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STRUCTURAL CLASSIFICATION OF ZEOLITES

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ABSTRACT

In the past ten years the structures of bikitaite, chabazite, dachiardite, erionite, faujasite, gismondine, gmelinite, harmotome, levyne, mordenite, phillipsite and Linde A have been determined. In addition, proposals have been made for NaP1 and heulandite. Although many structures remain undetermined, it is possible to extend the structural classification started by W. L. Bragg in "Atomic Structure of Minerals" on the basis of the determinations of analcime and the natrolite group.

The zeolites chabazite, gmelinite, erionite and levyne are based on different ways of linking together parallel six-membered rings. Harmotome, phillipsite, NaP1 and gismondine are based on parallel four-membered rings, and are related structurally to feldspar and paracelsian. The structures of faujasite and Linde A are both based on tetrahedra lying at the corners of truncated octahedra linked by other polyhedra, and are thus related to sodalite. The columns of linked five-membered rings in mordenite and dachiardite may also form the basis of other zeolites with a 7.5 Å repeat distance (laumontite and brewsterite) but probably not of ferrierite and heulandite.

INTRODUCTION

The most recent summary of the crystal structures of zeolites is that given by W. L. Bragg in "Atomic Structure of Minerals" published in 1937 by Cornell University Press. In the last decade, renewed interest in zeolites has led to the determination of the crystal structures of more than a dozen zeolites, and the time is ripe for a new summary.

Classification of structures serves two purposes: first, to make the data more readily available to a wider group of scientists, and secondly, to make it easier to see relationships between structures, thus encouraging the development of ideas on the nature of the crystal structures and on possible solutions of as yet unknown structures. Particular emphasis will be paid to this latter aspect for there are approximately fifteen zeolites whose structures have not been determined. Because zeolites bear important structural relations to other framework silicates such as feldspars, the present classification will be set in as wide a frame as possible.

Defining a zeolite is rather difficult because of the existence of gradational properties, and a broad definition will be used to avoid the danger of excluding a possible candidate from the group. The two characteristic physical properties of a zeolite are those of ion-exchange and reversible dehydration. Detailed study of zeolites has shown that the two phenomena are complex, and that many zeolites show incomplete ion-exchange, and that reversibility occurs only in the initial stage of dehydration. Possibly a more satisfactory definition of a zeolite will come from the nature of the crystal structure. Such a definition might be as follows: a zeolite is an alumino-silicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion-exchange and reversible dehydration. Because it is possible that materials with the typical physical properties of zeolites may not have framework structures, the above definition of a zeolite must be applied with caution.

In order to identify the types of linkage in the zeolite structures, and to depict the structures on a two-dimensional paper surface, it has been necessary to resort to various simplifying devices in which tetrahedra and other structural units are denoted by symbols specifying their orientation. Such devices often lead to idealization of the structures, but the details can be found from the original references.

For brevity, no attempt has been made to trace in detail the historical development of the determination of zeolite structures. However the references have been arranged in groups to correspond to the structural classification, and the historical sequence can be determined by inspection of the titles. The author wishes to pay tribute and make grateful acknowledgment to the following scientists who have contributed to this classification of zeolites: Dr. W. H. Taylor for his pioneering studies on analcime and the edingtonite group, Dr. D. W. Breck for ideas on the zeolites such as Linde A which are based on tetrahedra lying at the corners of convex polyhedra, Prof. R. M. Barrer and his group for their pioneering studies on molecular-sieve properties and associated structural effects, Drs. K. Fischer and W. M. Meier for their major contributions to the mordenite, gmelinite and gismondine groups, and also for the generous way in which they have communicated their data to the author.

STRUCTURAL CLASSIFICATION

Analcime group The analcime group of zeolites and related silicates consists of three types of analcime, wairakite, pollucite, leucite and viséite. Leucite is anhydrous, and viséite contains phosphorus, so neither fit a strict definition of a zeolite.

Analcime	$Na(AlSi_2O_6) \cdot H_2O$ Type (a): Isometric, *a* 13.72 Å, *Ia3d*, optically isotropic. Type (b): geometrically isometric, *a* 13.72 Å, not *Ia3d*, anisotropic. Type (c): geometrically rhombohedral or orthorhombic, if rhombohedral, *a* 13.71 Å, α 90° 31′, not *Ia3d*, optically anisotropic.
Wairakite	$Ca(AlSi_2O_6) \cdot 2H_2O$ pseudo-isometric, possibly monoclinic, *a* 13.69 *b* 13.68 *c* 13.56 Å, β 90.5°.
Pollucite	$Ca(AlSi_2O_6) \cdot xH_2O$ tetragonal, pseudo-isometric, *a* 13.77 Å.
Leucite	$K(AlSi_2O_6)$ Tetragonal, pseudo-isometric, *a* 12.98 *c* 13.68 Å, $I4_1/a$.
Viseite	$NaCa_5(Al_{10}Si_3P_5O_{30}(OH)_{18}) \cdot 8H_2O$ isometric, *a* 13.65 Å.

