

## Plenary Paper - Structure

# REVIEW OF NEW CRYSTAL STRUCTURES AND MINERALOGY OF ZEOLITES AND RELATED MATERIALS

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### ABSTRACT

Merlinoite, cowlesite, svetlozarite and amicite are new minerals. Structures of silicalite (ZSM-5) and ZSM-11 species were published. Systematic enumeration of framework topology continues. For dehydrated ion-exchanged mordenite, cation positions are complex, and the structural cause of small vs. large pore varieties remains unsolved. For A, zero-coordination is disproved. Possible techniques for structure analysis of small crystals are discussed.

### INTRODUCTION

This review describes (a) new minerals and petrogenesis, (b) crystal structure determinations of new structure types and modifications of known types, (c) systematic enumeration of framework topology and (d) possible ways of determining structures of fine-grained zeolites. It assumes data in Proceedings of the Tucson (1976) and Chicago (1977) conferences [1,2]:

### NEW MINERALS AND PETROGENESIS

Merlinoite,  $\sim(\text{K,Ca,etc.})_7(\text{Al}_9\text{Si}_{23}\text{O}_{64}) \cdot 23\text{H}_2\text{O}$ , [3], cowlesite,  $\sim\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ , [4], svetlozarite,  $\sim(\text{Ca,K,Na})(\text{Al}_2\text{Si}_{12}\text{O}_{28}) \cdot 6\text{H}_2\text{O}$ , [5], and amicite,  $\text{Na}_4\text{K}_4\text{Al}_8\text{Si}_8\text{O}_{32} \cdot 10\text{H}_2\text{O}$ , [6], are newly proposed minerals. Two new minerals in the cancrinite group - franzinite [7] and liottite [8] are also of interest.

The petrogenesis of zeolites was reviewed thoroughly in [1], and further data given in [9]. It is impossible to review here all the factors involved in crystallization and subsequent recrystallization of natural zeolites in sediments, but it is obvious that non-equilibrium kinetic factors are involved as well as controls from the chemical composition of the host rock and ionic solutions whereas

correlations between the occurrence of phillipsite and clinoptilolite in marine sediments with sedimentation rates and rock types were regarded as largely coincidental by [10], meaningful correlations with rock type, age and sedimentation rates were inferred by [11]. Occurrence of authigenic minerals in sediments of the Magadii basin, Kenya, was related to chemical compositions of starting materials, mainly volcanic glass, and infiltrating brines [12]. Sedimentary zeolites in Europe were reviewed [13]. Morphology of sedimentary zeolites was illustrated by SEM photography [14].

Multivariate factor analysis [15] demonstrated that most natural zeolites have restricted ranges of chemical composition, and systematic study is delineating composition ranges: mordenite has 80-85% occupancy of T sites by Si, and mainly Na and Ca in exchange sites [16]; stilbite, stellerite and barrerite have the same framework topology and Si/Al ratio but different space groups as cations vary in exchange sites [17]; gmelinite has both variable Si/Al and cation contents [18]; wellsite is retained as a chemical variant in the phillipsite-harmotome group [19]; ferrierite has a wide range of Si/Al and cation content, with a preference for Mg over coexisting zeolites [20]; composition ranges of heulandite-family minerals were extended, and a sub-group of natural Ca-heulandites (Ca-clinoptilolites) recognized [21]. Clinoptilolite [22], epistilbite [23] and Na,K-ferrierites [24] were synthesized.

