure is the well known sodalite type (PAULING, 1930), except that in the mineral sodalite one half of the tetrahedral sites are replaced by aluminum, so that the ring has the composition $[Si_2Al_2O_4O_{8/2}]$ and both the [Nb] and the [O] sites are occupied by this ring. The composition of the sodalite framework is therefore $[Al_6Si_6O_{24}]$ (Table 1). The crystal structure of sodalite has a magnification factor of 2.1 relative to NbO and a density of 17 Al and Si atoms per 1000 Å^3.

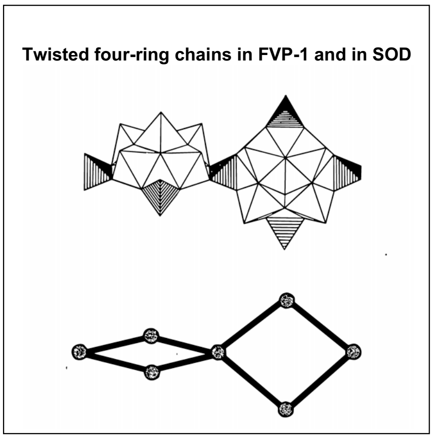

Fig. 5
Part of the twisted chain of four-connected $[V_5O_9(PO_4)_{4/2}]$ units in FVP-1 and of silicate four-rings in sodalite (after SCHINDLER & BAUR, 1997).

An extremely open framework with zeolitic properties can be built from $[V_5O_9(PO_4)_{4/2}]$ groups (SCHINDLER et al., 1997). The chemical composition of the compound is $Na_v[((V^{4+}{}_{4-w}V^{5+}{}_{1+w})O_9)(PO_4)_2] \,.\, (PO_4)_x \,.\, (OH)_y \,.\, zH_2O$ (or FVP-1 for short). The $V_5O_9(PO_4)_{4/2}$ group consists of five square pyramidal coordinations around tetra- and pentavalent vanadium and four phosphate groups (Table 1). The phosphate tetrahedra are the bonding sites between the groups and provide thus the 90° twist. Because of the peculiar shape of the group it has been called the spiked helmet, where the central spike is one of the vanadyl groups. The resulting framework is more open than the faujasite framework (Fig. 6). Its magnification relative to NbO itself is 3.8 and it has only 10.2 vanadium and phosphorus atoms per 1000 Å^3, as compared to 12.7 aluminum and silicon atoms per 1000 Å^3 for faujasite.

This is a good example for an increase in pore size with magnification factor. The framework of FVP-1 can be dehydrated and rehydrated in the same way as a zeolite. Unfortunately it is not as stable as faujasite at higher temperatures.

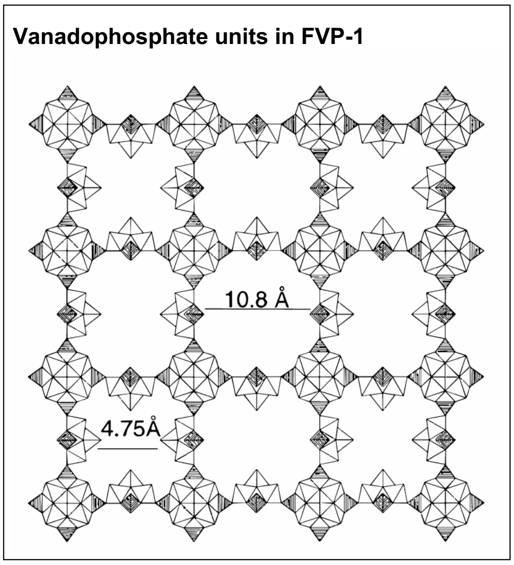

Fig. 6
Arrangement of spiked helmet units $[V_5O_9(PO_4)_{4/2}]$ in FVP-1 (after SCHINDLER et al., 1997).