All members of the groups have the same type of framework structure that was determined for analcime by Taylor (1930). Depiction of the structure is difficult because of the way in which the different rings of oxygen tetrahedra are twisted and interconnected. Figure 1 is an idealized view down a cube edge (say the *z*-axis). The tetrahedra have been placed into three groups, U (for upwards) with an apex pointing along +*z* and the base parallel to (001), D (for downwards) with the apex pointing along −*z*, and T (for tilted) in which one edge is parallel and one is perpendicular to *z*. Four-membered rings of type UDUD are connected by T tetrahedra to form rings of type UDTUDTUDTUDT. Each T tetrahedron is joined to a U and a D tetrahedron in a twelve-membered ring and to a U tetrahedron from a lower level and a D tetrahedron from a higher level. There are four levels of four- and twelve-membered rings in each unit cell, linked together by the T tetrahedra. The resultant framework structure has regular six-membered rings parallel to (111), and distorted eight-membered rings parallel to (110). The complex interaction of the 4-, 6-, 8- and 12-membered rings, and the severe distortion of the latter two rings from a regular shape is probably the reason why this structure is so hard to visualize.

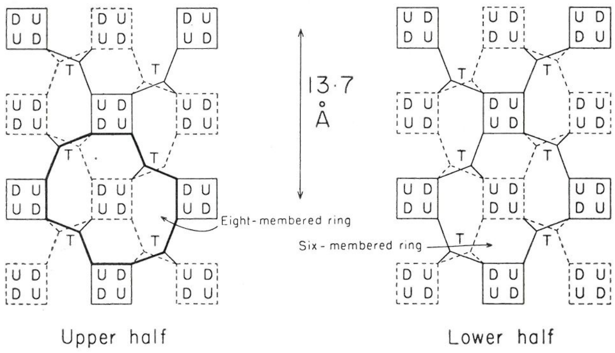


FIG. 1. Schematic crystal structure of analcime. A detailed explanation is given in the text of the method of linkage. The orientations of the terahedra are shown by the symbols U, D and T, and the positions of the tetrahedra are at the intersections of the lines. In each half of the unit cell there are two levels of tetrahedra shown by full (upper) and broken (lower) lines. One of the twelve-membered rings is emphasized by use of a heavy line. The 13.7 Å repeat of the isometric unit cell is shown. The vertical 4_1 symmetry axes pass between the T tetrahedra which lie at the corners of a square in projection. One each of the six-membered rings and eight-membered rings are pointed out: the six-membered ring is regular in shape, but the eight-membered ring is strongly distorted.

Some of the outstanding structural problems in this group concern the polymorphism of analcime (Coombs, 1955: is it caused by order-disorder of the aluminum and silicon atoms?), the location of cations and water molecules (Náray-Szabó, 1938b; Taylor, 1938; Beattie, 1954), the structural changes occurring between analcime with the usual composition of $NaAlSi_2O_6 \cdot H_2O$ and the uncommon silica-rich material (Saha, 1959, 1961) and the detailed structures of wairakite (Steiner, 1955; Coombs, 1955) and viséite (McConnell, 1952).

Sodalite group

Sodalite	Many chemical variants, one example is $Na_4(Al_3Si_3O_{12})Cl$ isometric, *a* 9.0 Å, $P\bar{4}3n$.
Linde A	$Na_{12}(Al_{12}Si_{12}O_{48}) \cdot 27H_2O$ isometric, *a* 12.32 Å, Pm3m (pseudo-cell): true cell has *a* 24.64 Å.
Faujasite	synthetic forms known as Linde X and Y $(Na_2, Ca)_{30}(Al, Si_{192}O_{384}) \cdot 260H_2O$ isometric, *a* 24.7 Å, *Fd3m*.

Although sodalite is not a zeolite, it is convenient to use it as a designation for this group of zeolites and related alumino-silicates. (Actually it is possible that a zeolite with the sodalite framework might occur either naturally or synthetically with a composition like $Na_3Al_5Si_3O_{12} \cdot H_2O$). All three known structural types in this group (Reed and Breck, 1956; Barrer, Bultitude and Sutherland, 1957; Bergerhoff, Koyama and Nowacki, 1956; Bergerhoff *et al.* 1956) are built from linked tetrahedra arranged at the corners of truncated octahedra. (The truncated octahedron is often called a cubo-octahedron: the nomenclature of Encyclopedia Britannica, 1958 edition, vol. 20, p. 945, is used here.) The truncated octahedron contains eight hexagonal faces (octahedral) and six square (cube) faces. In sodalite (Fig. 2) the truncated octahedra share both square and hexagonal faces. The model in Fig. 2 shows eight truncated octahedra arranged at the corners of the isometric unit cell. It will be seen that the truncated octahedra leave just sufficient space for another truncated octahedron at the body center of the cell. In Linde A the truncated octahedra also occupy the corners of the unit cell, but are now joined by cubes to produce a larger cell edge and a larger cavity at the center of the cell. The cavity has the shape of a truncated cubo-octahedron, consisting of six cube faces, eight octahedral faces and twelve dodecahedral faces, all with equal edges.

