

## Feldspathoids and their relationships to zeolites

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### ABSTRACT

The feldspathoids are defined as anhydrous framework aluminosilicates that contain alkali and alkali-earth elements, but contain no volatile anions and are similar in composition to the feldspars (*i.e.*, they contain the same or similar atoms), but contain less silica than the alkali feldspar. Thus the feldspathoids have an  $\text{Si}/(\text{Si} + \text{Al})$  ratio less than 0.75. Nepheline and leucite fit this definition.

Sodalites, cancrinites, and scapolites are commonly considered as feldspathoids. However, these are the only framework aluminosilicates that contain large volatile anions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ , and  $\text{H}_2\text{O}$ . These minerals have chemistries and structures that are quite different from that of the feldspars or the feldspathoids, proper. However, some of their structures are closely related to the zeolites, but they are not zeolites, proper.

The structures of the cancrinite-group minerals are characterized by stacking of six-membered rings in an AB . . . sequence. This stacking gives rise to large continuous channels that are formed by twelve-membered rings of alternating  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra. These are among the largest channels known, even for zeolites. The cancrinite structure also consists of small cages, known as  $\epsilon$ -cages in zeolite chemistry. The sodalite-group minerals have strong structural similarities to the cancrinite-group minerals, but the former have an ABC . . . stacking sequence that leads to cubic instead of hexagonal symmetry. This sequence leads to an offset of the C-type layer and gives rise to a network of large  $\beta$ -cages in the sodalite-group minerals. Some cancrinite-type minerals have structures that are based on more complicated stacking of six-membered rings. Examples of these minerals and their stacking sequences are liottite (ABABAC . . .), and afghanite (ABABACAC . . .). Some zeolites also have structures that are based on similar stacking of six-membered rings, *e.g.*, offretite (AAB . . .), erionite (AABAAC . . .), levynite (AABCCABBC . . .), and chabazite (AABBCC . . .). The  $\epsilon$ - and  $\beta$ -cages are also used as building blocks in many zeolite structures such as zeolite A, offretite, and faujasite.

As a family, sodalite, cancrinite, and scapolite, have a unique chemistry in that they are the only aluminosilicate minerals that contain large volatile anions and they have a close structural relationship to the zeolites, but not to the feldspars or the feldspathoids, proper. Therefore, a new group name, *e.g.*, *zeoloids*, may be appropriate for these minerals because they are not feldspathoids.

### INTRODUCTION

The framework aluminosilicates include the feldspars, feldspathoids, and zeolites. They are tectosilicates in which each oxygen atom of the  $\text{TO}_4$  ( $\text{T} = \text{Al}, \text{Si}, \dots$ ) tetrahedron is shared between two tetrahedra to give a continuous three-dimensional

network that extends throughout the structure. This feature results in a framework structure in which the ratio of T:O is 1:2.

Among the framework aluminosilicate minerals, the rings and size of the interstices vary greatly. In the feldspars and in certain feldspathoids (*e.g.*, nepheline, kalsilite, kaliophilite, leucite, and eucryptite) the frameworks are so compact that the interstitial cations at normal temperatures are trapped and immobile on interstitial sites. However, there are many more open frameworks so that in addition to the interstitial cations needed to neutralize the framework charge, there is room for 'salt molecules', as in sodalites, cancrinites, and scapolites; or for water molecules and often many other molecules as in the zeolites.

Division of the framework silicates into various subgroups is based mainly on structural differences and distinctive physical properties commonly result from these differences. An example is the zeolite-group minerals. The usual criteria for classifying a particular framework aluminosilicate as a zeolite is its ability to exchange cations and to gain or lose water without changing its structure. The mineral analcime has such properties, but its structure is more like the feldspathoid leucite, to which it has strong structural similarities. In some cases sodalite is considered as a zeolite, but it has no water; in other cases sodalite is considered as a feldspathoid, but sodalite has little structural or chemical similarities to the feldspars or other feldspathoids, proper. These irregularities lead to some fundamental questions.

What is a feldspathoid? Which minerals belong to the feldspathoid group? Are the feldspathoids related to the feldspars? How are they related? Some minerals (*e.g.*, sodalites and cancrinites) that are considered as feldspathoids are more closely related to the zeolites than to the feldspars; how are such minerals to be classified? To address these questions, the crystal chemistry of the appropriate mineral groups is considered and distinctive features are extracted.

The purpose of this paper is to clarify which minerals belong to the feldspathoids and to illustrate that sodalites, cancrinites, and scapolites are neither feldspathoids nor zeolites, although they are related to the zeolites. The unique chemical and structural features of the sodalites, cancrinites, and scapolites are also illustrated. The relationships between these mineral groups and the zeolites are also established, and their non-relationships to the feldspathoids are also discussed. A preliminary report of this work was given in Hassan (1994).

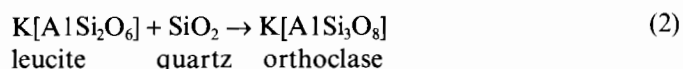
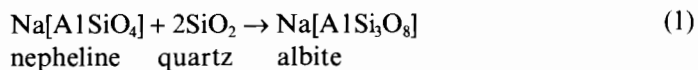
## FELDSPATHOIDS

The feldspathoids are a poorly-defined group of minerals. The word feldspathoids seems to have different meanings for different authors because of the absence of well-defined chemical or structural constraints, as there are for other silicates such as silica or feldspar minerals. The mineralogical literature does not contain a proper definition for feldspathoids. Thus, it is not clear which minerals belong to the feldspathoid group. Most silicate minerals are classified on a structural basis (*e.g.*, chain, sheet, or framework silicates) and their chemistry is well defined, as in the silica and feldspar minerals. However, the feldspathoids are defined mainly by chemical criteria.

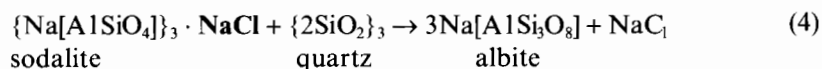
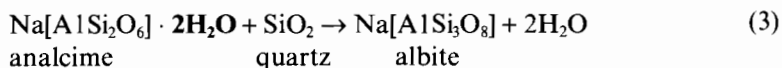
According to the *Dictionary of Geological Terms* (1960), feldspathoid is a name given to several minerals, aluminosilicates of Na, K, and Ca, that are similar in composition to the feldspars, but contain less silica than the corresponding feldspar.

Leucite and nepheline are the most common; others are melilite and sodalite. The German equivalent, *feldspatvertreter*, indicates the chief occurrence of these minerals; they take the place of feldspars in igneous rocks that are too low in silica for feldspar to form, or that contain more alkalis and aluminum than can be accommodated in the feldspars. The former definition is related to chemistry and the latter to occurrence. However, nepheline occurs with alkali feldspar in syenites and leucite occurs with sanidine in potassium-rich volcanic rocks. Thus, feldspathoids may occur with alkali feldspar. Therefore, the definition based on occurrence does not help to classify the feldspathoids.

The two main feldspathoids are nepheline and leucite, and their relations to the analogous alkali feldspar may be represented as follows:



Similar relationships can be given for other minerals, for example:



Because of the above relationships, feldspathoids normally never occur in rocks with quartz or its polymorphs. Most feldspathoids are, thus, the result of crystallization from a magma, which is relatively poor in silica and rich in alkali and alkali-earth elements. However, eucryptite and pollucite may coexist with quartz, which is in contrast with other feldspathoids.

Minerals usually considered as feldspathoids are listed in Table 1. For some minerals, their chemical compositions can be compared with nepheline (Ne) or the feldspars. This list is compiled from various sources (Deer *et al.* 1992; Klein & Hurlbut 1993; Zoltai & Stout 1984; Merlino 1984; Henderson 1984; Edgar 1984). Not all these minerals are feldspathoids, proper. The list can be reduced considerably if a more rigorous and appropriate definition is given for the feldspathoids.

The feldspathoids are best defined as anhydrous, non-volatile bearing, framework aluminosilicates of alkalis and alkali earths that contain the same or similar atoms as the feldspars, but contain less silica than the corresponding alkali feldspar. Thus, the feldspathoids have Si/(Si + Al) ratios that are less than 0.75. The structures of the feldspathoids are different from the feldspars.