5. Metastructures derived from the ReO_3-type

The ReO_3 structure type (MEISEL, 1932) can be seen as another defect structure of halite. It crystallizes ideally in space group $Pm\bar{3}m$. There is a cation, Re, at 0 0 0 in Wyckoff site 1(a), leaving three of the cation sites of halite vacant, and there are three oxygen atoms in Wyckoff site 3(d), leaving the anion site in halite at $^1/_2$ $^1/_2$ $^1/_2$ unoccupied. Again, as in the case of the NbO-type, the topology is entirely different from NaCl. In the ReO_3 type we see coordination octahedra of oxygen around Re sharing all corners with neighboring octahedra, while in NaCl the coordination octahedra share all their edges with neighboring octahedra. The ReO_3 structure type can be seen as one octahedrally 6-connected particle [Re] joined by three 2-connected [O] (Table 1).

There exist numerous metastructures of the ReO_3-type. I shall present here two groups of them. For one, all the boracite compounds are built on this principle. There is an $[OB_4]$ group at the black nodes surrounded by six $[BO_4]$ groups connecting to neighboring $[OB_4]$ clusters (Fig. 7). The $[B_4O(BO_4)_4]$ framework is filled in natural and synthetic boracites by various different cations and anions (Table 1). Depending on the symmetry of the boracites the central core could be either $[OB_4]$ or $[OB_3]$ clusters. This does not change the topology of the overall framework which depends on the topologically active connecting $[BO_4]$ groups, not on the topologically passive cores. The core can be viewed as mere decoration (SCHINDLER & HAWTHORNE, 1998). The boracite crystal structure is also adopted by a number of zincophosphates and -arsenates, one of which is listed in Table 1 (HARRISON et al., 1996).

Secondly there is the pharmacosiderite group, where the core consists of four fused coordination octahedra, $[Fe_4(OH)_4]$, around which six arsenate tetrahedra $[AsO_4]$ play the role of the topologically active 2-connected groups (Table 1). The coordination octahedra around Fe consist of OH groups and of oxygen atoms from the AsO_4 groups. This is the result of a crystal structure determination performed by ZEMANN (1947, 1950) on the mineral pharmacosiderite, $K[Fe_4(OH)_4(AsO_4)_3] . 6\text{-}8H_2O$ (Fig. 7). It was also ZEMANN (1959) who recognized the relationship of the pharmacosiderites to a series of curious germanates prepared by NOWOTNY & WITTMANN (Table 2). In these germanates germanium occurs both in octahedral and tetrahedral coordination substituting both for the As and the Fe in pharmacosiderite itself.