In faujasite the truncated octahedra are linked by hexagonal prisms at the octahedral faces in such a way as to place the centers of the truncated octahedra at the positions of the carbon atoms in diamond. Because the edges of the hexagons in truncated octahedra are alternatively of two types, those shared between two hexagons, and those shared between a hexagon and a square, adjacent truncated octahedra may be linked in two ways by hexagonal prisms. In faujasite, adjacent truncated octahedra are linked in such a way that the hexagons bordering on the hexagonal prism alternate to give an axis of inverse three-fold symmetry. In the other method of linkage the hexagons face each other across the hexagonal prism to give an axis of three-fold rotational symmetry. A framework can be built from truncated octahedra linked in this pattern, but it is necessary to distort the octahedra. It will be seen from Fig. 2 that large cages are formed, each one comprised of twenty truncated octahedra. There are twelve windows into the cage, each being a prism of ten-fold symmetry. At a casual glance, there are ten three-fold and six ten-fold axes of rotational symmetry, but this is an optical illusion. Ten-fold symmetry requires an angle of 108° between the faces of the prism. If the truncated octahedra are undistorted they are linked through an angle of 109°28′. In the model it is easy to distort the octahedra by 1°28′ thus permitting completion of the cage and yielding apparent high symmetry. It is possible that this unit (or a similar one obtained by removing the hexagonal prisms) may occur in amorphous and gel material where the lack of true symmetry would not matter.

In Fig. 2 is shown a model for a possible structure based on truncated octahedra linked partly in the faujasite manner and partly in the other manner. Dr. D. W. Breck of the Linde Company suggested to the author that there might be a wurtzite equivalent to the zinc blende (or diamond) arrangement found in faujasite, and he showed that if alternate layers of truncated octahedra lying parallel to the (111) planes of faujasite were rotated by 60° and fastened together again, a new framework was obtained which was the wurtzite analog. In this wurtzite form, the bonding between the layers is like that in the hypothetical amorphous variety, but the bonding in the layers is like that in faujasite. The symmetry of the wurtzite form is hexagonal and the cell dimensions are a 19.3 c 28.5 Å.

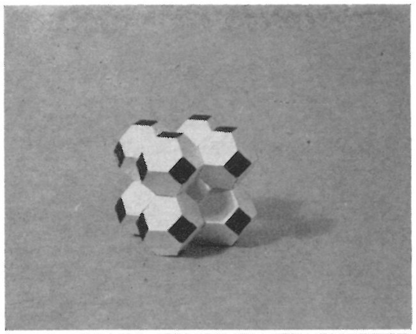
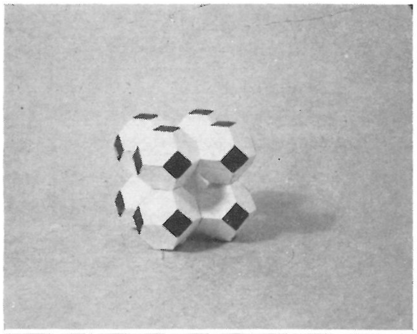
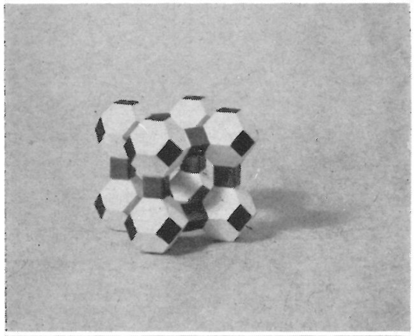
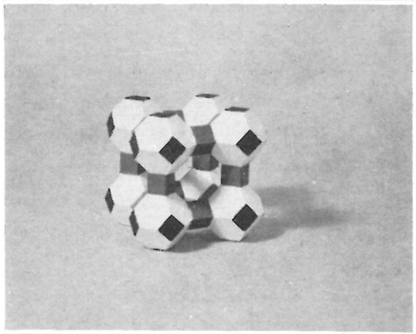
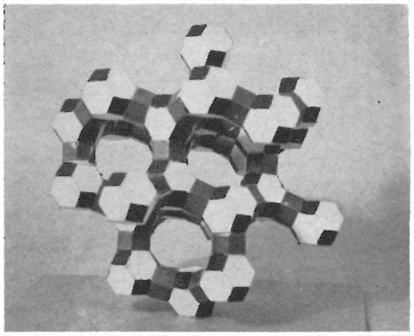
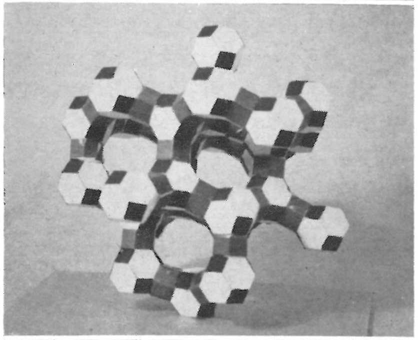
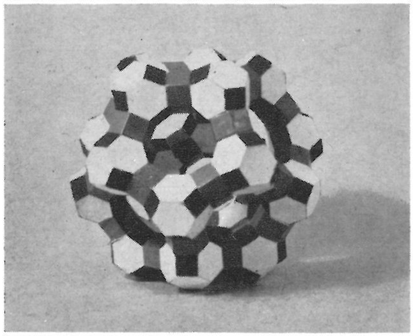
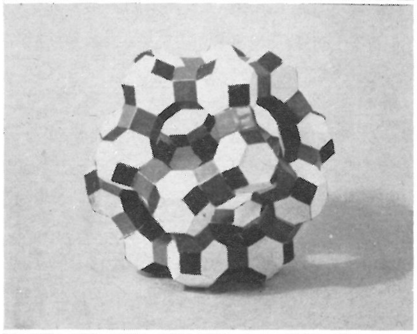
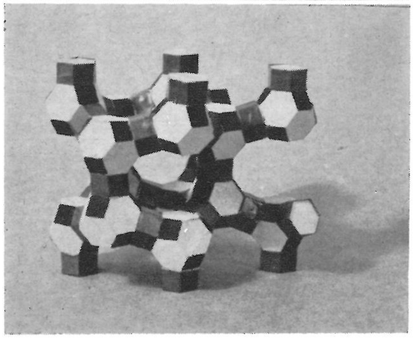
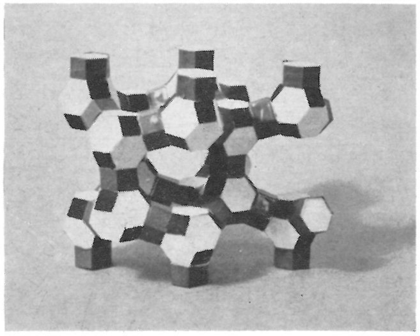
At the moment the author is studying the ways in which regular polyhedra can be linked together so that he can predict all possible structures of this type. He hopes that it will be possible to find the structures of paulingite and ashcroftine among these possible arrangements, and, indeed, has found a structure with the cell dimensions and symmetry of paulingite, but with too many tetrahedra for the chemical analysis.

