

## The crystal chemistry of natural zeolites

Glauco Gottardi

Istituto di Mineralogia e Petrologia, Università di Modena, Modena,  
Italy

**Abstract** - This is a review of new achievements in the field of crystal chemistry of natural zeolites after 1983. There are two new zeolites, willhendersonite and perliaite, and two new frameworks, those of parthéite and goosecreekite; gobbinsite has the framework of gismondine, and gonnardite that of natrolite. Bikitaite has been shown to have a triclinic symmetry and an ordered (Si,Al) distribution. T-O-T angles of 180° are not present in dachiardite and in a variety of ferrierite. Edingtonite may be (Si,Al) ordered or not. Structural study of a number of exchanged chabazites has put some light on the gas absorption behaviour of this zeolite. Neutron diffraction studies led to location of hydrogen atoms in many zeolites; in natrolite, scolecite, thomsonite, edingtonite, bikitaite, the water molecules are well ordered, but this is true only to a lesser extent in other non-fibrous zeolites, like brewsterite, yugawaralite, laumontite, gismondine. The H...O distances found to date are among the longest found in crystalline hydrates and indicate that the hydrogen bonds formed between water molecules and framework oxygens are rather weak. A new computing method has been devised to deduce the Al-content of the tetrahedra of a framework from T-O distances and T-O-T angles, because the contents obtained via Jones' linear relation are systematically too low. Newly assessed correlations between chemistry and genesis of zeolites raise intriguing problems on the possibility of explaining these correlations.

This review describes new structural and chemical achievements in the field of natural zeolites after the Conference held in Reno in 1983.

### NEW MINERALS AND NEW CRYSTAL STRUCTURES

The description of the new zeolite willhendersonite,  $KCa(Al_3Si_3O_{12})_5H_2O$ , already announced at the Reno conference, has been published [1,2]; samples of the new mineral were found at about the same time in a basic potassic lava from Central Italy and in the altered limestone inclusions in the lava flows of Etringer Bellerberg, Germany. The CHA framework of willhendersonite has Si:Al=1 and an ordered distribution given by the alternation of the two atoms. The topological symmetry of chabazite  $R\bar{3}m$  is reduced to a topochemical  $R\bar{3}$  in willhendersonite; further reduction to the real symmetry  $P\bar{1}$  is caused by (a) an ordered distribution of cations in the extraframework sites and (b) distorsion of the framework by a cation too small to fit an undistorted framework (effects B1 and B2 according to Gottardi [3]).

A brand new zeolite is perliaite,  $K_9Na(Ca,Sr)(Al_{12}Si_{24}O_{72})_{15}H_2O$  [4] found as radial microcrystalline aggregates in a nepheline-microcline vein in rischorrites (a kind of biotite-nepheline-syenite). Perliaite is the natural counterpart of zeolite L [5, 6], a K-rich zeolite with variable Si:Al ratio; the similarity of these phases is supported by the comparison of X-ray powder and IR data. It is a pity that the samples of perliaite are not suitable for single crystal structure analysis.

A new framework has been described for parthéite  $\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{15}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$  [7], a silicate which probably has zeolitic properties. A unit of three 4-rings (fig.1) can be used to assemble the framework which is actually interrupted at two tetrahedral nodes occupied by Al (two other Al are at the centre of normally 4-connected tetrahedra): the sharing coefficient according to Zoltai [8] is 1.9. This is the second zeolite-like mineral, after roggianite, to have an interrupted tetrahedral framework.

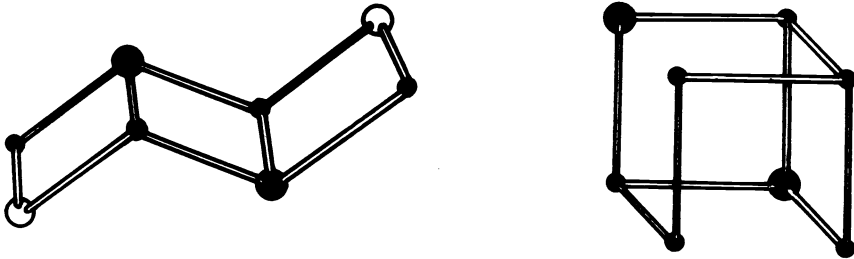


Fig. 1. The building blocks of parthéite (left) and goosecreekite (right). Small black dots = Si. Large black dots = Al. Large white dots = Al coordinating an unshared OH.