#### CRYSTAL STRUCTURE DETERMINATION.

Because of small crystal size, determination of the crystal structures of two members of the new class of high-silica zeolites with 10-ring windows was very difficult, and atomic coordinates are imprecise. The Na form of the ZSM-5 zeolite [25],  $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192} \cdot \sim 16\text{H}_2\text{O}$ ,  $n < 27$  and typically 3, and the silicalite polymorph of  $\text{SiO}_2$  [26] have the same framework topology. Whereas a structure with tetrahedral Al and corresponding exchange sites shows ion-exchange and reversible dehydration expected of an ideal zeolite, the Al-free structure does not show ion-exchange and is hydrophobic and organophilic: thus silicalite is a molecular sieve but not a zeolite. The channel system of silicalite (Fig. 1) consists of a 3D intersection of a straight channel with elliptical cross-section  $.51 \times .57 \text{ nm}$  along the orthorhombic  $b$  axis ( $1.98 \text{ nm}$ ) and a zig-zag channel along  $[101]$  and  $[10\bar{1}]$  directions ( $a$   $2.01$ ;  $c$   $1.34 \text{ nm}$ ). Four channels meet at each intersection (arrows, Fig. 1), and the synthetic precursor of silicalite contains an alkylammonium ion which probably resides at each channel intersection where it acted as a template during synthesis. Heating at  $600^\circ\text{C}$  destroys the organic cation leaving a 3D system of intersecting channels defined by 10-rings wide enough to adsorb molecules up to  $0.6 \text{ nm}$  diameter. The framework contains pairs of tetrahedra, 4-rings and corrugated bands of 6-rings, all cross-linked by 5-rings and occasional 6-rings. A secondary building unit contains 12 tetrahedra linked into five 5-rings and one 6-ring. Detailed structure refinement of silicalite and its precursor will be difficult because the true space group  $\text{P}112$  is a low sub-group of the ideal space group  $\text{Pnma}$  [27].

The structural sub-units of ZSM-5 and silicalite can be assembled into other structure types, one of which gives the new

framework of ZSM-11 [28] whose properties are somewhat similar to those of ZSM-5. The ZSM-11 framework has tetragonal symmetry, and the intersecting channels of elliptical 10-membered rings with cross-section  $.51 \times .55 \text{ nm}$  lie along the  $a$  and  $b$  axes. Stereoplots of all known zeolite structure types are given in [29]. The silica analog of ZSM-11 was denoted silicalite-2 [30].

The merlinoite structure [31] contains double-crankshaft chains cross-linked as in theoretical type 17 [32]; distortion lowers the ideal tetragonal symmetry to orthorhombic. The new zeolite amcicite has the same framework topology as gismondine [33], but ordering of both the Si,Al and Na,K atoms lowers the topologic tetragonal symmetry to monoclinic I2.

Structure refinements show that edingtonite [34] and scolecite [35] have the same Si,Al ordering as natrolite. Synthetic zeolite K-F has the same framework topology as edingtonite, but structural details differ considerably [36]. The role of K atoms in the thermal stability of clinoptilolite was determined [37]. The brewsterite framework fitted crystal-chemical modeling [38].

The occurrence [39], synthesis [40], and sodalite-type structure [41] of bicchulite,  $\text{Ca}_2\text{Al}_2\text{SiO}_6(\text{OH})_2$ , are of interest to zeolite scientists.

This review now turns to crystal structure determination of zeolites deliberately modified by chemical treatment. It emphasizes the problems caused by pseudo-symmetry and substitutional disorder.

Mordenite was chosen for a systematic survey of the location of exchangeable cations because it is a high-silica zeolite for which crystals occur large enough for single-crystal X-ray study. The space group  $\text{Cmcm}$  for the ideal tetrahedral framework certainly does not apply to some dehydrated ion-exchanged forms. By use of distance least-squares modeling in which the T-O distances were constrained to vary with T-O-T angles as in a molecular-orbital interpretation, natural mordenite was simulated by two structure types in  $\text{Cc}$ , each repeated four times by twinning to give an 8-domain intergrowth [42]. Al and Si atoms alternate in the 4-rings of both structure types, but the domain intergrowth need not have long-range order throughout an entire crystal.

Crystal-structure analyses of dehydrated ion-exchanged varieties were probably made on pseudo space groups, and caution is needed in interpretation of structural details; the location of cation sites is correct, but populations and distances are subject to an unknown error. The following table summarizes site occupancies:

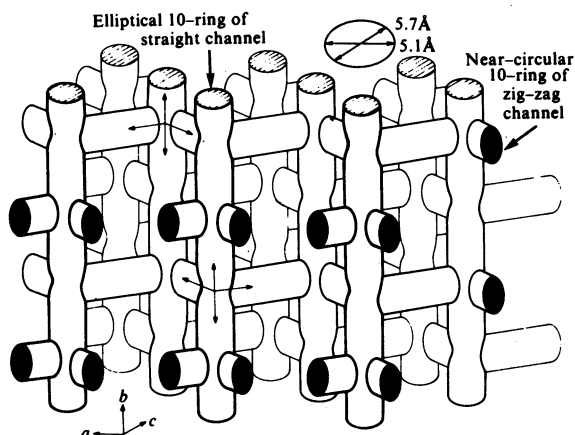


Fig. 1 Idealised channel system in silicalite. To avoid possible confusion caused by the perspective, the dimensions of the channels along  $b$  are shown at upper centre.