If we accept this definition, many minerals in Table 1 can be eliminated from the feldspathoids. For example, the melilite-group minerals (soda melilite, gehlenite, and akermanite) are not framework minerals because the ratio of T:O is not 1:2, so the minerals of this group are not feldspathoids. Petalite can be eliminated because it contains more silica than the alkali feldspars.

Anorthite is a well-known feldspar mineral, but it fits perfectly the definition of a feldspathoid. However, anorthite has never been considered a feldspathoid. Paracelsian and danburite have similar chemistries to the feldspars, but their structures are

different from that of feldspar. The inclusion or exclusion of the other minerals in Table 1 as feldspathoids requires detailed consideration of their crystal chemistry. Therefore, the necessary background data on their structures and chemistries are given below.

### Nepheline—Kalsilite series

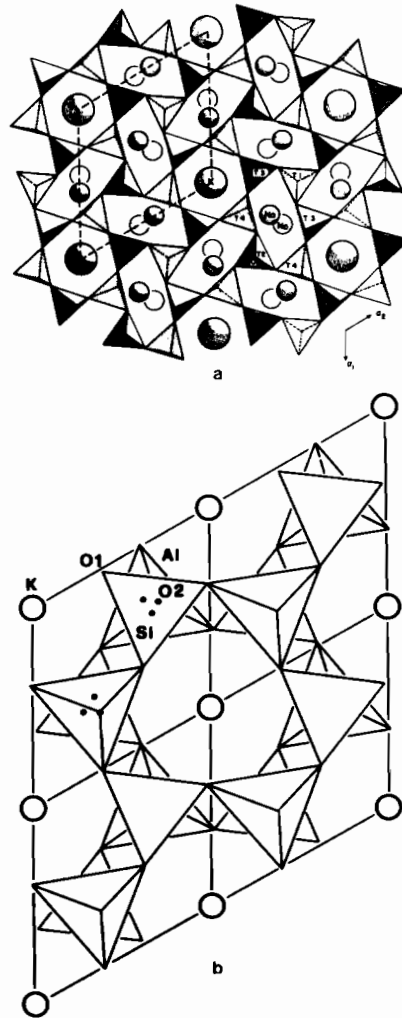
Natural nephelines,  $\text{Na}_3(\text{K}, \text{Na})[\text{AlSiO}_4]_4$  are intermediate members in a solid-solution series between the end-member  $\text{Na}[\text{AlSiO}_4]$  and  $\text{K}[\text{AlSiO}_4]$  (= kalsilite). Nepheline and kalsilite are not isostructural. However, both have structures based on the tridymite-type framework in which about one half of the Si atoms are replaced by Al atoms; the charge balance is achieved by interstitial alkali atoms in the structural cavities. Polymorphism gives rise to a number of species: different polymorphs occur at various specific compositions.

The structure of nepheline consists of four independent tetrahedral sites per unit cell. The apices of the tetrahedra occupied by T1 and T4 cations are arranged in one direction along the *c* axis, and those occupied by T2 and T3 point in the opposite direction (Fig. 1a). The T1 and T2 sites occur on the three-fold axes, and T3 and T4 occupy general positions.

The cavities in the framework are too large for the alkali atoms, in particular Na, to occupy their centers and maintain proper bonding to the framework oxygen atoms located in the channel walls. Therefore, the framework is distorted by rotation of the framework tetrahedra about the hexad axis, and so the apical

**Table 1.** Minerals usually considered as feldspathoids (feldspars included for comparison)

Mineral	Chemical Formula	Abbreviated formula	Si/(Si + Al) $\leq 0.75$	Feldspathoid?
Nepheline	$(\text{Na}, \text{K})[\text{AlSiO}_4]$	Ne	0.50	Yes
Kalsilite	$(\text{K}, \text{Na})[\text{AlSiO}_4]$		0.50	Yes
Eucryptite	$\text{Li}[\text{AlSiO}_4]$		0.50	Yes
Leucite	$(\text{K}, \text{Na})[\text{AlSi}_2\text{O}_6]$		0.67	Yes
Pollucite	$\text{Cs}[\text{AlSi}_2\text{O}_6] \cdot \text{H}_2\text{O}$		0.67	No
Analcime	$\text{Na}[\text{AlSi}_2\text{O}_6] \cdot 2\text{H}_2\text{O}$		0.67	No
Sodalite	$\{\text{Na}[\text{AlSiO}_4]\}_3 \cdot \text{NaCl}$	$\text{Ne}_3 \cdot \text{NaCl}$	0.50	No
Hauyne	$\{\text{Na}[\text{AlSiO}_4]\}_3 \cdot \text{CaSO}_4$	$\text{Ne}_3 \cdot \text{CaSO}_4$	0.50	No
Cancrinite	$\{\text{Na}[\text{AlSiO}_4]\}_3 \cdot \text{CaCO}_3 \cdot \text{H}_2\text{O}$	$\text{Ne}_3 \cdot \text{CaCO}_3 \cdot \text{H}_2\text{O}$	0.50	No
Marialite	$\{\text{Na}[\text{AlSiO}_3\text{O}_8]\}_3 \cdot \text{NaCl}$	$\text{Ab}_3 \cdot \text{NaCl}$	0.75	No
Meionite	$\{\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]\}_3 \cdot \text{CaCO}_3$	$\text{An}_3 \cdot \text{CaCO}_3$	0.50	No
Soda				
melilite	$\text{NaCa}[\text{AlSi}_2\text{O}_7]$		0.67	No
Gehlenite	$\text{Ca}_2[\text{Al}_2\text{SiO}_7]$		0.33	No
Akermanite	$\text{Ca}_2[\text{MgSi}_2\text{O}_7]$		0.67	No
Petalite	$\text{Li}[\text{AlSi}_4\text{O}_{10}]$		<b>0.80</b>	No
Paracelsian	$\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$		0.50	No
Danburite	$\text{Ca}[\text{B}_2\text{Si}_2\text{O}_8]$		0.50	No
Anorthite	$\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$	An	0.50	No
Orthoclase	$\text{K}[\text{AlSi}_3\text{O}_8]$	Or	0.75	No
Albite	$\text{Na}[\text{AlSi}_3\text{O}_8]$	Ab	0.75	No



**Fig. 1.** (a) Projection of the crystal of nepheline down  $c$ . A is the hexagonal site and B is the oval site (from Papike and Cameron, 1976); (b) projection of the crystal structure of kalsilite down  $c$  (from Merlino 1984).

oxygen atoms (O1 in nepheline and O2 in kalsilite) are distributed off the three-fold axis towards one of the three neighbouring alkali atoms (Fig. 1b). This distortion gives rise to the formation of different numbers of hexagonal, trigonal, and oval shaped rings and is responsible for the number of  $\text{Na}[\text{AlSiO}_4]$ — $\text{K}[\text{AlSiO}_4]$  species that are related either by re-constructive or displacive phase transitions (Table 2).

In nepheline, one quarter of the six-membered rings are hexagonal and three quarters are oval in shape, whereas in kalsilite all such rings are ditrigonal in shape. There are eight cavities per unit cell in nepheline and the Na atoms fully occupy the six small oval-shaped cavities, and the K atoms occupy the two hexagonal-shaped cavities, thus giving  $\text{Na}_3\text{K}[\text{Al}_4\text{Si}_4\text{O}_{16}]$  as a distinct ordered nepheline.

Other members in the nepheline-kalsilite series have different numbers of hexagonal, ditrigonal, and oval-shaped rings and different ways of linking succeeding layers.

**Table 2.** (Na,K)[AlSiO<sub>4</sub>]minerals: symmetry and cell parameters

Mineral	Wt.%	Symmetry	Space Group	Cell parameter (Å)			Reference
	NaAlSiO <sub>4</sub>			a	b	c	
Nepheline	100–30	hexagonal	<i>P</i> 6 <sub>3</sub>	10.000		8.381	Simmons & Peacor (1972)
High-temperature carnegieite	100–90	cubic		7.362			
Kalsilite	0–20	hexagonal	<i>P</i> 6 <sub>3</sub>	5.16		8.69	Perrotta & Smith (1965)
Orthorhombic NaAlSiO <sub>4</sub>	0–10	orthorhombic	<i>Pn</i> 2 <sub>1</sub> <i>m</i>	9.07	15.67	8.56	See Merlino (1984)
Trikalsilite	≈30	hexagonal	<i>P</i> 6 <sub>3</sub>	15.4		8.6	Sahama & Smith (1957)
Tetrakalsilite	≈25	hexagonal	<i>P</i> 6 <sub>3</sub>	20.513		8.553	Benedetti <i>et al.</i> (1977)
Kaliophilite	0–10	hexagonal	<i>P</i> 6 <sub>3</sub> 22	26.93		8.522	Smith & Tuttle (1957)

All their frameworks contain stacking of layers of six-membered rings of tetrahedra, with layers of different topology in the different members of the series.