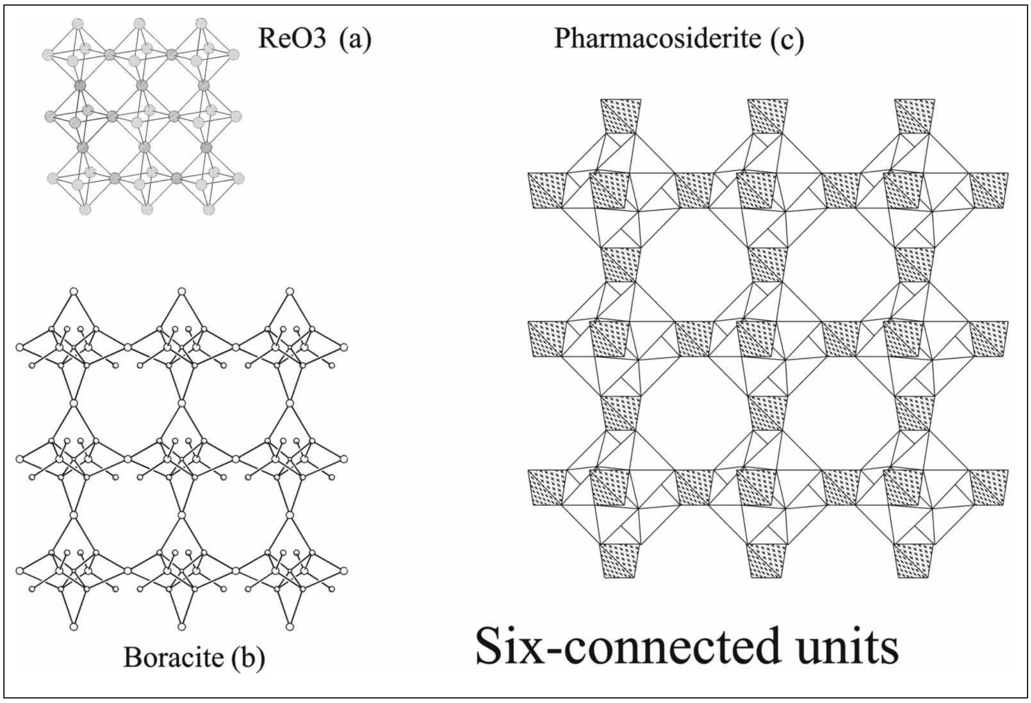

Fig. 7
Arrangement of six-connected units in ReO_3, boracite and pharmacosiderite (after SCHINDLER et al., 1999).

ZEMANN (1959) predicted that further examples of this crystal structure type would be found. In fact numerous additional pharmacosiderites with other chemical compositions have been prepared in the meantime (Table 2). The octahedral sites can be occupied by Al, Fe, Ge, Mo or Ti, the tetrahedral sites by As, Ge, P or Si. The nonframework cations can be Ag, Ba, Cs, H, K, Li, Na, NH_4, Pb, Rb and Tl (Table 3). Various cation-exchange experiments have been performed on natural (MUTTER et al., 1984) and synthetic (NENOFF et al., 1994) pharmocosiderite-type compounds. The titanosilicate analog of pharmacosiderite was in addition exchanged with Mg and Ca, and furthermore used to remove trace amounts of Cs and Sr, which makes it interesting for the removal of radioactive isotopes of these elements (DYER et al., 1999). Three additional minerals have been found to belong to the pharmacosiderite group (Table 4).

Compound	Unit cell constants	References
$K[Al_4(OH)_4(AsO_4)_3] . 6\text{-}8H_2O$	7.72	HÄGELE & MACHATSCHKI (1937)
Pharmacosiderite, $K[Fe_4(OH)_4(AsO_4)_3] . 6\text{-}8H_2O$	7.91	ZEMANN (1947,1950)
$Na_3H[Ge_4O_4(GeO_4)_3] . 4H_2O$	7.67	NOWOTNY & WITTMANN (1953)
$(NH_4)_3H[Ge_4O_4(GeO_4)_3] . 4H_2O$	7.70	NOWOTNY & WITTMANN (1953)
$Li_3H[Ge_4O_4(GeO_4)_3] . 4H_2O$	7.66	NOWOTNY & WITTMANN (1954)
$Ag_3H[Ge_4O_4(GeO_4)_3] . 4H_2O$	7.65	WITTMANN & NOWOTNY (1956)
$Ba_2[Ge_4O_4(GeO_4)_3] . 7H_2O$	7.65	EULENBERGER et al. (1961)
$Pb_{2.2}[Ge_4O_4(GeO_4)_3](OH)_{0.4} . 6.6H_2O$	7.639	EULENBERGER et al. (1961)
$Tl_3H[Ge_4O_4(GeO_4)_3] . 4H_2O$	7.695	PAPAMANTELLOS &WITTMANN (1965)
$Cs_3[Mo_4O_4(PO_4)_3]$	7.728	HAUSHALTER (1987)
$(NH_4)_3[Mo_4O_4(PO_4)_3]$	7.736	KING et al. (1991)
$Na_3H_x(H_2PO_4)_x [Ge_4O_4(GeO_4)_3] . 4H_2O$	7.7121	NENOFF et al. (1994)
$Cs_3H[Ti_4O_4(SiO_4)_3] . 4H_2O$	7.8301	HARRISON (1995)
$K_3H[Ge_4O_4(GeO_4)_3] . nH_2O$	15.34960	ROBERTS & FITCH (1996)
$Rb_3H[Ge_4O_4(GeO_4)_3] . nH_2O$	15.45998	ROBERTS & FITCH (1996)
$Cs_3H[Ge_4O_4(GeO_4)_3] . nH_2O$	15.56660	ROBERTS & FITCH (1996)
$Na_3H[Ti_4O_4(SiO_4)_3] . 6H_2O$	7.8124	DADACHOV & HARRISON (1997)

Table 2

Selection of pharmacosiderite compounds presently known.

