

ON THE CATION AND WATER POSITIONS IN FAUJASITE<sup>1</sup>WERNER H. BAUR<sup>2</sup>, *Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, New York.*

## ABSTRACT

The structure of faujasite has been refined using least squares applied to three-dimensional Weissenberg film data, and exchangeable cation and water positions determined using Fourier and difference syntheses. Faujasite has the most open silicate framework known. Approximately 40% of exchangeable cations occupy a position (occupancy 0.54) within the cubeoctahedral aluminosilicate cage, whereas 16% of the water molecules occupy one position within and one outside of the cage. The remaining cations and water molecules are randomly distributed through the aluminosilicate framework.

The zeolite mineral faujasite has the most open silicate framework known so far. This fact becomes clearer by comparing the calculated densities of the aluminosilicate framework of different zeolites, than by

TABLE 1. COMPARISON OF THE X-RAY DENSITIES OF SOME FRAMEWORK SILICATES

	Composition	Density (g. cm <sup>-3</sup> )			
		Overall	Water	Cation	Frame- work
faujasite	(Na <sub>2</sub> Ca) <sub>0.075</sub> (Al <sub>0.3</sub> Si <sub>0.7</sub> )O <sub>2</sub> · 1.37H <sub>2</sub> O	1.91	0.52	0.14	1.25
zeolite type A	Na <sub>12</sub> Al <sub>12</sub> Si <sub>12</sub> O <sub>24</sub> · 27H <sub>2</sub> O	1.97	0.44	0.25	1.28
chabasite	Ca <sub>2</sub> Al <sub>4</sub> Si <sub>8</sub> O <sub>24</sub> · 13H <sub>2</sub> O	2.09	0.48	0.16	1.45
natrolite	Na <sub>2</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> · 2H <sub>2</sub> O	2.25	0.21	0.27	1.77
bikitaite	LiAlSi <sub>3</sub> O <sub>6</sub> · H <sub>2</sub> O	2.28	0.20	0.08	2.00
sanidine	KAlSi <sub>3</sub> O <sub>8</sub>	2.56	—	0.36	2.20
quartz	SiO <sub>2</sub>	2.65	—	—	2.65
coesite	SiO <sub>2</sub>	2.91	—	—	2.91

comparing the densities of the whole crystals, which include the contribution of the water molecules and the exchangeable cations as well (Table 1). Less than one half of the volume of faujasite is occupied by the framework. The crystal structure determination of the naturally occurring mineral faujasite (Bergerhoff, *et al.*, 1956; Bergerhoff, *et al.*, 1958) and of the synthetic molecular sieve X (Broussard and Shoemaker, 1960) yielded practically identical results for the aluminosilicate framework, but are at variance with regard to the cation positions. Neither of the studies gave information on the locations of the water molecules. In order

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to resolve these questions the single crystal data of Bergerhoff *et al.* (1958) were refined further.

The 829  $F_{hkl}$  (Weissenberg, Cu-K $\alpha$ , photographic intensities measured by microphotometer, non-observed reflections inserted with  $\sqrt{\frac{1}{2}I_{\min} \cdot Lp^{-1}}$ ) were refined by the method of least squares. The weighting scheme of Hughes (1941) was applied throughout the calculations. Several Fourier and difference syntheses were computed in order to find the locations of the exchangeable cations and the water molecules. Refinement using isotropic temperature factors lowered  $R$  ( $\sum ||F_o| - |F_c|| / \sum |F_c|$ ) from 0.32 to 0.149. Further refinement employing anisotropic thermal parameters brought  $R$  to 0.133 (including unobserved reflections). The results

TABLE 2. PARAMETERS<sup>1</sup> FOR THE FAUJASITE STRUCTURE

$a = 24.74 \text{ \AA}$ , space group  $Fd3m$ , origin at center of symmetry, cell contents  
 $192 \times (\text{Na}_2\text{Ca})_{0.075}(\text{Al}_{0.3}\text{Si}_{0.7})\text{O}_2 \cdot 1.37\text{H}_2\text{O}$