Another new framework, which is also (Si,Al) ordered, has been described [9] for goosecreekite. It can be assembled using the units shown in fig.1, and it is not related to any other known framework.

Gobbinsite discovered as a new mineral four years ago, was known to be related to zeolite P-1, and hence to have the GIS framework. Now it has been shown [10] that this is indeed true, but the topochemical symmetry  $I4_1/amd$  had to be lowered to  $Pmn2_1$  to permit a successful refinement with a disordered (Si,Al) distribution, Na and K being ordered in separate sites. It is worth noting that now phases with the GIS framework are known with several symmetries:  $I4_1/amd$  (garronite),  $I\bar{4}$  (Na-P1),  $P2_12_12_1$  (Na-P2),  $Pmn2_1$  (gobbinsite),  $I2$  (amicite),  $P2_1/c$  (gismondine). The formula of this gobbinsite, schematically  $\text{Na}_2\text{K}_2\text{Ca}(\text{Al}_6\text{Si}_{10}\text{O}_{32})12\text{H}_2\text{O}$ , is different from that formerly known for other samples of this mineral,  $\text{Na}_4(\text{Ca,Mg})_6(\text{Al}_6\text{Si}_{10}\text{O}_{32})10\text{H}_2\text{O}$ , which are K-poor and hence possibly pertaining to still another symmetry.

Gonnardite, a fibrous zeolite which was considered as probably related to thomsonite, has now been demonstrated to have a NAT framework [11] and to be strictly related to tetranatrolite, because having a (Si,Al) disordered distribution in the tetrahedra; gonnardite also features a full diadochy of Na and Ca, in contrast to natrolite and mesolite, in which this diadochy is very restricted.

### OLD MINERALS: NEW STRUCTURAL AND CHEMICAL STUDIES

Bikitaite [12] was known to have symmetry  $P2_1$  and a partial order in its framework, and namely no Al in its "pyroxene chains", and a statistical distribution of 50%Al and 50%Si in its "tridymite sheet". If the ratio Si:Al=1 in the sheet, then Loewenstein's rule implies a perfect alternation of the two atoms in the tetrahedra: apparent combination of perfect disorder and perfect order could be reconciled assuming a non-coherence between adjacent sheets [13]. As a matter of fact, a new accurate refinement [14] in space group P1 on crystals of the original occurrence revealed the existence of crystals with a perfect (Si,Al) ordered structure, with the expected alternation of Si and Al in the sheets with hexagonal meshes. The existence of other bikitaite crystals with apparently disordered or partially ordered sheets has also been ascertained by the authors of this refinement. Similar results were announced [15] as obtained by neutron diffraction, but no details of this second research have been published so far. The structure of a synthetic analogue of bikitaite  $\text{Cs}_{0.35}(\text{Al}_{0.35}\text{Si}_{2.65}\text{O}_6)$  [16] does not have any (Si,Al) order in its framework, quite in accordance with the higher Si-content (88% of the tetrahedra are Si-occupied).

Dachiardite [17] has a texture with two acentric domains: on the average the crystal seems to be centric because the two domains have opposite patterns and are present in 50% of the crystal volume each. One important point is that the T-O-T angle of  $180^\circ$  present in the average structure, becomes  $146^\circ$  or  $172^\circ$  in the two domains. Epistilbite, with a structure similar to that of dachiardite, was believed up to then to have a symmetry  $C2/m$  and two T-O-T angles of  $180^\circ$ . Now it has been shown [18] to have, like dachiardite, a texture with two acentric domains where the above mentioned T-O-T angles become  $149^\circ$ ; however, unlike dachiardite, these two domains do not have the same volume, but 80% the one and 20% the other, so that the average structure is now acentric  $C2$ . Another T-O-T angle of  $180^\circ$  had been measured in ferrierite (space group  $Immm$ ): now this is not true at least for a rare Mg-poor variety [19], in which this angle becomes  $168^\circ$  or  $172^\circ$  in view of the lower symmetry  $P2_1/n$  of the crystals. For normal Mg-rich ferrierites, space group  $Immm$  [20], is confirmed and also their energetically unfavourable T-O-T angles of  $180^\circ$ ; on the other hand these "normal" ferrierites were shown to have structures faulted on the planes (010) and (110) by sigma transformations, by studying the streaks of electron diffractions.