Nepheline and its analogs fit the definition of a feldspathoid perfectly, and thus they are proper feldspathoids.

#### Leucite—analcime group minerals

This discussion of the structural and chemical features of the leucite-analcime group minerals closely follows the review presented by Merlino (1984). The framework structure of the leucite-analcime group is intricate (Galli *et al.* 1978); it can be described in terms of the prismatic cage (Fig. 2). The bases of the prismatic cage are formed by four-membered rings with  $\bar{4}$  symmetry, and two additional tetrahedra occur on opposite edges (Fig. 2a, b). The cages formed infinite columns through base sharing; succeeding cages in each column invert the position of the missing edges. Each column is connected to four adjacent parallel columns, thus building up a three-dimensional framework with Ia3d topological symmetry (TS). The connection of two adjacent columns and the formation of helical 4<sub>1</sub> and 4<sub>3</sub> chains of four-membered rings and chair-shaped six-membered rings are shown in Fig. 2c.

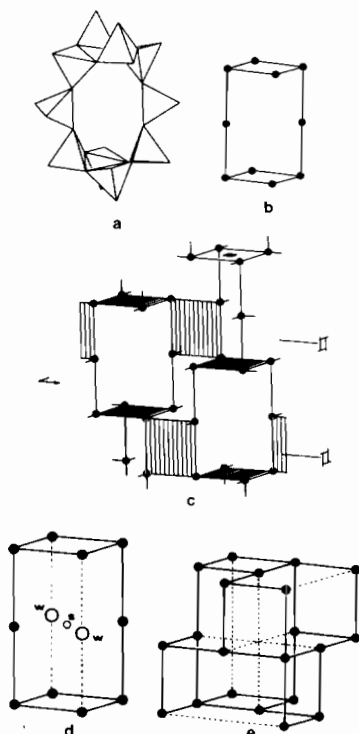
The interstitial sites on the 'missing' edges and inside the prismatic cage are called W and S, respectively (Fig. 2d). Different members in the family are characterized by different occupancies of these sites by cations, water molecules, and vacancies. The relative position of cages oriented in three different directions shows how each W site is at the intersection of the edges of three interwoven cages in the centre of the cubic unit (Fig. 2e). The multiplicities of W and S sites are 16 and 24, respectively, in space group Ia3d.

The natural phases with a leucite framework are given in Table 3. The interstitial cations occur in the W sites and vacancies occur in the S sites in the leucite-type structures. However, cations occur in S sites and water molecules occur in W sites in the analcime-type structures.

#### *Leucite-type structures:*

The composition of leucites does not depart significantly from the ideal formula K[AlSi<sub>2</sub>O<sub>6</sub>]; the Si/Al ratio is close to 2:1 and the replacement of K for Na rarely exceeds 10 per cent.

Leucite is tetragonal with pseudocubic symmetry and it inverts to a cubic form at about 600°C. The real symmetry of high-leucite coincides with the TS



**Fig. 2.** (a) Prismatic cage representing part of the leucite structure; (b) its simplified representation revealing the topology of the tetrahedral nodes and their connectivity; (c) the connection between two adjacent columns of prismatic cages; (d) 24-fold S and 16-fold W sites in the prismatic cage; and (e) relative positions of three adjacent cages enclosing a W site at their common intersection point (from Merlino 1984).

symmetry and the  $K^+$  cations occur in the 16-fold W site, while the S sites are empty. Low-leucite has space group  $14_1/a$  and the reduction in symmetry is related to the collapse of the framework around the  $K^+$  cations.

Pollucite is isostructural with leucite. The water molecules are located in W sites not occupied by  $Cs^+$  cations and the  $Na^+$  cations are located in S sites within the cages and forming  $H_2O-Na-H_2O$  clusters.

#### *Analcime-type structures:*

Analcime presents the same framework as leucite. The water molecules occur in 16-fold W sites and  $Na^+$  cations and vacancies are distributed on 24-fold S sites. Wairakite and hsianghualite are isostructural with analcime. In hsianghualite, the  $Ca^{2+}$  cations fully occupy the S sites in the cages;  $F^-$  anions occupy the slightly displaced W sites instead of water molecules. The small  $Li^+$  cations are stuffed in the structure and are tetrahedrally coordinated by a fluorine and three framework oxygen atoms of the hexagonal ring.

Based on the anhydrous condition in the definition of a feldspathoid, pollucite and analcime can be eliminated from the feldspathoids, even though they are structurally related to the feldspathoid leucite. Therefore, pollucite and analcime-group minerals should not be considered as feldspathoids, but leucites are proper feldspathoids.

**Table 3.** Minerals with leucite framework (TS = *Ia3d*): composition and cell parameters

Mineral	Chemical formula	Space Group	Cell parameters (Å)				Reference
			a	b	c	$\beta$	
<i>Leucite-type structures</i>							
Leucite (high)	$K_{16}[Al_{16}Si_{32}O_{96}]$	<i>Ia3d</i>	13.43				Peacor (1968)
Leucite (low)	$K_{16}[Al_{16}Si_{32}O_{96}]$	<i>I4<sub>1</sub>/a</i>	13.04		13.85		Mazzi <i>et al.</i> (1976)
Pollucite	$Cs_{12}Na_4[Al_{16}Si_{32}O_{96}] \cdot 4H_2O$	<i>Ia3d</i>	13.69				Berger (1969)
<i>Analcime-type structures</i>							
Analcime	$Na_{16}[Al_{16}Si_{32}O_{96}] \cdot 16H_2O$	<i>I4<sub>1</sub>/acd</i>	13.78				Mazzi & Galli (1978)
Wairakite	$Ca_8[Al_{16}Si_{32}O_{96}] \cdot 16H_2O$	<i>I2/a</i>	13.69	13.64	13.56	90.5°	Takéuchi <i>et al.</i> (1979)
Hsianghualite	$Li_{16}Ca_{24}[Be_{24}Si_{24}O_{96}]F_{16}$	<i>I2<sub>1</sub>3</i>	12.88				

### Cancrinite-group minerals

The structures of the cancrinite-group minerals are characterized by parallel six-membered rings consisting of alternating  $AlO_4$  and  $SiO_4$  tetrahedra. The hexagonal symmetry is the result of the stacking of such six-membered rings in an AB . . . sequence. This stacking gives rise to large continuous channels that are formed by twelve-membered rings of alternating  $AlO_4$  and  $SiO_4$  tetrahedra (Fig. 3a). These are among the largest channels known, even for zeolites. The cancrinite structure also consists of small cages, known as  $\epsilon$ -cages in zeolite chemistry. The  $\epsilon$ -cage is also known as a cancrinite cage or 'undecahedral' cage, which is bounded by 5 six-membered and 6 four-membered rings and, thus, the  $\epsilon$ -cage is also known as 11-hedral cage (Fig. 3b). The  $\epsilon$ -cages occur along the three-fold axes (Fig. 3a).

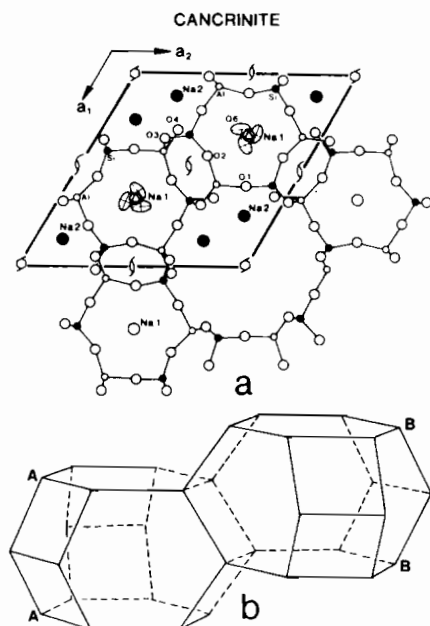
The most important members of the cancrinite group-space group, R-values, unit cell information,  $\epsilon$ -cage content and selected references are given in Table 4a. The stacking of six-membered rings in all these cancrinites is the AB . . . sequence. In general, the  $\epsilon$ -cages contain atoms or clusters of atoms that have a net charge difference of 1 + valence units. The  $[Na \cdot H_2O]^+$  clusters occur in the  $\epsilon$ -cages of cancrinite, hydroxy cancrinite, vishnevite, and pitiglianoite, but  $[Ca \cdot Cl]^+$  clusters occur in davyne, quadri-davyne, and microsommite. Tiptopite, the beryllophosphate analog of hydroxy cancrinite, contains a K cation. The other interstitial cations and anions occur in the large channels that are parallel to the  $6_3$  axes (Fig. 3a).