Table 1. Cation populations in mordenite.

Site	H	Na	K	Rb	Cs	Ca	Ba
I or I'	0.6Na	3.1Na	-	-	-	1.7Ca	0.3Ca
II	-	-	3.3K	3.6Rb	3.8Cs	-	1.9Ba
III	-	-	-	-	-	0.6Ca	0.3Ba
IV	-	2.6Na	3.0K	3.1Rb	1.9Cs	0.5Ca	1.1Ba
VI	-	1.5Na	0.9K	0.7Rb	1.7Cs	0.6Ca	-
S.G.	Cmcm	Pbcn	Pbcn	Pbcn	P2 <sub>1</sub> cn?	Cmcm	Pbcn
Ref.	[43]	[44]	[45]	[46]	[47]	[48]	[49]

Site I lies at the end of the side pocket, and occupancy by more than two cations results in strong electrostatic repulsion, as indicated by displacement of 0.5Å into I' for dNa-mordenite which has 3.1Na at the end of the side pocket. An ordered domain structure with  $a' = 5a$  occurs for one crystal of dNa-mordenite. Site I is too small for large cations, and K, Rb, Cs and Ba atoms go instead into II which lies in the side pocket at the center of an elliptical 8-ring.

Site IV lies at the center of another elliptical ring at the junction of the side pocket with the main channel, and is partly occupied by all types of cations. Atoms at site VI have a very one-sided coordination to oxygens of the wall of the main channel. There are many subtle features, but the main conclusion is that the cations are distributed over several sites in order to minimize the electrostatic potential associated with occupancy of tetrahedral nodes by Al. At least one cause of lowering of space-group symmetry is displacement of cations from positions with high point symmetry.

Structural analysis of dehydrated H-mordenite produced by HCl treatment of Na-exchanged mordenite was consistent with extraction of Al from tetrahedral sites coupled with migration of Si to "heal" vacated sites, but subtle complications require cautious interpretation [50]. Similar treatment of natural mordenite did not remove 1.4Ca atoms per cell [51].

Dehydration of offretite with stacking faults of erionite type [52] and of erionite with stacking faults of offretite type [53] causes internal ion-exchange in which Ca displaces K from the cancrinite cage. In unheated erionite, K is locked into the cancrinite cage and is unavailable for conventional ion exchange [54]. The unusually long Ca-O distance of 2.73Å to oxygens of the cancrinite cage of dehydrated offretite may result from forces resisting crumpling of the cage around the small divalent Ca<sup>2+</sup> ion [53]. Magnesium lies nearly in the plane of a 6-ring in dehydrated offretite where it is bonded to three oxygens, and upon adsorption of CO moves slightly to become tetrahedrally coordinated to three framework oxygens at 2.08Å and a C atom at 2.16Å [55].

Chabazite has optical and X-ray evidence of symmetry lower than rhombohedral, and brevity forbids description of details of the refinements on the pseudo-cell of dehydrated Ca-exchanged [56], CO-complexed [57], dehydrated Na-exchanged [58], and both hydrated and dehydrated Cu-exchanged [59] varieties. Again a warning is desirable on problems caused by refinement in a pseudo space group.