Location	Chemical elements or groups
Octahedral site	Al, Fe, Ge, Mo, Ti
Tetrahedral site	As, Ge, P, Si
Pore-filling	Ag, Ba, Ca, Cs, H, H_2O, K, Li, Mg, Na, NH_4, Pb, Rb, Sr, Tl

Table 3

Site-occupations observed in pharmacosiderite-type compounds.

Mineral name	Composition	References
Pharmacosiderite	$K[Fe_4(OH)_4(AsO_4)_3] . 6H_2O$	ZEMANN (1947,1950)
Ba-pharmacosiderite	$Ba[Fe_4(OH)_5(AsO_4)_3] . 5H_2O$	WALENTA (1966)
Alumopharmacosiderite	$K[Al_4(OH)_4(AsO_4)_3] . 6.5H_2O$	SCHMETZER et al. (1981)
Sodium-pharmacosiderite	$(Na,K)_2[Fe_4(OH)_5(AsO_4)_3] . 7H_2O$	PEACOR & DUNN (1985)

Table 4

Minerals of the pharmacosiderite group.

Pharmacosiderites are an excellent example for a nontetrahedral framework structure with obvious zeolitic properties. Like the zeolites proper, it is extremely tolerant of exchanges of its pore-filling. In addition the constituent cations of the framework can be very variable. It almost appears as if the topology of the framework were more important than its chemical composition. Despite all the differences in the chemistry of the framework the unit cell constants vary only by 3.5 % (Table 2). All this makes them similar to some of the tetrahedral zeolitic frameworks.

6. Outlook

The consideration of metastructures leads us to additional zeolite-like compounds. What more is there in the story? For one it is fun to look for patterns in nature. Presently I do not know of any method to search out systematically, using the computer, the relationships between simple Wells-nets and complex metastructures. It has to be done by hand and head. Secondly it is in principle possible and some people are attempting it, to engage in crystal engineering. You choose groups of atoms in the right proportion and with the correct number and geometry of the binding sites to achieve a desired result. A recent example of that is the $[Cu_6(CO_3)_{12}]$ potassium guanidinium hydrate with sodalite topology (ABRAHAMS et al., 2003).

Apparently similar principles apply at different scales. In the examples shown here the factor is only seven from the smallest to the largest. Higher magnifications are being reached by combining supertetrahedra, that is groups of general tetrahedral shape consisting of several tetrahedra bonded together. Examples are compounds built of $[In_{10}S_{20}]^{10-}$ supertetrahedra (CAHILL & PARISE, 2000) or of $[In_3GeS_8]^{3-}$ supertetrahedra (ZHENG et al., 2002), both papers include numerous earlier references in this direction as does SCHINDLER et al. (1999). No doubt even larger magnifications will be reached in the future. All we have to do is to compare the assembly of metal atom spheres (ca. 10^{-10} m), with spheres of $SiO_2 \, . \, nH_2O$ in opal (JONES et al., 1964) and manipulated polystyrene beads (PARK, et al., 1998), both about 10^{-7} m, with macroscopic objects (10^{-2} m) to realize how far this can go.

References

ABRAHAMS, B. F., HAYWOOD, M. G., ROBSON, R. & SLIZYS, D. A. (2003): New tricks for an old dog: the carbonate ion as a building block for networks including examples of composition $[Cu_6(CO_3)_{12} \, . \, \{C(NH_2)_3\}_8]_4$ - with the sodalite topology. - Angew. Chem. Int. Ed. 42, 1111-1115.