Microsommite has a *c* parameter that is similar to that of cancrinite. However, its unit cell is three times ( $Z = 3$ ) that of cancrinite, with  $a_m = \sqrt{3} a_c$ .

The sodalite-group minerals have strong structural similarities to the cancrinite-group minerals, but the former have an ABC . . . stacking sequence that lead to cubic instead of hexagonal symmetry. This sequence leads to an offset of the C-type layer and gives rise to a network of large  $\beta$ -cages in the sodalite-group minerals.

Some cancrinite minerals have structures that are based on more complicated stacking of six-membered rings and, thus, they have more complex aluminosilicate frameworks than either cancrinite with AB . . . sequence or sodalite with ABC . . . sequence (Table 4b). Some examples of these minerals and their stacking sequences are liottite (ABABAC . . .) and afghanite (ABABACAC . . .). The 'crystals' and 'domains' were first observed in other cancrinites by Rinaldi using transmission electron microscopy and, subsequently, found also as single crystals (see Merlino 1984).





**Fig. 3.** (a) Crystal structure of cancrinite showing four-, six-, and twelve-membered rings of alternating silicon and aluminum tetrahedra (after Grundy and Hassan, 1982). (b) Schematic illustration of the two  $\epsilon$ -cages per unit cell in cancrinite.

The chemical formulae of these minerals has been normalized to that of the smaller cancrinite cell for the purpose of comparison. Their formula unit per unit cell is  $Z (= n)$ . Except for synthetic losod, which is a zeolite, the other minerals have formulae that contain similar cations and anions as cancrinite with the AB . . . stacking sequence. All the cancrinites have the same  $a$  parameter, but their  $c$  parameter is some multiple,  $n$ , of the basic cancrinite  $c$  parameter (Table 4b). Cancrinites with AB . . . stacking sequence have superstructures that also give multiples,  $n$ , of the substructure  $c$  parameter.

The difficulties found in refining the structures of these cancrinites are related not only to possible stacking faults or stacking variations, but also to disorder in the distribution of the interstitial cations (K, Na, Ca), anions (Cl, CO<sub>3</sub>, SO<sub>4</sub>) and H<sub>2</sub>O.

### Sodalite-group minerals

Many materials have the sodalite, Na<sub>8</sub>[Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>]Cl<sub>2</sub>, structure. It is characterized by a framework of corner-linked TO<sub>4</sub> tetrahedra (T = Si<sup>4+</sup>, Al<sup>3+</sup>, Be<sup>2+</sup>, B<sup>3+</sup>, Ga<sup>3+</sup>, and Ge<sup>4+</sup>) and intervening large cavities, called  $\beta$ -cages in zeolite chemistry (Fig. 4a, b). The  $\beta$ -cages occur as building blocks for many zeolites. The structures are characterized by six-fold rings of TO<sub>4</sub> tetrahedra parallel to {111} planes in the cubic structure. These rings are stacked in a cubic ABCABC . . . sequence. The structures also contain four-fold rings of TO<sub>4</sub> tetrahedra parallel to {100} planes. The cations in the TO<sub>4</sub> tetrahedra are fully ordered in the different sodalite minerals (Table 5a, b).

The  $\beta$ -cage is sometimes described on the basis of the well-known truncated octahedron or cubo-octahedron that is bounded by 8 six-membered and 6 four-membered rings and is, thus, called 14-hedron (Type 1) in zeolite chemistry (Fig. 4b).

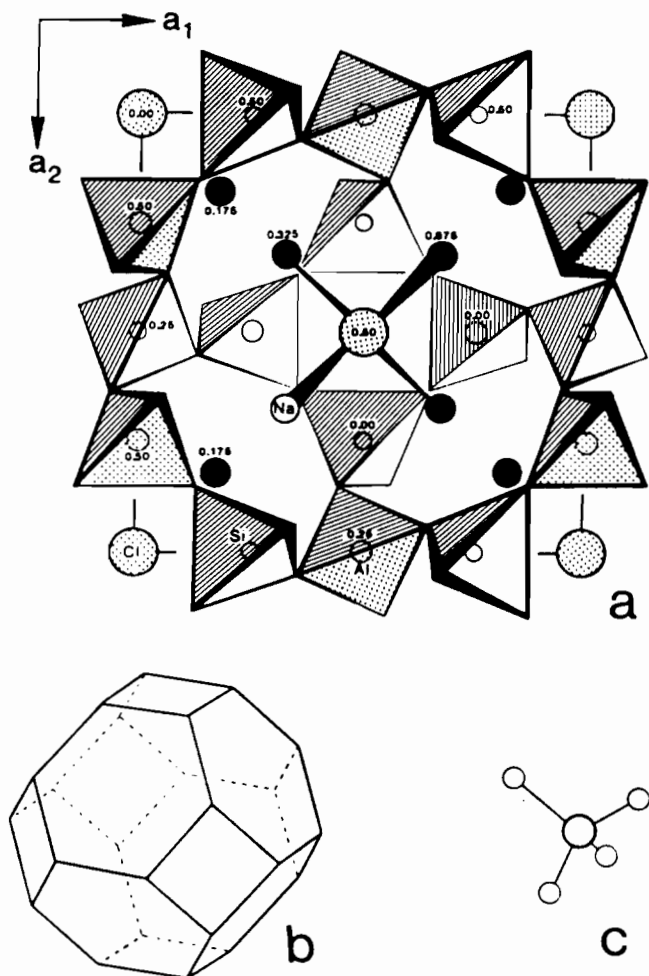
Table 4a. Cancrinite-group minerals: composition,  $\epsilon$ -cage clusters, symmetry, cell parameters, and R value

Mineral	Chemical Formula	$\epsilon$ -Cage Clusters	Space Group	Cell ( $\text{\AA}$ ) a c	R	Selected Reference
Cancrinite	$\text{Na}_6\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$	$[\text{Na} \cdot \text{H}_2\text{O}]^+$	$P6_3$	12.590 5.117	0.028	Grundy & Hassan (1982)
Hydroxy (basic) cancrinite	$\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{OH})_2 \cdot 3\text{H}_2\text{O}$	$[\text{Na} \cdot \text{H}_2\text{O}]^+$	$P6_3$	12.664 5.159	0.047	Hassan & Grundy (1991c)
Vishnevite	$\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{SO}_4 \cdot 2\text{H}_2\text{O}$	$[\text{Na} \cdot \text{H}_2\text{O}]^+$	$P6_3$	12.685 5.179	0.037	Hassan & Grundy (1984b)
Pitiglianoite	$(\text{Na}, \text{K})_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{SO}_4 \cdot 2\text{H}_2\text{O}$	$[\text{Na} \cdot \text{H}_2\text{O}]^+$	$P6_3$	22.121 5.221	0.065	Merlino <i>et al.</i> (1991)
Davyne	$\text{Na}_6\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2(\text{OH})_2$	$[\text{Ca} \cdot \text{Cl}]^+$	$P6_3$	12.793 5.367	0.048	Hassan & Grundy (1990)
Quadridavyne	$(\text{Na}, \text{K})_6\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_4$	$[\text{Ca} \cdot \text{Cl}]^+$	$P6_3/m$	22.771 5.3371	?	Bonaccorsi <i>et al.</i> (1994)
Microsommitte	$\text{Na}_4\text{K}_2\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{SO}_4\text{Cl}_2$	$[\text{Ca} \cdot \text{Cl}]^+$	$P6_3$	22.160 5.346	?	See Merlino <i>et al.</i> (1991)
Tiptopite	$\text{K}_2\text{Li}_{2.9}\text{Na}_{1.7}\text{Ca}_{0.7}[\text{Be}_6\text{P}_6\text{O}_{24}](\text{OH})_2 \cdot 1.3\text{H}_2\text{O}$	$[\text{K}]^+$	$P6_3$	11.665 4.962	0.048	Peacor <i>et al.</i> (1987)