It is now necessary to turn to a painful subject. The remarkable claim of zero coordination or near zero coordination of cations in several varieties of A zeolite was made by K. Seff and coworkers [60-65]. Such a proposal that cations float in space instead of bonding to framework oxygens was so remarkable that scepticism was expressed about technical problems: (a) lack of an

independent determination of the chemical composition of crystals used for X-ray analysis, (b) refinement of irregular, weak electron-density peaks as atoms when other residual peaks were not ascribed to atoms, and (c) refinement of a pseudostructure ( $a$  1.2nm,  $Pm\bar{3}m$ ) rather than the superstructure with ordered Si and Al ( $a$  2.4nm,  $Pm\bar{3}c$ ). Fortunately for the credibility of standard chemical theory, new refinements of high accuracy by Pluth and me of dehydrated K-exchanged [66] and Na-exchanged [67] A zeolite have demonstrated that the original evidence for zero coordination of cations is false, and is the result merely of incorrect interpretation of poor-quality diffraction data. Further measurements are needed to check the claim of zero or near-zero coordination in other exchanged varieties of A zeolite.

The new refinements confirm the long-standing conclusion that some cations in dehydrated, but not hydrated, zeolites have unusual coordinations because of geometrical restrictions caused by limited flexibility of aluminosilicate tetrahedral frameworks. Figs. 2 and 3 show stereo plots for dK- and dNa-A zeolites.

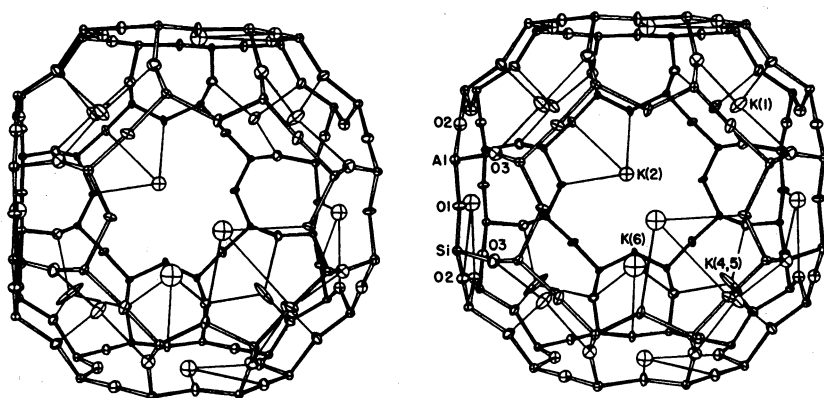


Fig. 2 Stereo-plot of atomic positions in the large cage of dK-A zeolite. Displacement ellipsoids at 30% probability level.

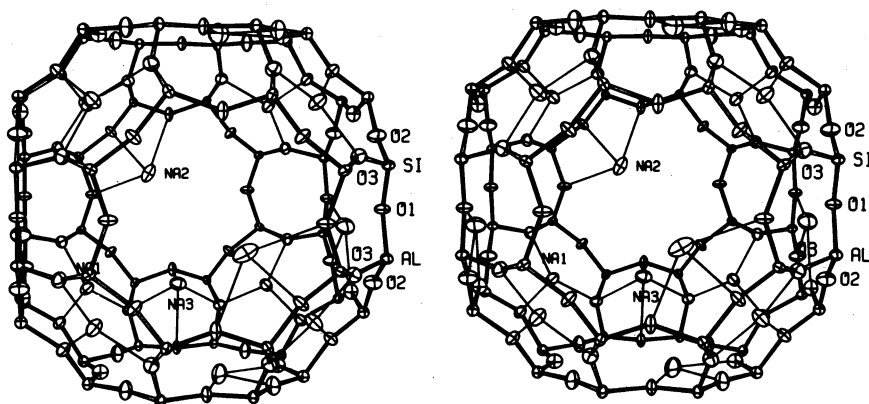


Fig. 3 Stereo-plot of atomic positions in the large cage of dehydrated Na-A zeolite. Displacement ellipsoids at 30% probability level.

In dNa-A zeolite (using the pseudo-cell for convenience), 7.8 Na atoms occupy 8-fold site (1) near the center of a puckered 6-ring with bonding to three oxygens in near-triangular coordination at .232nm; 2.9 Na atoms occupy 12-fold site (2) which lies 0.13nm off-center of an 8-ring with one-sided bonding to one oxygen at 0.24 and two oxygens at ~0.26nm. Readers should be aware, of course, that in disordered structures the true distance between atoms with low fractional occupancy may differ from distances measured between electron density maps which are averaged over all unit cells irrespective of occupancy. There is room for only one Na per 8-ring, and the one-quarter occupancy of a 12-fold site causes uncertainty in the interatomic distances. The remaining 0.8 Na atom lies in a 12-fold site (3) inside the large cavity opposite a 4-ring. Apparent distances of ~0.26nm to four oxygens may be affected by considerable uncertainty because of the low occupancy (7%) by Na(3). A plausible argument suggests that framework oxygens may move away from the Na(3) position when the Na(3) site is not occupied, thereby resulting in reduction of the actual Na(3)-O distances from the value obtained from the electron density. The combined Na content of 11.6 atoms is consistent with electron microprobe analysis.