The chabazite group

Chabazite	near $Ca_2(Al_4Si_8O_{24})\cdot 13H_2O$ rhombohedral or pseudo-rhombohedral, possibly monoclinic or triclinic, a 9.44 Å, α 94° 28′, $R\bar{3}m$.
Gmelinite	near $Na_2(Al_2Si_4O_{12})\cdot 6H_2O$ hexagonal, a 13.72 c 10.02 Å, $P6_3/mmc$.
Erionite	$(Ca, etc.)_{4.5}(Al_9Si_{27}O_{72})\cdot 27H_2O$ hexagonal, a 13.62 c 15.12 Å, $P6_3/mmc$.
Levyne	near $Ca(Al_2Si_4O_{12})\cdot 6H_2O$ rhombohedral, a 10.75 Å, α 76° 25′, $R\bar{3}m$.

The structures of the four members of this group were determined in the last four years (Dent and Smith, 1958; Nowacki *et al.*, 1958; Barrer and Kerr, 1959; Staples and Gard, 1959; Fischer, 1960 and personal communication), and are based on parallel six-membered rings of tetrahedra. The group is named from the most commonly-occurring member.

The relations between the structures are shown in Fig. 3 (see Barrer and Kerr, 1959, for additional diagrams). The horizontal six-membered rings of Si, Al tetrahedra are linked either to other rings vertically superimposed giving hexagonal prisms or through tilted four-membered rings to the other horizontal hexagonal rings displaced both vertically and sideways. In projection the centers of the six-membered

rings lie in the same pattern as close-packed spheres, thus permitting a simple terminology. As is well-known, cubic and hexagonal close-packing can be represented as ABC and AB, where A, B and C represent the three possible horizontal projections of the layers. A similar terminology can be used for the zeolites in the chabazite group if the centers of the hexagonal rings of tetrahedra are specified by the alphabetical symbol. When adjacent layers have the same symbol hexagonal prisms are formed: when they have different symbols, the hexagonal rings are linked by tilted four-membered rings. The possible structures that can be built from parallel six-membered rings are infinite in number, and the simplest are enumerated in the following table. In compiling the list, it should be noted that combinations with three or more identical symbols in sequence are omitted, even though they are possible theoretically.

AB	
ABC*	
AAB	
AABC	
AABB	gmelinite
ABAC	
ABABC	
AABBC	
AABAC	
AABBCC*	chabazite
AABAAC	erionite
AABCCB	
AABACC	
AABCBB	
AABABC	
.	
.	
.	
AABCCABBC*	levyne

All the structures have hexagonal symmetry and a 120° prism for a unit cell except for the three starred ones which have a rhombohedral unit cell. These three structures have a unit cell only one-third as large as that for related structures with the same number of alphabetical symbols. Thus chabazite and levyne have simpler structures than would appear from their position in the list. The combination ABC is the incorrect structure that was proposed for chabazite (Wyart, 1931) thirty years ago.