Table 4b. Additional cancrinite-type minerals: composition, stacking sequence, symmetry, cell parameters, and R value

Mineral	Chemical Formula	$nc$ $n$	Stacking Sequence	Space Group	Cell (Å)		R	Selected Reference
					$a$	$c$		
Cancrinite†	Na <sub>6</sub> Ca <sub>2</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ](CO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	1	AB ...	$P6_3$	12.590	5.117	0.028	Grundy & Hassan (1982)
Sodalite	Na <sub>8</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ]Cl <sub>2</sub>	1.5	ABC ...	$P\bar{4}3n$	8.882	—	0.017	Hassan & Grundy (1984a)
Losod (syn)	Na <sub>6</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ]·9·5H <sub>2</sub> O	2*	ABAC ...	$P6_3/mmc$	12.906	10.541	0.400	Sieber & Meier (1974)
Liotite	Na <sub>3.1</sub> Ca <sub>3.6</sub> K <sub>1.3</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ]Cl <sub>0.9</sub> (SO <sub>4</sub> ) <sub>1.3</sub> (CO <sub>3</sub> ) <sub>0.6</sub> ·1.2H <sub>2</sub> O	3	ABABAC ...	$P6m2$	12.842	16.091	0.140	Merlino & Orlandi (1977a)
Afghanite	Na <sub>4.9</sub> Ca <sub>3.5</sub> K <sub>0.7</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ]Cl <sub>1.6</sub> (SO <sub>4</sub> ) <sub>1.3</sub> (CO <sub>3</sub> ) <sub>0.1</sub> ·0.5H <sub>2</sub> O	4	ABABACAC ...	$P6_3mc$	12.847	21.464	0.160	Merlino & Mellini (1976)
Franzinite	Na <sub>4.3</sub> Ca <sub>2.5</sub> K <sub>1.0</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ]Cl <sub>0.1</sub> (SO <sub>4</sub> ) <sub>1.5</sub> (CO <sub>3</sub> ) <sub>0.4</sub> ·1.2H <sub>2</sub> O	5*	ABCABCACA ... ?	$P\bar{3}m1$	12.884	26.58	0.270	Merlino & Orlandi (1977b)
'crystal'		6	Unknown	?	12.88	31.75	?	see Merlino (1984)
'crystal'		7*	Unknown	?	12.9	37.3	?	see Merlino (1984)
Giuseppettite	Na <sub>5.0</sub> Ca <sub>0.9</sub> K <sub>1.8</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ]Cl <sub>0.24</sub> (SO <sub>4</sub> ) <sub>1.34</sub> (CO <sub>3</sub> ) <sub>0.24</sub>	8*	ABABABCBABABABC	$P\bar{6}2c$	12.85	42.22	?	Mazzi & Tandini (1981)
'crystal'		9	Unknown	?	12.89	47.90	?	see Merlino (1984)
'domains'		12	Unknown	?	12.77	63.90	?	see Merlino (1984)
Sacrofanite	Na <sub>6.3</sub> Ca <sub>1.8</sub> K <sub>1.4</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ]Cl <sub>0.2</sub> (SO <sub>4</sub> ) <sub>1.1</sub> (CO <sub>3</sub> ) <sub>0.3</sub> ·3·2H <sub>2</sub> O	14*	Unknown	$P6_3mc$	12.865	72.24	?	Burrigato <i>et al.</i> (1980)

†  $n \times c$ : = 2, 5, 7, 8, 14, 16 for cancrinites with AB ... stacking sequence; the number of layers in a sequence is  $2n$  and  $Z$ , the unit-cell content is  $n$ .



**Fig. 4.** (a) Crystal structure of sodalite (after Pauling, 1930). (b) Truncated-octahedral or  $\beta$ -cage in sodalite-type structures. (c) Tetrahedral  $\beta$ -cage clusters (e.g.,  $[\text{Na}_4\text{Cl}]$ ) located in the centre of the cage.

The  $\beta$ -cages are stacked in eight fold coordination with each six-membered ring shared between two  $\beta$ -cages. The six-membered rings form channels parallel to the cube diagonals.

Crystal-chemical data for members of the sodalite group are given (Tables 5a, b). The  $\beta$ -cages contain clusters of atoms, for example, in sodalite, hackmanite, and tugtupite, each cage contains  $[\text{Na}_4\text{Cl}]^{3+}$  clusters (Fig. 4c); that is, the chlorine at the center of the cage is tetrahedrally coordinated by four sodium cations that are on the cube diagonals (Fig. 4a,c). The cage clusters contain a net charge difference of  $3^+$  valence units and all the clusters are of the same type, but nosean, hauyne, and lazurite contain different clusters in different proportions (Table 5a, b). These different clusters may be ordered and rise to antiphase domain boundaries, and superstructures also occur in these minerals.

Table 5a. Minerals with sodalite-type structure:  $\beta$  cage clusters, symmetry, cell parameters, and R value

Mineral	Chemical Formula	$\beta$ -Cage Clusters	Space Group	Cell $a(\text{\AA})$	R	Selected Reference
Sodalite	$\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$	$100\%[\text{Na}_4\text{Cl}]_3 +$	$P\bar{4}3n$	8.882	0.017	Hassan & Grundy (1984a)
Hackmanite	$\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$	$100\%[\text{Na}_4\text{Cl}]_3^{3+}$	$P\bar{4}3n$	8.877	0.035	Peterson (1983)
Hydroxy sodalite	$\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{OH})_2 \cdot 2\text{H}_2\text{O}$	$100\%[\text{Na}_4\text{OH} \cdot \text{H}_2\text{O}]_3^{3+}$	$P\bar{4}3n$	8.890	0.028	Hassan & Grundy (1983)
Nosean	$\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{SO}_4 \cdot \text{H}_2\text{O}$	$50\%[\text{Na}_4\text{SO}_4]_2^{2+}$ $50\%[\text{Na}_4\text{H}_2\text{O}]_4^{4+}$	$P\bar{4}3n^*$	9.084	0.057	Hassan & Grundy (1989)
Haüyne	$\text{Na}_{4.5}\text{Ca}_2\text{K}[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_{1.5}(\text{OH})_{0.5}$	$75\%[\text{Na}_3\text{Ca} \cdot \text{SO}_4]_3^{3+}$ $25\%[\text{K}_2\text{Ca} \cdot \text{OH}]_3^{3+}$	$P\bar{4}3n^*$	9.166	0.036	Hassan & Grundy (1991a)
Lazurite	$\text{Na}_6\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_{1.4}\text{SO}_6$	$71\%[\text{Na}_3\text{Ca} \cdot \text{SO}_4]_3^{3+}$ $29\%[\text{Na}_3\text{Ca} \cdot \text{S}]_3^{3+}$	$P\bar{4}3n^*$	9.105	0.070	Hassan <i>et al.</i> (1985)
Bicchulite	$\text{Ca}_8[\text{Al}_8\text{Si}_4\text{O}_{24}](\text{OH})_8$	$100\%[\text{Ca}_4\text{OH}]_4^{4+}$	$I\bar{4}3m$	8.825	0.012	Sahl (1980)
Synthetic	$\text{Zn}_8[\text{B}_2\text{O}_7]_2\text{O}_2$	$100\%[\text{Zn}_4\text{O}]_6^{6+}$	$I\bar{4}3m$	7.480	0.044	Smith-Verdier & Garcia-Blanco (1980)
Synthetic	$\text{Na}_8[\text{Al}_6\text{Ge}_6\text{O}_{24}](\text{OH})_2$	$100\%[\text{Na}_4\text{OH}]_3^{3+}$	$P\bar{4}3n$	9.029	0.048	Belokoneva <i>et al.</i> (1982)
Synthetic	$\text{Na}_8[\text{Ga}_6\text{Si}_6\text{O}_{24}](\text{OH})_2 \cdot 6\text{H}_2\text{O}$	$100\%[\text{Na}_4\text{OH} \cdot 3\text{H}_2\text{O}]_3^{3+}$	$P\bar{4}3n$	8.856	0.084	McCuster <i>et al.</i> (1986)
Synthetic	$\text{Cr}_8[\text{Al}_{12}\text{O}_{24}](\text{WO}_4)_2$	$100\%[\text{Cr}_4 \cdot \text{WO}_4]_6^{6+}$	$I\bar{4}3m$	9.300	0.040	Depmeier (1988)

\* Average space groups because these minerals may contain antiphase domain boundaries; the space group for each domain is  $P2_3$ .