Refinement in the true cell yielded two sizes of tetrahedra which confirms the Si,Al alternation found earlier for hydrated A [68].

Particularly important was the discovery that least-squares refinement of Na(2) in the pseudo-cell gave an impossibly high population of  $4.4 \pm 0.1$  for the effectively 3-fold site (actually 12-fold, but cation repulsion forbids more than 3 atoms), whereas refinement in the true cell gave an equivalent population of 2.9 atoms. This provides a serious warning that problems can arise in least-squares refinements of population factors in pseudo-cells.

For dK-A, the distribution of K atoms is more complex than for dNa-A, probably because  $K^+$  is a larger ion than  $Na^+$ . Two small electron-density peaks indicate 0.5 atom of K displaced into the main cage at ~0.29nm to four oxygens of a 4-ring (i.e. similar to Na(3) in dNa-A), and 0.15 atom of K displaced into the sodalite cage at ~0.30nm to four oxygens. In addition, 6.3 atoms lie at site (1) displaced into the large cage from a 6-ring, 3 atoms lie at site (2) off-centered from each 8-ring, and 1.5 atoms lie in an elongated peak displaced into the sodalite cage from a 6-ring. Calculations of electrostatic potential are needed to explain this complex distribution.

Many papers by Seff and co-workers can be located from indexes in J. Am. Chem. Soc. and J. Phys. Chem. Space restriction forbids description here.

#### SYSTEMATIC ENUMERATION OF FRAMEWORK TOPOLOGY.

Although an infinity of topologies exists, it is important to enumerate those 4-connected 3-dimensional nets in which simple rules describe the linkage of sub-units. This leads to rational classification and allows prediction of new structure types, some of which might be matched by cell dimensions and space group symmetry with materials of unknown structure. The pioneering studies of A. F. Wells [e.g. 69] were used as a basis for systematic

enumeration using various sub-units. Use of a perpendicular linkage from a simple hexagonal two-dimensional net [70] yielded various frameworks, one of which matches that of zeolite Li-A(BW). Addition of a perpendicular or near-perpendicular linkage to  $4.8^2$ ,  $3.12^2$  and  $4.6.12$  2D nets yielded 79 simpler nets [71] of which five are represented by merlinoite, gismondine, harmotome/phillipsite, gmelinite and chabazite. Combination of a helix or zigzag, crankshaft and saw chains with simple 2D nets yielded various 3D nets including ones for cancrinite, bikitaite and offretite [72]. Still in progress is enumeration of frameworks based on polyhedra, and on non-simple 2D nets. Enumeration with the 4-4-1 unit of linked tetrahedra yielded many frameworks including ones for heulandite, stilbite, and brewsterite [73].

The Wells symbol for 3D nets is non-definitive because more than one net can occur with the same set of adjacent circuits. A unique symbol is needed, perhaps one using a matrix of inter-nodal separations arranged in a standard orientation.

Most frameworks found in actual structures are simple and elegant, and those simple and elegant frameworks not found in actual structures are obvious candidates for synthesis. Unfortunately the frameworks of the ZSM-5 and ZSM-11 zeolites are not simple, and a complex theoretical framework cannot be ruled out automatically as a target for synthesis.

A detailed theoretical study is needed of (a) interrupted tetrahedral frameworks (e.g. wenkite [74,75]) and (b) frameworks of non-tetrahedral type or of mixed type such as tetrahedra plus triangles, pyramids or octahedra (e.g. hilgardite [76], chilgardite [77], and verplanckite [78]). Furthermore there are intriguing structures with linked heteropoly complexes (e.g. sherwoodite [79]).