The gismondine, found several years ago [21] as "low-potash" samples, was thought to be an exception. Now a thorough study [22] of the crystal chemistry of samples from 17 localities has shown that the K-content is always quite low (nearly  $1/3$  of the high values previously reported); the old wet analyses were wrong because made on samples of gismondines intergrown with K-rich phillipsite; these new microprobe analyses were made also on some samples, which before were believed to be "high-potash", in areas selected for their absence of phillipsite. On the whole, gismondines are always very near to the stoichiometric formula  $Ca_4(Al_8Si_{32}O_{32})16H_2O$ . Two gismondines [23], selected from the preceding 17, have been refined: the good accuracy achieved allowed location not only of all water molecules, but also of some hydrogens; no difference in their nearly perfect (Si,Al) order was observed in spite of their different Si:Al ratios: the sample with higher Si:(Si+Al)=51% has the same tetrahedra dimensions as the sample with Si:(Si+Al)=53%, so the degree of order is not influenced by the slightly increased Si-content.

After merlinoite was described as a new mineral, it was emphasized [24] that merlinoite phillipsite intergrowths should be frequent; as a matter of fact, there are only few peaks in the powder pattern which allow distinction the two minerals, and these key-peaks are often weak in synthetic and sedimentary phillipsites. Now an anomalous phillipsite has been described [25] in the vugs of a French basalt: it gives no such key-peaks, so, from this point of view, the mineral cannot be classified as merlinoite or phillipsite. The sample is microcrystalline, the crystallite size being 35 nm; it has been interpreted as a submicroscopic intergrowth of the two minerals, the name phillipsite being preferred for the whole sample because some chemical and physical properties are more similar to those of this zeolite.

The STI framework may be found in nature as Ca-form (stellerite, space group  $Fmmm$ ) and as Na-form (barrerite, space group  $Amma$ ); now a structural study [26] has shown that Ca-exchanged barrerite fully corresponds to stellerite, unlike Na-exchanged stellerite, which shows, at least from a statistical point of view, a symmetry higher than barrerite [27], because of the random distribution of Na-atoms on both sides of a mirror plane. Five stilbites have been refined [28]: one is near to the stoichiometric formula  $NaCa_4(Al_9Si_{27}O_{72})30H_2O$ , the other four are more Na-rich. All five structures are very similar, with small but constant variations of the Al-fraction in the different tetrahedra. In spite of the different cation contents, the cation sites are the same in all samples, although their population factors are obviously different. A simple explanation of the sector twinning of stilbite was given in the refinement of the structure [29]. Now a new detailed study [30] has been devoted to this problem. Different (monoclinic and orthorhombic) symmetries, not related to chemical changes, are present in the different growth sectors; from the optical point of view, also sectors with triclinic symmetries are present; a detailed structural explanation of the experimental data support the whole interpretation.

Edingtonite, a fibrous zeolite, has been shown [31] to have two structural varieties: besides the already known orthorhombic (Si,Al) ordered form, there are also crystals which are tetragonal and (Si,Al) disordered. So, up to now, only four frameworks have been found in nature with both ordered and disordered (Si,Al) distributions: ANA (analcime may be very near to full disorder, wairakite is well ordered), NAT (natrolite, mesolite, scolecite are perfectly ordered, tetranatrolite-gonnardite is disordered), EDI (orthorhombic ordered,

tetragonal disordered), GIS (gismondine and amicitite perfectly ordered, garronite and gobbin-site disordered). For other zeolites various degrees of order in a restricted range have been found, but not the extreme types. Different growth conditions, more than different temperature values, are probably responsible for the growth of crystals with or without order, but the field is still open for further fruitful experimental research. Anyway this irrelevance of temperature on the degree of order of the zeolite, always growing at a fairly moderate temperature, is supported by at least two facts, which are described in the following. The only case for which information on the laboratory growth conditions of the two forms is known, is wairakite [32]: the first material to crystallize, also at low temperature, is disordered (cubic or tetragonal) and it takes a month or two of continuous hydrothermal treatment at 623K (350°C) and 200 Mpa (2 Kbar) to transform the crystals into their monoclinic ordered modification. The geological and laboratory evidence for the feldspar albite is similar: the "low T" synthesis and the sedimentary genesis both may lead to the disordered forms, and the order is favoured not only by time, obviously, but also by some peculiarities of the system (for instance silica-excess, or also high-pressure).