**Table 5b.** Helvite-group and tugtupite minerals (sodalite-type structure)

Mineral	Ideal Chemical Formula	$\beta$ -Cage Clusters	Space Group	Cell $a(\text{\AA})$	$R$	Selected Reference
Helvite	$\text{Mn}_8[\text{Be}_6\text{Si}_6\text{O}_{24}]\text{S}_2$	100% $[\text{Mn}_4\text{S}]^{6+}$	$P\bar{4}3n$	8.291	0.024	Hassan & Grundy (1985)
Danalite	$\text{Fe}_8[\text{Be}_6\text{Si}_6\text{O}_{24}]\text{S}_2$	100% $[\text{Fe}_4\text{S}]^{6+}$	$P\bar{4}3n$	8.232	0.024	Hassan & Grundy (1985)
Genthelvite	$\text{Zn}_8[\text{Be}_6\text{Si}_6\text{O}_{24}]\text{S}_2$	100% $[\text{Zn}_4\text{S}]^{6+}$	$P\bar{4}3n$	8.109	0.028	Hassan & Grundy (1985)
Tugtupite	$\text{Na}_8[\text{Al}_2\text{Be}_2\text{Si}_8\text{O}_{24}]\text{Cl}_2$	100% $[\text{Na}_4\text{Cl}]^{3+}$	$I\bar{4}$	8.640†	0.023	Hassan & Grundy (1991b)

† Tetragonal:  $a = b = 8.640$ ;  $c = 8.873 \text{ \AA}$

## SCAPOLITES

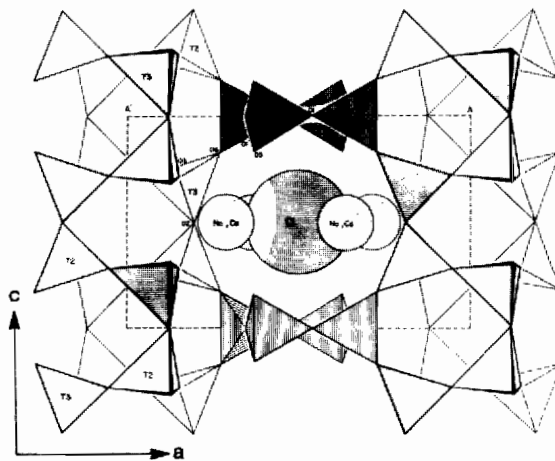
The framework aluminosilicate structure of scapolite consists of four-membered, oval-shaped six-membered and five-membered rings made up of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra. The structure consists of large cages that contain anions ( $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ ) that are surrounded by four (Na,Ca) cations, thus forming clusters of atoms (Fig. 5). The chemical composition of scapolites is very similar to that of cancrinites and sodalites.

Scapolite composition varies between that of the end-member marialite and meionite (Table 6). Two solid-solution series exist between the end members: series (a) occurs between 0 and 75 Me, and series (b) occurs between 75 and 100 per cent Me. Two types of substitutions occur (Table 6). Because the point 75 Me is a valid end-member composition, it should be given a proper mineral name.

Ordering of  $[\text{Na}_4\text{Cl}]^{3+}$  and  $[\text{NaCa}_3\text{CO}_3]^{5+}$  clusters occurs in compositions between 0 and 75 Me, and disordering of  $[\text{NaCa}_3\text{CO}_3]^{5+}$  and  $[\text{Ca}_4\text{CO}_3]^{6+}$  clusters occurs for compositions between 75 and 100 per cent Me.

## ZEOLITES

Zeolites are best-defined as hydrous aluminosilicates with a framework structure enclosing cavities and channels occupied by alkali and alkali-earth cations and water



**Fig. 5.** Projection of the  $P4_2/n$  marialite scapolite down  $a$  and onto the  $AA'$  plane (from Levien & Papike 1976).

Table 6. Scapolite-group minerals

Mineral	Chemical Formula	Cage Clusters
Marialite [Me <sub>0</sub> ]	Na <sub>4</sub> [Al <sub>3</sub> Si <sub>9</sub> O <sub>24</sub> ]Cl	[Na <sub>4</sub> ·Cl] <sup>3+</sup>
Name? [Me <sub>75</sub> ]	NaCa <sub>3</sub> [Al <sub>5</sub> Si <sub>7</sub> O <sub>24</sub> ]CO <sub>3</sub>	[NaCa <sub>3</sub> ·CO <sub>3</sub> ] <sup>5+</sup>
Meionite [Me <sub>100</sub> ]	Ca <sub>4</sub> [Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> ]CO <sub>3</sub>	[Ca <sub>4</sub> ·CO <sub>3</sub> ] <sup>6+</sup>
Substitution between Me <sub>0-75</sub> : Si <sub>2</sub> [Na <sub>4</sub> ·Cl] <sup>3+</sup> ↔ Al <sub>2</sub> [NaCa <sub>3</sub> ·CO <sub>3</sub> ] <sup>5+</sup>		
Substitution between Me <sub>75-100</sub> : Si[NaCa <sub>3</sub> ·CO <sub>3</sub> ] <sup>5+</sup> ↔ Al[Ca <sub>4</sub> ·CO <sub>3</sub> ] <sup>6+</sup>		

molecules, both of which have considerable freedom of movement permitting ion exchange and reversible dehydration without changing its structure. Chemically, they are related to feldspars, but they contain water molecules and have much more open structures; they may be transformed to feldspars when subjected to thermal metamorphism.

Although analcime is commonly included as a member of the zeolite group, it has close affinities with the feldspathoid leucite, and often has a somewhat higher-temperature paragenesis than the other zeolites.

The zeolites are characterized also by having the molecular ratio (Ca, Sr, Ba, Na<sub>2</sub>, K<sub>2</sub>)O/AlO<sub>3</sub> equal to unity. A general formula can be written M<sub>x</sub>D<sub>y</sub>[Al<sub>x+2y</sub>Si<sub>z</sub>O<sub>2x+4y+2z</sub>]·nH<sub>2</sub>O, where M = Na, K or other monovalent cations and D = Mg, Ca, Sr, Ba and other divalent cations. Thus, the ideal formula of the natural zeolite heulandite, for example, can be written as CaO·Al<sub>2</sub>O<sub>3</sub>·7SiO<sub>2</sub>·6H<sub>2</sub>O or as Ca<sub>4</sub>[Al<sub>8</sub>Si<sub>28</sub>O<sub>72</sub>]·24H<sub>2</sub>O on a unit-cell basis, the cations, in the first group being the exchangeable ions and those in the square brackets representing the structural cations, which with oxygen atoms make up the tetrahedral framework of the structure. The ratio SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is always ≥ 2:1. The chemistry of many zeolites is rather variable and sometimes deviates considerably from schematic formulae, which are at best only an approximation of what the composition of a particular zeolite may be (Table 7).

Many zeolites have structures that are based to stacking of six-membered rings, as is cancrinites and sodalites, e.g., offretite (AAB . . .), erionite (AABAAC . . .), levynite (AABCCABBC . . .), and chabazite (AABBCC . . .) (Table 7). This feature indicates a strong structural similarity among all of these minerals. However, the zeolites contain water molecules instead of CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> found in sodalites, cancrinites, and scapolites.

In addition, many other zeolites have structures that contain ε- and β-cages. These cages are used as building blocks in many zeolite structures such as zeolite A, and faujasite (Table 7; Fig. 6a, b).

As a family, sodalite, cancrinite, and scapolite have a unique chemistry in that they are the only aluminosilicate minerals that contain large volatile anions and they have a close structural relationship to the zeolites, but not to the feldspars or the feldspathoids, proper. Therefore, a new group name, *i.e.*, *zeoloids*, may be appropriate for these minerals.