BAERLOCHER, C., MEIER, W. M. & OLSON, D. H. (2001): Atlas of Zeolite Framework Types. 5th ed. - Elsevier: Amsterdam.

BATTEN, S. R., HOSKINS, B. F. & ROBSON, R. (1998): Synthesis and rutilelike structure of $[Cd(tcm)(hmt)(H_2O)](tcm)$ (tcm^- = tricyanomethanide, $C(CN)_3^-$; hmt = hexamethylenetetramine). - Inorg. Chem. 37, 3432-3434.

BAUR, W. H. (1956): Über die Vefeinerung der Kristallstrukturbestimmung einiger Vertreter des Rutiltyps: TiO_2, SnO_2, GeO_2 und MgF_2. - Acta Cryst. 9, 515-520.

BAUR, W. H. (1964): On the cation and water positions in faujasite. - Am. Mineral. 49, 697-703.

BAUR, W. H. (1977): Computer simulation of crystal structures. - Phys. Chem. Minerals 2, 3-20.

BAUR, W. H. & FISCHER, R. X. (2002): Zeolite-Type Crystal Structures and their Chemistry. Zeolite Structure Codes DAC to LOV. Subvolume C in Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, Group IV: Physical Chemistry, Volume 14, Microporous and other Framework Materials with Zeolite-Type Structures, eds. W. H. Baur, R. X. Fischer, 459 pp. - Springer, Berlin.

BAUR, W. H. & OHTA, T. (1982): The Si_5O_{16} pentamer in zunyite refined and empirical relations for individual silicon oxygen bonds. - Acta Cryst. B38, 390-401.

BOWMAN, A. L., WALLACE, T. C., YARNELL, J. L. & WENZEL, R. G. (1966): Crystal Structure of niobium monoxide. - Acta Cryst. 21, 843.

BRAGG, W. H. & BRAGG, W. L. (1913): The structure of the diamond. - Proc. Roy. Soc. London, Series A, 89, 277-291.

BRAGG, W. L. (1914): The analysis of crystals by the X-ray spectrometer. - Proc. Roy. Soc. London, Series A, 89, 468-489.

BRAGG, W. L. (1920): The arrangement of atoms in crystals. - Phil. Mag. [6], 40, 169-189.

CAHILL, C. L. & PARISE, J. B. (2000): On the formation of framework indium sulfides. - J. Chem. Soc. Dalton Trans. 1475-1482.

DYER, A., PILLINGER, M. & AMIN, S. (1999): Ion exchange of caesium and strontium on a titanosilicate analogue of the mineral pharmacosiderite. - J. Mater. Chem. 9, 2481-2487.

EULENBERGER, G., NOWOTNY, H. & WITTMANN, A. (1961): Ein Beitrag zur Strukturchemie der Germanatzeolithe von Barium und Blei. - Monatsh. Chem. 92, 949-955.

GRAMLICH, V. & MEIER, W. M. (1971): The crystal structure of hydrated NaA: a detailed refinement of a pseudosymmetric zeolite structure. - Z. Kristallogr. 133, 134-149.

HÄGELE, G. & & MACHATSCHKI, F. (1937): Synthese des Alumopharmakosiderits; Formel und Struktur des Pharamakosiderits. - Fortschr. Mineral. 21, 77-78.

HARRISON, W. T. A., BROACH, R. W., BEDARD, R. A., GIER, T. E., BU, X. H. & STUCKY, G. D. (1996): Synthesis and characterization of a new family of thermally stable open-framework zincophosphate/-arsenate phases: $M_3Zn_4O(XO_4)_3 . nH_2O$ (M = Na, K, Rb, Li, …; X = P, As; ~ n = 3.5-6). Crystal structures of $Rb_3Zn_4O(PO_4)_3 . 3.5H_2O$, $K_3Zn_4O(AsO_4)_3 . 4H_2O$, and $Na_3Zn_4O(PO_4)_3 . 6H_2O$. - Chem. Mater. 8, 691-700.