Atom	Symmetry position	x	y	z	B( $\text{\AA}^2$ )	( $e \cdot \text{\AA}^{-3}$ )
(Si, Al)	192 (i) 1	0.12544 (6)	0.94655 (7)	0.03626 (6)	1.2 (1)	39
O <sub>1</sub>	96 (g) m	0.1742 (2)	0.1742 (2)	0.9680 (3)	2.8 (2)	16
O <sub>2</sub>	96 (g) m	0.1773 (2)	0.1773 (2)	0.3232 (3)	2.5 (2)	16
O <sub>3</sub>	96 (g) m	0.2527 (2)	0.2527 (2)	0.1435 (3)	2.5 (2)	15
O <sub>4</sub>	96 (h) 2	0.1053 (2)	0.8947 (2)	0.0	2.8 (2)	16
O <sub>w1</sub>	32 (e) 3m	0.1673 (3)	0.1673 (3)	0.1673 (3)	3.2 (3)	12
O <sub>w2</sub> × 0.333	32 (e) 3m	0.272 (1)	0.272 (1)	0.272 (1)	3.9 (9)	3
(Na, Ca) × 0.5	32 (e) 3m	0.0699 (3)	0.0699 (3)	0.0699 (3)	2.6 (3)	10

<sup>1</sup> Here and in Table 3 the estimated standard deviations, obtained from the least squares refinement, are given in parentheses following the value. They correspond to the last significant digits of these values.

are shown in Table 2. Except the atoms of the framework only three atomic positions could be located. Two of them are identical with the positions which were named "Alkali 1" and "Alkali 2" by Bergerhoff *et al.* (1958). The estimated standard deviation of  $\rho$  is  $0.8 e \cdot \text{\AA}^{-3}$ , therefore the highest peak in the last difference synthesis, which is only  $1.4 e \cdot \text{\AA}^{-3}$ , is not significant. There are a number of locations with electron densities around  $1.0 e \cdot \text{\AA}^{-3}$ . Some of them are arranged in such a way around the positions of (Si, Al) and O that they suggest residual electron densities due to anisotropic thermal motion of these atoms. However, these peaks remained in the difference syntheses even after the anisotropic refinement. They are believed to be caused by the Al/Si disorder in the structure. According to Smith and Bailey (1963) in three dimensional framework silicates the average distances (in tetrahedral coordina-

tion) are  $\text{Al}-\text{O}=1.75 \text{ \AA}$ ,  $\text{Si}-\text{O}=1.61 \text{ \AA}$ ; depending upon whether an Al or Si atom is in the center of the coordination tetrahedron, the oxygen atoms will occupy different positions. From the distribution of the residual electron densities it can be concluded that the  $\text{AlO}_4$ -tetrahedron is rotated and displaced slightly with respect to the  $\text{SiO}_4$  tetrahedron. The refined positions correspond to mean positions between these two extremes. The Al content of the crystal has been estimated in three ways: a) from the mean (Si, Al)-O distance of  $1.647 \text{ \AA}$  it is found to be about 26% (Smith and Bailey, 1963); b) from the variation of the cell constants with chemical composition this follows for  $a=24.74 \text{ \AA}$ , a value of 32%; c) upon variation of the form factor curve for (Si, Al) the best fit was found for 25% Al.

From the heights of the largest electron density maxima in the last difference synthesis it is estimated that no atomic positions, except those given in Table 2, can be occupied by more than one seventh of a water molecule (or by an even smaller fraction of a cation).