Studies on hydrated and de-hydrated chabazites [33, 34, 35, 36, 37, 38, 39] have shown how cation sites may change and influence gas adsorption. In hydrated forms, exchangeable cations occupy four sites: III in the D6R, I and II on three-fold axis, and IV on the S8R window. Charge, dimension and hydration of the cation influence the site population and hence the self-diffusion. Dehydration always causes de-stabilizing of site II where the cation is bound only to water molecules; the other sites are also affected by some population change. Framework deformation induced by dehydration increases with decreasing dimension of the exchangeable cation; extreme cases are obtained with Ag- (strongly deformed S8R and monoclinic symmetry) and Cs-chabazite (roundly shaped S8R, whose center is filled by the cation, which coordinates 4 oxygens of the ring). The dehydrated forms of large cations (Cs, Ba) have the S8R completely blocked and feature a low gas adsorption capacity, whereas the dehydrated forms of small cations (Ag, Co, Mn, all bond to only 3 oxygens of the S8R) have larger gas adsorption; the trigonal pyramidal coordination of these cations in sites I and IV could be a good premise for a high reactivity of small molecules inside the chabazitic cage.

Mazzite has a framework with two symmetrically independent tetrahedra: their dimensions [40] are slightly different, nevertheless lattice energy calculations [41] and MASNMR data [42] support the significance of this small difference as an indicator of different Al-fractions. Now a synthetic Ga-mazzite has been structurally investigated [43], but no clear evidence for order in the sites has been found, although Ga, because of its larger ionic radius, should have a greater tendency to order with respect to Si, than Al.

### NEUTRON DIFFRACTION STUDIES: THE HYDROGEN BOND IN ZEOLITES

A number of papers have been devoted to single crystal neutron studies of natural zeolites: Natrolite [44, 45], scolecite [46, 47, 48], edingtonite [49], thomsonite [50], heulandite [51], stellerite [52], brewsterite [53], cancrinite [54], bikitaite [55], yugawaralite [56], gismondine [57], laumontite [58].

Although most of the zeolites other than the fibrous ones show disorder in the water oxygen and hydrogen sites, several of the refinements produced data accurate enough for a general discussion of the hydrogen bonding systems in zeolites. Since the hydrogen bond is essentially electrostatic in character, the length of the H...O contact is usually assumed to be an indication of the bond strength. The H...O distances found to date in zeolite are among the longest found in crystalline hydrates and indicate that the hydrogen bonds formed by water molecules are rather weak. There is also a continuous variation of H...O distances between weakly-bonded and non-bonded molecules, indicating that the H-bond formation is subordinated with respect to the major forces acting between water molecules, extraframework cations and framework oxygens. The strong asymmetry detected in several configurations of the bonds formed by the same water molecule, is another indication of the packing constraints imposed on the water molecules.

Disorder in the water sites and geometry of the hydrogen bonds is related to the framework density, the size of the extraframework cations and the framework topology. The (Si, Al) distribution in the framework tetrahedral nodes has a minor influence on the water molecule configurations.

In the fibrous zeolites complete order is present both in the water oxygen and hydrogen sites. All of the water molecules are bonded to extraframework cations and every hydrogen atom is H-bonded to framework oxygens. Their topology allow all of the framework oxygens to coordinate the cations in the channels or to act as hydrogen bond acceptors.