HARRISON, W. T. A., GIER, T. E. & STUCKY, G. D. (1995): Single-crystal structure of $Cs_3HTi_4O_4(SiO_4)_3]$. $4H_2O$, a titanosilicate pharmacosiderite analog. - Zeolites, 15, 408-412.

HAUSHALTER, R. C. (1987): Mo_4 O^{46+} cubes in $Cs_3Mo_4P_3O_{16}$. - J. Chem. Soc. Chem. Comm. 1566-1568.

JONES, J. B., SANDERS, J. V. & SEGNIT, E. R. (1964): Structure of Opal. - Nature, 204, 990-991.

KIM, C. H. & IWAMOTO, T. (1997): Crystal structure and rutile-mimetic framework in cyanocadmate clathrate $[Cd\{Cd(CN)_3(imH)\}_2].p\text{-}C_6H_4Me_2$ involving unidentate imidazole (imH = $C_3H_4N_2$) ligand. - Bull. Korean Chem Soc. 18, 791-793.

KING, H. E., MUNDI, L. A., STROHMAIER, K. G. & HAUSHALTER, R. C. (1991): A synchrotron single crystal X-ray structure determination of $(NH_4)_3Mo_4O_4(PO_4)_3$: a microporous molybdenum phosphate with Mo_4 O^{46+} cubes. - J. Solid State Chem. 92, 154-158.

MEISEL, K. (1932): Rheniumtrioxyd. III. Mitteilung. Über die Kristallstruktur des Rheniumtrioxyds. - Z. Anorg. Allgem. Chem. 207, 121-128.

MUTTER, G., EYSEL, W., GREIS, O. & SCHMETZER, K. (1984): Crystal chemistry of natural and ion-exchanged pharmacosiderites. - N. Jahrb. Mineral. Monatsh. 183-192.

NENOFF, T. M., HARRISON, W. T. A. & STUCKY, G. D. (1994): $Na_3H_x(H_2PO_4)_x[(GeO)_4(GeO_4)_3]$. $4H_2O$: a rhombohedrally-distorted germanium pharmacosiderite analog with anion/cation exchange capabilities. - Chem. Mater. 6, 525-530.

NOWOTNY, H. & WITTMANN, A. (1953): Alkaligermanate vom Typ $MH_3Ge_2O_6$. - Monatsh. Chem. 84, 701-704.

NOWOTNY, H. & WITTMANN, A. (1954): Zeolithische Alkaligermanate. - Monatsh. Chem. 85, 559-574.

PAPAMANTELLOS, P. & WITTMANN, A. (1965): Einkristalluntersuchungen am Zeolithgermanat $Tl_3H[Ge_4$ O4 $(GeO_4)_3]$. $4H_2O$. - Monatsh. Chem. 96, 1014-1015.

PARK, S. H., QIN, D. & XIA, Y. (1998): Crystallization of mesoscale particles over large areas. - Adv. Mater. 10, 1028-1032.

PAULING, L. (1930): The structures of the minerals of the sodalite family. - Z. Kristallogr. 83, 405-414.

PEACOR, D .R. (1973): High-temperature single-crystal study of the cristobalite inversion. - Z. Krist. 138, 274-298.

PEACOR, D. R. & DUNN, P. J. (1985): Sodium-pharmacosiderite - a new analog of phramacosiderite from Australia and new occurences of barium-pharmacosoderite. - Mineral. Record, 16, 121-124.

ROBERTS, M. A. & FITCH, A. N. (1996): The crystal structures of hydrated and partially dehydrated $M_3H[Ge_7 O_{16} . nH_2O$, (M = K, Rb,Cs), determined from powder diffraction data using synchrotron radiation. - Z. Kristallogr. 211, 378-387.