There is optical and *x*-ray evidence that suggests reduction of symmetry of chabazite from the ideal configuration (possibly to the monoclinic or triclinic systems), and ordering of the silicon and aluminum atoms has been suggested as the cause. The complete structures of hydrated, dehydrated and Cl_2-bearing varieties of chabazite have been determined, but only the shape of the framework is known for the other zeolites of this group. Intergrowths of gmelinite and chabazite have been found, indicating stacking errors in the sequence of hexagonal prisms.

Natrolite group

Natrolite	$Na_2(Al_2Si_3O_{10})\cdot 2H_2O$ orthorhombic, *a* 18.30 *b* 18.63 *c* 6.60 Å, *Fdd*2.
Scolecite	$Ca(Al_2Si_3O_{10})\cdot 3H_2O$ probably monoclinic, *a* 18.52 *b* 18.99 *c* 6.56 Å, *Cc*.
Mesolite	$Na_2Ca_2(Al_2Si_3O_{10})_3\cdot 8H_2O$ monoclinic (?), *a* 56.8 *b* 6.55 *c* 18.48 Å, β 90° 00′.
Edingtonite	$Ba(Al_2Si_3O_{10})\cdot 3H_2O$ probably orthorhombic pseudo-tetragonal, *a* 9.58 *b* 9.70 *c* 6.54 Å, $P\bar{4}2_1m$ (pseudo ?).
Thomsonite	near $NaCa_2(Al_5Si_5O_{20})\cdot 6H_2O$ orthorhombic, *a* 13.0 *b* 13.0 *c* 13.3, *Pn*2*n*.
Gonnardite	$(Ca, Na)_{6-8}(Si, Al_{20}O_{40})\cdot 12H_2O(Al\sim 9)$ orthorhombic, *a* and *b* like thomsonite, *c* 6.6 Å.
Metanatrolite	natrolite dehydrated at 300° C. monoclinic (?) *a* 16.3 *b* 17.1 *c* 6.6 Å, γ 90°, *F*112.

Because the structural properties of this group are so well described in Bragg's "Atomic Structure of Minerals," readers are referred there first. The following additional comments may prove useful. All structures are based on cross-linking of columns of tetrahedra and the three possible ways of doing this are all found in nature: edingtonite; natrolite, scolecite and mesolite; thomsonite and gonnardite. Thus this group of zeolites is complete, apart from the possible discovery of further compositional variants. (To prove that there are only three ways of cross-linking the columns, examine Fig. 139 in Bragg's book and subtract 3 from each number in the edingtonite diagram, 2 from the thomsonite and 1 from the natrolite. The numbers around the diamond-shaped

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FIG. 2. Stereoscopic pairs of models of structures built from truncated octahedra: from top to bottom, sodalite, Linde A, faujasite, amorphous variety, wurtzite analog of faujasite. To aid in visualization, the square faces of the truncated octahedra are painted black and the square faces of the linking cubes and hexagonal prisms are covered in a neutral tone. The intersection of four edges marks the center of a tetrahedron where a silicon or aluminum atom resides, while oxygen atoms occur near, but not on, the centers of the edges. The sodalite and Linde A models are resting on a (100) face. The faujasite model is arranged with a [111] axis vertical to permit easy comparison with the model of the wurtzite-analog which has an [0001] axis vertical.

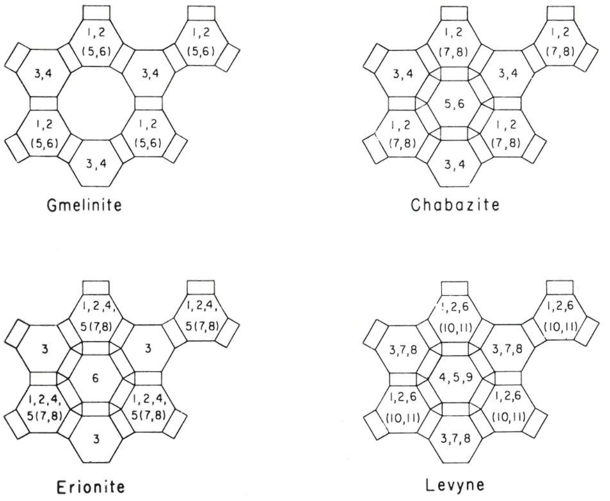


FIG. 3. Schematic representations of the gmelinite, chabazite, erionite and levyne structures. The heights of the six-membered rings of tetrahedra are shown by the numbers, and the positions of the tetrahedra by the intersections of the lines. The structural pattern may be visualized by following the sequence of the numbers. Where adjacent six-membered rings are vertically superimposed, hexagonal prisms are formed: where they are displaced sideways, they are linked by tilted four-membered rings. The number in brackets denotes the next unit cell. Large cavities, linked by apertures, are formed in the framework: see Barrer and Kerr (1959) for perspective drawings.

units become 0202 for edingtonite, 0242 for thomsonite and 0246 for natrolite. Because the numbers must change by 2, and 8 is the unit cell repeat of 0, these are the only three combinations.)