## COMPARISON OF THE FRAMEWORK ALUMINOSILICATES

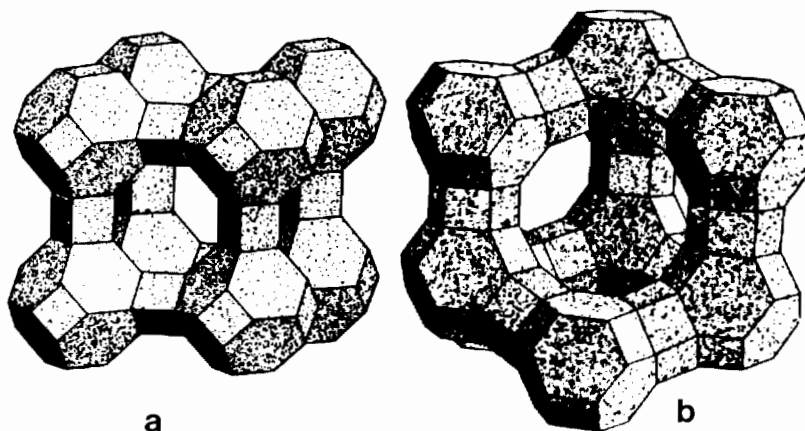
The basic feature of all framework structures is an aluminosilicate framework composed of (Si, Al)O<sub>4</sub> tetrahedra, each oxygen of which is shared between two tetrahedra. The net negative charge on the framework is balanced by the presence of cations, in most cases Ca, Na, or K, which are situated in cavities and channels within it. This feature is embodied in the structures of the feldspar, feldspathoid, zeoloid, and zeolite

Table 7. Zeolites containing stacking of six-membered rings and zeolites containing  $\beta$ - and  $\epsilon$ -cages

Mineral	Chemical Formula	$nc$	Stacking Sequence	Space Group	Cell ( $\text{\AA}$ )				Rings				n-hedron n	Minimum channel dimension
					$a$	$c$	4	6	8	12				
Cancrinite	$\text{Na}_6\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{OH})_2 \cdot 3\text{H}_2\text{O}$	1	AB...	$P6_3$	12.664	5.159	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	11 = $\epsilon$	6.2 $\text{\AA}$	
Sodalite	$\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{OH})_2 \cdot 2\text{H}_2\text{O}$	1.5	ABC...	$P4_3n$	8.890	—	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	14 (I) = $\beta$	2.2	
Offretite	$(\text{K}_2\text{MgCa})_2[\text{Al}_5\text{Si}_{13}\text{O}_{36}] \cdot 15\text{H}_2\text{O}$	1.5	AAB...	$P6m2$	13.29	7.58	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\epsilon$ , 14 (II)	6.4	
Losod	$\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot 9.5\text{H}_2\text{O}$	2	ABAC...	$P6_3/mmc$	12.91	10.54	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\epsilon$ , 17 (II)	2.2	
Gmelinite	$\text{Na}_2[\text{Al}_2\text{Si}_4\text{O}_{12}] \cdot 6\text{H}_2\text{O}$	2	AABB...	$P6_3/mmc$	13.75	10.05	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	14 (II)	7.0	
Chabazite	$\text{Ca}_2[\text{Al}_4\text{Si}_8\text{O}_{24}] \cdot 12\text{H}_2\text{O}$	3	AABBCC...	$R\bar{3}m$	13.78	15.06	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	20	3.7 $\times$ 4.2	
TMA-E(AB)		3	ABBACC...		13.27	15.23	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$			
Erionite	$(\text{NaK}_2\text{MgCa}_{1.5})[\text{Al}_8\text{Si}_{28}\text{O}_{72}] \cdot 28\text{H}_2\text{O}$	3	AABAAC...	$P6_3/mmc$	13.26	15.12	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\epsilon$ , 23	3.6 $\times$ 5.3	
Linde T	$\text{Na}_{1.2}\text{K}_{2.8}[\text{Al}_4\text{Si}_{14}\text{O}_{36}] \cdot 14\text{H}_2\text{O}$	3	AABAAC...	$P6_3/mmc$			$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\epsilon$ , 23	3.6 $\times$ 5.2	
Lecynite	$\text{Ca}_3[\text{Al}_6\text{Si}_{12}\text{O}_{36}] \cdot 18\text{H}_2\text{O}$	4.5	AABCCABBC...	$R\bar{3}m$	13.32	22.51	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	17	3.2 $\times$ 5.1	
Faujasite	$(\text{Na}_2, \text{Ca})_{30}[\text{Al}_{60}\text{Si}_{132}\text{O}_{384}] \cdot 260\text{H}_2\text{O}$	—	—	$Fd\bar{3}m$	24.67	—	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\beta$ , 26(II)	7.4	
Linde X	$\text{Na}_{86}[\text{Al}_{86}\text{Si}_{106}\text{O}_{348}] \cdot 264\text{H}_2\text{O}$	—	—	$Fd\bar{3}m$	25.02	—	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\beta$ , 26(II)	7.4	
Linde Y	$\text{Na}_{56}[\text{Al}_{56}\text{Si}_{136}\text{O}_{384}] \cdot 250\text{H}_2\text{O}$	—	—	$Fd\bar{3}m$	24.85	—	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\beta$ , 26(II)	7.4	
Linde A	$\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}] \cdot 27\text{H}_2\text{O}$	—	—	$Fm\bar{3}c$	24.64	—	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	26(I) = $\alpha, \beta$	4.2	
ZK-4	$\text{Na}_8\text{TMA}[\text{Al}_9\text{Si}_{15}\text{O}_{48}] \cdot 28\text{H}_2\text{O}$	—	—	$Fm\bar{3}c$	—	—	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\alpha, \beta$	4.2	
N-A	$\text{Na}_4\text{TMA}_3[\text{Al}_7\text{Si}_{17}\text{O}_{48}] \cdot 21\text{H}_2\text{O}$	—	—	—	—	—	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\alpha, \beta$	4.2	
Zeolite L	$\text{K}_9[\text{Al}_9\text{Si}_{27}\text{O}_{72}] \cdot 22\text{H}_2\text{O}$	—	—	—	18.4	7.5	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\epsilon$	7.1	

After Breck (1974); cancrinite or  $\epsilon$ -cage is called 11-hedron; sodalite or  $\beta$ -cage is 14-hedron (Type I); TMA = tetramethylammonium





**Fig. 6.** Arrangements of  $\beta$ -cages to enclose large central cavities. (a)  $\beta$ -cages connected by double four-membered rings of oxygen atoms in the structure of zeolite A. (b)  $\beta$ -cages connected by double six-membered rings of oxygen atoms in the structure of faujasite (from Meier 1968).

minerals. The feldspars have compact structures in which the (Na, Ca, K) ions are in relatively small cavities and are completely surrounded by oxygen atoms of the framework: the cations and framework are strongly interdependent so that cations cannot easily move unless framework bonds are broken, and replacement of Na or K by Ca necessarily involves a change in the Si/Al ratio. Similar features occur in the feldspathoids nepheline and leucite. The zeoloids have somewhat more open aluminosilicate frameworks, and their Na, Ca, K ions (and in some cases certain anions) occupy, but do not always fill, larger cavities and channels, which are intercommunicating. Thus, in the zeoloids there are channels through which ions can be either extracted or introduced, and some through which small molecules may pass, without disruption of the framework. The zeolite aluminosilicate frameworks are similar but many are still more open, containing larger cavities and larger channels (specific gravity of zeolites 2.0–2.3, zeoloids 2.3–2.5, feldspathoids 2.5–2.6, feldspars 2.6–2.7); zeolites may therefore exhibit to a greater extent the properties of ion exchange and molecular absorption. An additional feature which differentiates the zeolites still further from minerals of the other three groups is the presence of water molecules within the structural channels. These water molecules are loosely bound to the framework and cations, and like the cations can be removed and replaced without disrupting framework bonds. Because the zeolite framework is structurally almost independent of the (Na, Ca, K) cations, and because the latter do not fill all the cavities and channels, replacements of the type  $\text{Ca} \leftrightarrow 2(\text{Na}, \text{K})$  can occur as well as the more usual  $\text{CaAl} \leftrightarrow (\text{Na}, \text{K})\text{Si}$ .