Most of the non-fibrous zeolites (brewsterite, yugawaralite, gismondine, laumontite) for which an accurate water geometry was determined, show disorder either in the water oxygen or in the water hydrogen sites, or both. Also many of the hydrogen positions are too distant from framework oxygens or from water oxygens to be considered H-bonded. In these zeolites not every framework oxygen has a charge compensation from the cations or from hydrogen bonds. Brewsterite has ordered water sites but shows multiple proton positions. Yugawaralite shows multiple proton positions for one of the water molecules, split oxygen positions for two of the other water molecules, and a partially occupied water site which is not connected with the Ca-atom, and is not H-bonded to framework oxygens and other water molecules. Gismondine shows multiple hydrogen and oxygen positions for two of the water molecules. Laumontite presents a multiplicity of water oxygen sites in a circular arrangement on one site of the cation in the channel. Each oxygen has a low occupancy and shares multiple proton positions with the neighbouring water oxygens. The coordination spheres of two adjacent cation sites are connected by H-bonded water molecules in the center of the channel.

Bikitaite has completely ordered water sites, in a chain arrangement in the centre of the main structural channel. The water molecules are H-bonded to each other, and connected to framework through the Li coordination.

## FRAMEWORK MODELLING

The average Al-content in a zeolite framework, calculated using Jones' linear relation [59], is systematically lower (ca. 5%) than the same content given by the chemical analysis, if the (Si,Al) distribution in the T-sites is disordered; the agreement is satisfactory when Si and Al are well ordered within the framework. This systematic difference has been attributed [60] to an error in the evaluation of the oxygen positions due to static disorder related to the disordered (Si,Al) distribution; this error increases (a) when the T-O-T angle increases, (b) when the (Si,Al) distribution in the T-sites is completely random, (c) when in a T-O-T bridge the disordered oxygen sites do not lie all in the same plane. With an average Al-fraction of 25%, a random distribution could produce a calculated Al-content of 24% with T-O-T=120°, and only 13% with T-O-T=180°.

Starting from these premises, a computer program has been written [61] to calculate the T-O distances in a framework whose T-coordinates and Al-content are known (viceversa, the method does not permit calculation of the Al-content from interatomic distances and angles). A cyclic computation is performed, changing the Al-content until the calculated T-O distances match as closely as possible the T-O distances measured via the structural study. The final Al-contents so obtained are in good agreement with the chemical values for zeolites (the agreement is not yet satisfactory for other framework silicates).

The validity of Dempsey's rule [62] (also called "extended Loewenstein's rule 13") has been the object of mathematical analyses [63, 64, 65] to foresee most probable (Si,Al) distributions and to interpret Silicon-29 NMR data. The predicted distributions are observed in most cases, but exceptions are possible both in natural (scapolite) and in synthetic (faujasite) phases.

Extensive modelling of the zeolite structures has been developed [66] for various purposes: a better understanding of cation siting, accommodation of guest reactant, occurrence of various kinds of intergrowths (twin- and fault-planes). This modelling is certainly very useful in the interpretation of High Resolution Electron images, as those obtained on zeolite L and synthetic mazzite [67], or on offretite, chabazite and similar ABC-zeolites [68]. The advantage in observing the real structure of zeolites with HREM microscopy is obvious, but this kind of investigation is hindered by the low stability of zeolites under the electron beam, so that the flow of new results with this well established technique is rather low.

Two new contributions have been made to the enumeration of the 3-dimensional 4-connected nets [69, 70], : the model structures so described now should reach a total not far from 500. The problem now could be how to retrieve a given structure in such a great number of described structures; this problem is in turn related to another and still more difficult one: how to condense in a mathematical formula all data necessary to describe a framework. Sooner or later this question will be answered, and than the first problem, too, will be resolved.

### CORRELATION BETWEEN CHEMISTRY AND GENESIS OF ZEOLITES

It was long known that zeolites crystallized in sedimentary environment have an average chemical composition different from the average chemical composition of zeolites from vugs and fissures of massive rocks, these last usually being classified as "hydrothermal". So microcrystalline sedimentary clinoptilolite is on the average more alkali- and silica-rich than heulandite from vugs; similar trends are known for other zeolites. Now it has been shown [71] for heulandite, chabazite, erionite, phillipsite, analcime that a discriminant analysis of chemical data is able to assign to the right genesis, "sedimentary" or "hydrothermal", each zeolite on the basis of its chemical composition, the probability of error being as low as 5%. A further approach [72] has shown that even the type of diagenesis of a sedimentary zeolite ("closed system", "open system", "burial diagenesis", "deep sea genesis") may be deduced from its chemical analysis with a low probability of error.

The meaning of the existence of these statistical correlations is a field open for further research.

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