Meier (1960) has shown that the silicon and aluminum atoms in natrolite are ordered, and is known to have a paper in preparation on the ordering in mesolite and scolecite. It seems likely that gonnardite with a 6.6 Å *c*-axis and thomsonite with a 13.2 Å repeat are related by order-disorder of the tetrahedrally-coordinated atoms.

Phillipsite group

Phillipsite	$(K, Na)_5(Al_5Si_{11}O_{32}) \cdot 10H_2O$ orthorhombic, *a* 9.96 *b* 14.25 *c* 14.25 Å, *B2mb* or monoclinic, *a* 10.02, *b* 14.28 *c* 8.64 Å, β 125° 40′, $P2_1$ or $P2_1/m$.
Harmotome	$Ba_2(Al_4Si_{12}O_{32}) \cdot 12H_2O$ monoclinic (pseudo-orthorhombic), *a* 9.87 *b* 14.14 *c* 8.72 Å, β 124° 50′, $P2_1$.
Gismondine	$Ca(Al_2Si_2O_8) \cdot 4H_2O$ monoclinic, *a* 9.84 *b* 10.02 *c* 10.62 Å, γ 92.4°, $P112_1/a$.
Garronite	$(NaCa_{2.5})(Al_6Si_{10}O_{32}) \cdot 13\frac{1}{2}H_2O$ Tetragonal (?), *a* 10.01 *c* 9.87 Å.
NaP1	(named by Barrer *et al.*; identical with Linde B and Saha's B) $Na_2(Al_2Si_3O_{10}) \cdot 5H_2O$ isometric, *a* 10.0 Å (numerous cationic variants also occur).

The structures of this group are based on parallel four- and eight-membered rings of tetrahedra. The first structure of this group of zeolites to be determined in detail was that of harmotome (Sadanaga, *et al.*, 1961), who found that it consisted of cross-linked chains of tetrahedra of the same kind as those already found in the alumino-silicates feldspar and paracelsian (Fig. 4). It had long been suspected that harmotome and phillipsite were iso-structural, and this was confirmed by the publication of the structure of phillipsite by Steinfink (1961). (This structure is more regular, and based on an orthorhombic unit cell: it is possible that it may need minor modification to fit the monoclinic (pseudo-orthorhombic) geometry generally found for phillipsite.) Upon learning that the harmotome structure was built from the double-crankshaft chains of the feldspar structure, Smith and Rinaldi (1962) developed all the simple structures that could be built from cross-linked feldspar chains. Of the seventeen that resulted, one of

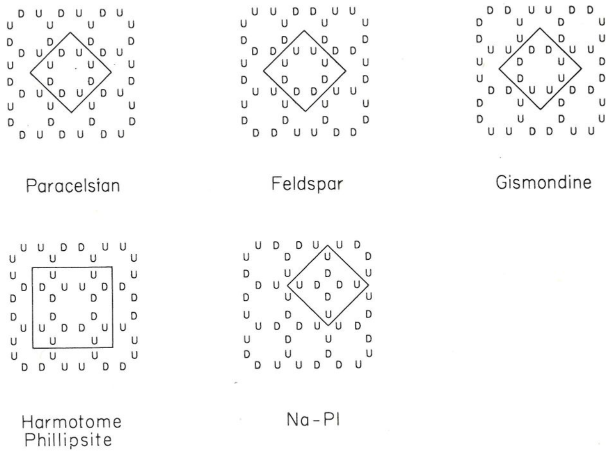


FIG. 4. Schematic representation of members of the harmotome group and the related silicates, feldspar and paracelsian. In each structure four-membered rings of tetrahedra are formed, of type UUDD in paracelsian, feldspar, gismondine and harmotome (or phillipsite), and type UUUU or DDDD in Na-P1. By sharing an oxygen atom between U and a superimposed D tetrahedron infinite chains perpendicular to the plane of the paper are formed in the first four structures, and cubes in the fifth structure. Sharing of oxygen atoms in the plane of the paper leads to eight-membered rings of type UUDUDDUD in paracelsian, and so on in the other structures. The smallest unit cell that is obtained for a regular structure is shown by the squares. Actually the structures of the anhydrous forms, paracelsian and feldspar, collapse in a non-symmetrical way so that a larger unit cell is formed. The structures of gismondine, harmotome (phillipsite) and Na-P1 expand to permit entry of water molecules, but the axes of the unit cell maintain the position shown in these idealized diagrams. Detailed explanation of these structures is given by Rinaldi and Smith (1962).