SCHINDLER, M. & BAUR, W. H. (1997): Inserting functional groups into square-planar units: a new construction principle for open microporous framework structures. - Angew. Chem. Int. Ed. 36, 91-93.

SCHINDLER, M., JOSWIG, W. & BAUR, W. H. (1997): The $Na/V/P/N(C_2H_5)_3/H_2O$ System at 473 K and the New Open Framework Structure of the Vanadium Phosphate Phase $Na_v[((V^{4+}_{4-w}V^{5+}_{1+w})O_9)(PO_4)_2] \cdot (PO_4)_x \cdot (OH)_y \cdot zH_2O$ (with v = 2.8 to 4.0, w = -0.1 to 1.1, x = 0 to 0.2, y = 0 to 2.1 and z=7 to 10). - Z. anorg. allgem. Chem. 623, 45-54.

SCHINDLER, M. & HAWTHORNE, F. C. (1998): The crystal structure of trembathite, $(Mg_{1.55}Fe_{1.43}Mn_{0.02})B_7O_{13}Cl$, a mineral of the boracite group: an example of the insertion of a cluster into a three-dimensional net. - Can. Mineral. 36, 1195-1201.

SCHINDLER, M., HAWTHORNE, F. C. & BAUR, W. H. (1999): Metastructures: homeomorphisms between complex inorganic structures and three-dimensional nets. - Acta Cryst. B55, 811-829.

SCHMETZER, K., HORN, W. & BANK, H. (1981): Alumopharmakosiderite, $K[Al_4(OH)_4(AsO_4)_3] . 6.5H_2O$, ein neues Mineral. - N. Jahrb. Mineral. Monatsh. 97-102.

SMITH, J. V. (2000): Tetrahedral Frameworks of Zeolites, Clathrates and Related Materials. - vol. A in "Microporous and other framework materials with zeolite-type structures", Baur, W. H., Fischer, R. X. (eds.), Landolt-Börnstein / New Series IV/14, -Springer: Berlin.

TILLMANNS, E., GEBERT, W. & BAUR, W. H. (1973): Computer simulation of crystal structures applied to the solution of the superstructure of cubic silicon diphosphate. - J. Solid State Chem. 7, 69-84.

WALENTA, K. (1966): Beiträge zur Kenntnis seltener Arsenatmineralien unter besonderer Berücksichtigung von Vorkommen des Schwarzwaldes. - Tschermaks Mineral. Petrogr. Mitt. 11, 121-164.

WELLS, A. F. (1954): The geometrical basis of crystal chemistry. - Part 1.-Acta Cryst. 7, 535-544.

WELLS, A.F. (1976): The geometrical basis of crystal chemistry. XII. Review of structures based on three-dimensional 3-connected nets. - Acta Cryst. B32, 2619-2626.

WELLS, A. F. (1977): Three-dimensional Nets and Polyhedra. - Wiley: New York.

WELLS, A. F. (1984): Structural Inorganic Chemistry. - Clarendon: Oxford.

WITTMANN, A. & NOWOTNY, H. (1956): Über zeolithische Germanate mit einwertigen Kationen. - Monatsh. Chem. 87, 654-661.

ZEMANN, J. (1947): Über die Struktur des Pharmakosiderits. - Experientia, 3, 452.

ZEMANN, J. (1950): Formel und Struktur des Pharmakosiderits. - Tschermaks Mineral. Petrogr. Mitt. 1, 1-13

ZEMANN, J. (1959): Isotypie zwischen Pharmakosiderit und zeolitischen Germanaten. - Acta Cryst. 12, 252.

ZEMANN, J. (1991): Nichtsilikatische Zeolithe. - Mitt. Österr. Mineral. Ges. 136, 21-34.

ZEMANN, J. (1993): Non-silicate zeolites (non-silicate microporous phases) in mineralogy. - Romanian J. Mineral. 76, 53-55.

ZHENG, N., BU, X., WANG, B. & FENG, P. (2002): Microporous and photoluminescent chalcogenide zeolite analogs. - Science, 298, 2366-2369.