#### THE FUTURE OF CRYSTAL STRUCTURAL STUDIES OF ZEOLITES.

Now that so many zeolite frameworks are known, and there is considerable understanding of crystal-chemical principles, it is desirable to discuss the most desirable directions for future research. Of course, it is necessary to systematically carry out "bread-and-butter" studies of natural and synthetic zeolites simply to extend the data base, but the present discussion is focused on ideas for extending the range of crystal structure studies.

Many zeolites have been synthesized only as crystals ( $\sim 0.1$  to  $10\mu\text{m}$ ) far too small for conventional single-crystal X-ray structural analysis, and at least one natural zeolite (cowlesite) is also too small. With a rotating-anode X-ray generator it should be possible to achieve a 20-fold increase of sensitivity, but this decreases the minimum crystal diameter only from  $\sim 50$ - $100\mu\text{m}$  to  $\sim 20$ - $40\mu\text{m}$ . Use of synchrotron radiation is being explored, but it seems unlikely that the  $10^5$  intensity gain required for  $1\mu\text{m}$  crystals can be achieved easily. Accordingly it seems desirable to explore the potential of electron diffraction, even though dynamical scattering causes severe problems in obtaining accurate structure amplitudes [refs. in 80]. Two possible approaches involve (a) ion thinning of zeolite crystals to optimum thickness, and (b) systematic recording by an area detector of the variation of intensity of 2D diffractions, as a crystal is rotated slightly, followed by computer-aided

interpretation of dynamical scattering. Perhaps electron-diffraction data of moderate accuracy can be used to deconvolute overlapping peaks in X-ray powder diffraction data of high accuracy.

Neutron diffraction requires even larger crystals than for single-crystal X-ray diffraction, and new sources are unlikely to reduce the minimum size below 500 $\mu$ m diameter. With this limitation, only some unusually large crystals of natural zeolites are suitable: these include natrolite [81], scolecite and thomsonite (now under study), chabazite (except for problem of mimetic twinning), analcime, faujasite (a few crystals 1mm diameter exist), and some lamellar zeolites. All known synthetic crystals are too small.

Scanning transmission electron microscopy has reached a level of sophistication in which an isolated single atom can be imaged. Discussion is in progress with A. V. Crewe to determine whether STEM would be useful for imaging atoms lying in zeolite channels, e.g. a Pt atom or cluster in a zeolite catalyst. The major snag is low penetration of the electron beam, amounting to the equivalent in stopping power of 20nm of carbon. For zeolites, the equivalent is near 10nm, or about 10 unit cells. Perhaps ion-beam thinning would allow preparation of suitable specimens.

Various techniques (e.g. X-ray photon spectroscopy; Auger electron spectroscopy) allow study of chemical properties of zeolite surfaces, and others (e.g. nuclear quadrupole resonance spectroscopy, electron spin resonance) of atomic environments; they are not discussed in detail here because they do not yield atomic coordinates in unit cells.

Returning to conventional single-crystal X-ray structure analysis, it seems necessary to emphasize the following propositions: (a) positions of at least most cations and molecules will be subjected to an unknown error in structures with disordered Al and Si atoms, (b) refinement in pseudo-cells may lead to systematic error in population densities, (c) even for structures with complete framework order refined in the correct unit cell and space group, interatomic distances may not correspond to distances between centroids of electron-density peaks for partly-occupied sites. In attempting to go further in understanding the crystal chemistry of zeolites, it seems desirable to focus attention on structures with complete Si,Al order and with full site occupancy, if possible. At the moment the Type A zeolite is probably best, but a new batch of crystals with complete Si/Al order is needed to replace the present batch of crystals with Si/Al > 1 [66]. Several natural zeolites with ordered Si,Al atoms (natrolite and other fibrous zeolites; gismondine; etc.) are worth detailed crystal-chemical study, especially of variants ion-exchanged to end-member compositions. Structures with sorbed molecules should probably be studied at low temperature to minimize atomic motions. If data of really high quality can be obtained, it should prove possible to test electrostatic-potential and molecular-orbital models. Such an approach, when combined with resonance techniques, should allow a few, but not most, zeolites to be used as containers for exploration of chemical reactions.

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