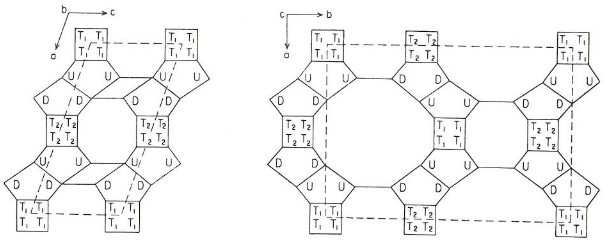
the fourteen that remained after assignation of three structures to feldspar, paracelsian and harmotome was suggested as a possible structure for gismondine. Fischer (private communication) independently showed that this hypothesis was correct, and has refined the atomic coordinates to a high degree of precision. The four structures are shown in Fig. 4, where U and D have the same significance as earlier.

Barrer, *et al.* (1959) reported on the synthesis and ion-exchange properties of various phases that gave *x*-ray powder patterns related to those of harmotome. One of these, denoted Na-P1, has also been prepared by the Linde Company (denoted Zeolite B), and by Saha (also called B). Barrer *et al.* indexed the powder pattern with an isometric unit cell and proposed a crystal structure based on parallel four- and eight-membered rings, but with UUUU rings instead of the UUDD rings in feldspar. The linkage of these rings leads to the formation of cages with tetrahedra lying at the corners of cubes. At the same time, Dr. G. P. L. Walker of Imperial College, London, was discovering a new zeolite, named garronite, in his study of the vug minerals of the Tertiary basalts of Ireland. Barrer *et al.* synthesized a sodium zeolite Na-P2 which was tetragonal, but otherwise similar to Na-P1. The Ca-exchanged product of Na-P2 gave an *x*-ray powder pattern identical with that of garronite. In addition, Barrer *et al.* made a third sodium zeolite, Na-P3, which is similar to the sodium-exchanged form of harmotome. Smith and Rinaldi extended their study of framework structures built from rings of type UUDD and UUUU to include UDUD and UUUD rings. Three of the resulting structures (labelled 2, β and γ in their paper) would give cell dimensions and powder patterns similar to those for Na-P1 and garronite. Thus there is still some uncertainty about the structures of these zeolites, but there seems no reasonable doubt that they belong to this structural group because of the general similarities of the *x*-ray powder patterns.

Mordenite group

Mordenite (ptilolite) $Na(AlSi_5O_{12}) \cdot 3H_2O$
orthorhombic, *a* 18.13 *b* 20.49 *c* 7.52 Å, $Cmc2_1$,
Dachiardite $(Na_2, Ca)_2(Al_4Si_{20}O_{48}) \cdot 12H_2O$
monoclinic *a* 18.35 *b* 7.54 *c* 10.25 Å, β 107° 49′, *C2/m*.

The structure of mordenite (Fig. 5), as determined by Meier (1961), consists of columns of five-membered rings of type UDDTT (or DUUTT) which are cross-linked by four-membered rings in one direction and by sharing of oxygen atoms in the other direction. Meier showed that there was another way of joining the columns together by four-membered rings, and this has turned out to be the structure of dachiardite (Gottardi and Meier, 1962).



Dachiardite Mordenite

FIG. 5. Schematic representation of the structures of dachiardite and mordenite (ptilolite). The tilted T_1 and T_2 tetrahedra have a relative displacement of half the repeat distance of the 7.5 Å axis (*b* in dachiardite, *c* in mordenite).

Both structures have a 7.5 Å repeat distance along the columns, which is the length obtained for the total vertical height of three linked tetrahedra, one each with the U, D and T orientations. Other zeolites—heulandite, ferrierite, laumontite (leonhardite) and brewsterite—have this repeat distance and it is tempting to suggest that they may be based on different ways of cross-linking columns of the mordenite type: indeed Rinaldi (personal communication) has discovered several ways of cross-linking these columns with six- and eight-membered rings. One of these fits the cell dimensions, symmetry and cell contents of heulandite, but did not explain the Patterson projection. It seems that at least heulandite is based on a framework that does not contain a mordenite type column: study of the Patterson projection suggests that the structure of this important zeolite will be solved by Rinaldi soon (see later for further discussion of heulandite, ferrierite, laumontite and brewsterite).

Bikitaite

Bikitaite $LiAlSi_2O_6 \cdot H_2O$
monoclinic, *a* 8.61 *b* 4.96 *c* 7.61 Å, β 114° 26′, $P2_1$.

Although an abstract announcing the solution of the structure of bikitaite has been published (Appleman, 1960), a detailed account of the structure has not yet appeared in press. Dr. Appleman has kindly allowed me to see his drawings of the crystal structure: neither he nor I have been able to find any obvious relation to the structures of other zeolites. However, detailed examination of a three-dimensional model may permit later recognition of a relationship.