The channel systems in the various zeolites are formed by different combinations of linked rings of tetrahedra; the wider the channels at their narrowest parts, the larger the cation that can be introduced into the structure. Those with eight- and twelve-membered rings have channels large enough for the admission of organic molecules as well as cations; thus zeolites can act as ion or molecular sieves, each having its characteristic upper limit for the size of ion or molecule to which it is permeable. A grading of some zeolites according to the openness of structure is given in Table 7.

Channel width, however, is not the only criterion for permeability, because the presence of many cations may block the channels, and ionic or molecular diffusion is also affected by water content. Cation exchange capacity in general diminishes with loss of water; cations are most mobile in zeolites with low cation content. Na is more mobile than Ca because it is monovalent and is thus held by a weaker electrostatic bond.

In most zeolites the water molecules are probably distributed among a number of possible sites and can jump from one to another. In general the Ca zeolites absorb more water, and in chabazite, heulandite and stilbite, water retentivity is greater with Ca than with K in the framework.

## CONCLUSIONS

The feldspathoids are best defined as anhydrous framework aluminosilicates that contain alkali and alkali-earth elements, but contain no volatile anions and are similar in composition to the feldspars (*i.e.*, they contain the same or similar atoms), but contain less silica than the alkali feldspar. Thus the feldspathoids have Si/(Si + Al) ratio less than 0.75. Nepheline and leucite best fit this definition.

Sodalite, cancrinites, and scapolites are the only framework aluminosilicates that contain large volatile anions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ , and  $\text{H}_2\text{O}$ ; all of which are important structural components. These minerals have chemistries and structures that are quite different from that of the feldspars or the feldspathoids. However, some of their structures are closely related to the zeolites, but they are not zeolites, proper.

The structures of the cancrinite-group minerals are characterized by parallel six-membered rings consisting of alternating  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra. The hexagonal symmetry is the result of the stacking of such six-membered rings in an AB . . . sequence. This stacking gives rise to large continuous channels that are formed by twelve-membered rings of alternating  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra. These are among the largest channels known, even for zeolites. The cancrinite structure also consists of small cages, known as  $\epsilon$ -cages in zeolite chemistry. The sodalite-group minerals have strong structural similarities to the cancrinite-group minerals, but the former have an ABC . . . stacking sequence that leads to cubic instead of hexagonal symmetry. This sequence leads to an offset of the C-type layer and gives rise to a network of large  $\beta$ -cages in the sodalite-group minerals. Some cancrinite-type minerals have structures that are based on more complicated stacking of six-membered rings. Some examples of these minerals and their stacking sequences are liottite (ABABAC . . .) and afghanite (ABABACAC . . .). Some zeolites also have structures that are based on similar stacking of six-membered rings, *e.g.*, offretite (AAB . . .), erionite (AABAAC . . .), levynite (AABCCABBC . . .), and chabazite (AABBCC . . .). The  $\epsilon$ - and  $\beta$ -cages are also used as building blocks in many zeolite structures such as zeolite A, offretite, and faujasite.

As a family, sodalite, cancrinite, and scapolite have a unique chemistry in that they are the only aluminosilicate minerals that contain large volatile anions and they have a close structural relationship to the zeolites, but not to the feldspars or the feldspathoids, proper. Therefore, a new group name, *i.e.*, *zeoloids*, may be appropriate for these minerals because their present classification as *feldspathoids* is not appropriate.

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## الفلدسباتويدات وعلاقتها بالزيوليت

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## خلاصة

يتم تعريف الفلدسباتويدات على أنها شبكة فراغية للسيليكات الألومينية اللامائية الحاوية على عناصر قاعدية وقاعدية أرضية ولكنها خالية من الأنونات المتطايرة، وهي شبيهة في تركيبها بالفلدسبار (حيث أنها يحتويان على نفس الذرات أو ذرات شبيهة). ففي الفلدسباتويدات تقل نسبة السيليكون والألومينيوم  $Si/(Si+Al)$  عن 0,750. وينطبق هذا التعريف على النيفيلين واللويسيت.

ويعتبر في العادة أن السوداليت والكانكرينيت والسكادوليت من الفلدسباتويدات. إلا أن هذه المعادن هي وحدها التي لها تركيب فراغي للألومينو سيليكات يحتوي على مثل هذه النسبة العالية للأنونات المتطايرة مثل  $Cl^-$ ،  $SO_4^{2-}$ ،  $CO_3^{2-}$ ،  $OH^-$  و  $H_2O$ . وهذه المعادن صفات كيميائية وتركيبية مختلفة تماما عن الصفات المميزة للفلدسبار أو للفلدسباتويد الحقيقية. وتكون بعض الملامح التركيبية لهذه المعادن قريبة من ملامح الزيوليت، إلا أنها ليست زيوليت حقيقية. تتميز تركيبات معادن مجموعة الكانكرينيت بتراكم حلقات ذات الأجزاء الستة في تتابع AB... ويؤدي هذا التراكم إلى ظهور قنوات كبيرة ومستمرة مكونة من حلقات ذات اثني عشر جزءا بأشكال رباعية متبادلة من الـ  $AlO_4$  و الـ  $SiO_4$ . وهذه أكبر القنوات المعروفة، حتى في الزيوليت. وتتكون تراكم الكاكرينيت أيضا من أقفصة صغيرة معروفة باسم الأقفصة E- في علم كيمياء الزيوليت. لمجموعة معادن السوداليت تشابه تركيبها كبير مع مجموعة معادن الكاكرينيت، ولكنها تحتوي على تراكم تراكمي ABC... يؤدي إلى تماثل مكعبي بدلا من التماثل السداسي للكاكرينيت. ينتج عن هذا التتابع زخرفة للمستوى C... وهذا يؤدي إلى شبكة فراغية لأقفاص كبيرة من النوع  $\beta$  في مجموعة معادن السوداليت. ولبعض المعادن الشبيهة بالكاكرينيت تراكم أكثر تعقيدا بها تراكم حلقات سداسية. ومثال هذه المعادن ولتتابعاتها التراكمية معدن الليوتيت (ABABAC...) والأفغانيت (ABABACAC...). ولبعض الزيوليت أيضا تراكم يعتمد على تراكم حلقات سداسية شبيهة بالتراكم السالف الذكر وأمثلة لذلك معادن الأوفروتيت (AAB...)، الأريونيت (AABAAC...)، الليفينيت (AABCCABBC...)، والشبازيت (AABBCC...). وتستخدم أيضا الأقفاص من طراز  $\epsilon$  و  $\beta$  لتكوين وحدات بنائية في تراكم الكثير من الزيوليت A والأونريتيت والفوجازيت.

وللعائلة المكونة من السوداليت والكانكرينيت والسكابوليت كيمياء خاصة حيث أنها المجموعة الوحيدة من معادن السيليكات الألومينية التي تحتوي أنيونات متطايرة كبيرة وبذلك فلها علاقة وثيقة بالزيوليت وليس بالفلدسباتويد الحقيقية. ولذلك يقترح اسم جديد لهذه المجموعة وهو الزيولويدات لأنها ليست فلدسباتويدات.



Feldspathoids are framework aluminosilicates which comprise at least three distinct groups: the leucite, nepheline-kalsilite and sodalite-cancrinite groups. Leucite group. All phases have the same... Cite this chapter as: Merlino S. (1984) Feldspathoids: Their Average and Real Structures. In: Brown W.L. (eds) Feldspars and Feldspathoids. NATO ASI Series (Series C: Mathematical and Physical Sciences), vol 137. Springer, Dordrecht.

feldspathoid The name for a group of framework silicate minerals which are similar to feldspars in their structure but contain less silica per formula unit. Source for information on feldspathoid: A Dictionary of Earth Sciences dictionary. The mineral analcime, although a zeolite, is closely related to the feldspathoids and often described with them. Minerals within the feldspathoid group crystallize from silica-deficient (silica undersaturated) melts and can occur instead of, or with, feldspar. A Dictionary of Earth Sciences. —. Hassan, I. (1997) Feldspathoids and their relationships to zeolites. Kuwait Journal of Science and Engineering, 24, 163–87. Haüy, R.J. (1797) Analcime. Hazen, R.M. and Finger, L.W. (1979) Polyhedral tilting: a common type of pure displacive phase transition and its relationship to analcite at high pressure. Phase Transitions, 1, 1–22. Heaney, P.J. and Veblen, D.R. (1990) A high-temperature study of the low-high leucite phase transition using the transmission electron microscope.