Zeolites with unknown structures

Paulingite	near (K, Ca, Na)$_{120}$(Al, Si)$_{580}$O$_{1160}\cdot$690H$_2$O isometric, *a* 35.1 Å, probably *Im3m*.
Ashcroftine	near (K, Na, Ca)$_{120}$(Al$_{160}$Si$_{200}$)O$_{720}\cdot$320H$_2$O tetragonal, *a* 34.0 *c* 17.5 Å.
Thaumasite	near Ca$_3$H$_2$(CO$_3$)(SO$_4$)(SiO$_4$)$\cdot$13H$_2$O hexagonal, *a* 11.0 *c* 10.4 Å, *P*6$_3$.
Ferrierite	near (Na, K)$_4$Mg$_2$(Al$_6$Si$_{30}$)O$_{72}$(OH)$_2\cdot$18H$_2$O orthorhombic, *a* 19.12 *b* 14.4 *c* 7.48 Å, *Immm, I*222, *I*2$_1$2$_1$2$_1$ or *Imm*2.
Heulandite and Clino-ptilolite (a compositional variant)	near (Ca, K, Na)(Al$_2$Si$_7$)O$_{18}\cdot$6H$_2$O monoclinic, *a* 15.85 *b* 17.9 *c* 7.45 Å, β 91° 24′, *I*2/*m*.
Laumontite	near (Ca, Na, K)(Al$_2$Si$_4$)O$_{12}\cdot$4H$_2$O monoclinic, *a* 14.90 *b* 13.17 *c* 7.55 Å, β 111° 30′, *C*2 or *Cm*. leonhardite, the partially dehydrated form of laumontite, has: *a* 14.75 *b* 13.10 *c* 7.55 Å, β 112° 0′.
Brewsterite	(Sr, Ba, Ca)(Al$_2$Si$_6$)O$_{16}\cdot$5H$_2$O monoclinic, *a* 6.77 *b* 17.41 *c* 7.66 Å, β 93° 04′.
Stilbite	near Na$_2$Ca$_4$(Al$_{10}$Si$_{26}$)O$_{12}\cdot$28H$_2$O monoclinic, *a* 13.6 *b* 18.2 *c* 11.3 Å, β 129° 10′, *C*2/*m*.
Epistilbite	near Ca(Al$_2$Si$_6$)O$_{10}\cdot$5H$_2$O monoclinic *a* 8.9 *b* 17.7 *c* 10.2 Å, β 124° 20′.
Yugawaralite	Ca$_4$(Al$_7$Si$_{20}$)O$_{54}\cdot$14H$_2$O monoclinic, *a* 13.26 *b* 13.65 *c* 9.73 Å, β 111° 30′.
Rhodesite	(Ca, Na, K)$_8$Si$_{16}$O$_{40}\cdot$11H$_2$O orthorhombic, *a* 23.8 *b* 6.54 *c* 7.05 Å.
Mountainite	(Ca, Na, K)$_8$Si$_{16}$O$_{40}\cdot$12H$_2$O monoclinic, *a* 13.51 *b* 13.10 *c* 13.51 Å, β 104°.

Although the structures of none of these minerals are known, there are some interesting relations between the cell dimensions of some of them. The *a* dimension of ashcroftine is similar to that of paulingite, and the *c* dimension is halved, suggesting that that there may be a structural relationship. A structure has been suggested for heulandite by Ventriglia (1955), but comparison of its vectors with the Patterson projection prepared by Rinaldi (private communication) shows no correspondence. The pseudo-orthorhombic cell of heulandite is similar in dimensions to the truly orthorhombic cell of ferrierite and there is a fair correspondence between the intensities. Consequently it seems likely that these two zeolites have the same structural framework. Dr. K. Fischer is trying to determine the structure of laumontite at the present time, and Dr. F. Rinaldi has taken preliminary measurements of brewsterite. Strunz and Tennyson (1956) have shown that there are interesting geometrical relations between heulandite, stilbite and epistilbite, the most obvious one being the presence of an axis with an 18 Å repeat distance. Three minerals (thaumasite, rhodesite and mountainite) which are not strictly zeolites are included: it was thought best to include them because their water is partly of zeolite type. Hydro-nepheline was not included because there is considerable doubt concerning its identity. At least one other probable zeolite is known to the author (it has cell dimensions similar to those of thomsonite, and it occurs in veins in Oregon granite), and several others are suspected by other zeolite investigators. It seems likely that the list of zeolites will become considerably larger than that given here.

CONCLUSION

The first classifications of zeolites were based on external morphology and proved of considerable value in directing the attention of structural crystallographers to zeolites with related structures. Thus the members of the natrolite group have similar morphology, and phillipsite and harmotome were suspected correctly by the morphologists to be isostructural. However, it is unlikely that erionite with its fibrous habit would be linked with the equant zeolite, chabazite. Study of the structural units of zeolites has revealed many other possible arrangements and it seems possible that some of these will be found to fit as yet unknown zeolites.

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Note Added After Submission of the Paper

In preparing this paper, the work of Barrer and White (*Jour. Chem. Soc. London,* 1952, 1561–1571) was accidentally overlooked. They prepared a hydroxy-sodalite whose water was zeolitic in nature, a sodium alumino-silicate labelled L which was monoclinic *a* 8.10 *b* 6.10 *c* 4.88 Å, *β* 105° 20′ and another one labelled M which was orthorhombic *a* 11.75 *b*5.81 *c* 8.52 Å.