The structural unit of the faujasite structure is a cubeoctahedral aluminosilicate cage consisting of 24 (Si, Al) atoms and 36 oxygen atoms. The (Si, Al) positions of this sodalite unit (it was first observed in the crystal structure of sodalite) outline a cubeoctahedron. These sodalite cages are stacked in the faujasite structure in the same way as the carbon atoms in diamond: they are centered around symmetry position 8(a) and have the point symmetry  $\bar{4}3m$ . They are joined by the bridging oxygen atoms  $\text{O}_4$  which (together with two (Si, Al) $_6\text{O}_6$  faces of the cubeoctahedral cages) outline a hexagonal prism. This arrangement of sodalite units joined by the hexagonal prisms forms a very open framework with large cages in it. The large cages have a diameter of  $16.34 \text{ \AA}$  measured from center to center of two opposing oxygen atoms; they are interconnected by holes outlined by 12-membered (Si, Al) $_{12}\text{O}_{12}$  rings which measure  $10.12 \text{ \AA}$  across from center to center of the oxygen atoms. There are 8 sodalite cages, 8 large cages and 16 hexagonal prisms per unit cell. This open framework can accommodate up to 260 water molecules per unit cell and, varying with the Si:Al ratio, different amounts of exchangeable cations. For bond distances and angles see Table 3.

Figure 1 shows a cross section through a sodalite cage in faujasite. The cation position and the two water positions found in the course of this refinement are all connected with this cubeoctahedral cage.  $\text{O}_{w1}$  and the cation position are both arranged tetrahedrally inside the sodalite cage. The cation position is surrounded by a distorted octahedron of three  $\text{O}_1$  and three  $\text{O}_{w1}$ . The structure factor calculations were performed using a mixed form factor curve for the cation position:  $(2f_{\text{Na}} + f_{\text{Ca}}) \times 0.333$ , corresponding to the  $\text{Na}:\text{Ca}=2:1$  ratio in the chemical analysis of faujasite by Damour (1848). Assuming this ratio the occupancy of the cation position was refined and turned out to be 0.54, which means

that only every other cation position is occupied. Since no chemical analysis of the material used for collecting the intensity data is available, this number is subject to a large error. However, this half occupancy is reasonable when one considers that a likely hydrogen bonding scheme can be constructed only as long as there are not more than two cations

TABLE 3. INTERATOMIC DISTANCES (Å) AND BOND ANGLES (IN DEGREES) IN FAUJASITE.

(a) (Si, Al)O <sub>4</sub> tetrahedron			
(Si, Al)-O <sub>1</sub>	1.657 (3)	∠(Si, Al)-O <sub>1</sub> -(Si, Al)	140.6° (0.5°)
(Si, Al)-O <sub>2</sub>	1.642 (3)	∠(Si, Al)-O <sub>2</sub> -(Si, Al)	140.3° (0.5°)
(Si, Al)-O <sub>3</sub>	1.645 (3)	∠(Si, Al)-O <sub>3</sub> -(Si, Al)	145.1° (0.5°)
(Si, Al)-O <sub>4</sub>	1.643 (3)	∠(Si, Al)-O <sub>4</sub> -(Si, Al)	140.6° (0.5°)
Mean value:	1.647	Mean value:	141.6°
O <sub>1</sub> -O <sub>2</sub>	2.710 (8)	∠O <sub>1</sub> -(Si, Al)-O <sub>2</sub>	110.5° (0.4°)
O <sub>1</sub> -O <sub>3</sub>	2.666 (5)	∠O <sub>1</sub> -(Si, Al)-O <sub>3</sub>	107.7° (0.4°)
O <sub>1</sub> -O <sub>4</sub>	2.708 (7)	∠O <sub>1</sub> -(Si, Al)-O <sub>4</sub>	110.3° (0.3°)
O <sub>2</sub> -O <sub>3</sub>	2.687 (6)	∠O <sub>2</sub> -(Si, Al)-O <sub>3</sub>	109.7° (0.4°)
O <sub>2</sub> -O <sub>4</sub>	2.653 (4)	∠O <sub>2</sub> -(Si, Al)-O <sub>4</sub>	107.7° (0.3°)
O <sub>3</sub> -O <sub>4</sub>	2.710 (7)	∠O <sub>3</sub> -(Si, Al)-O <sub>4</sub>	111.0° (0.3°)
Mean value:	2.689	Mean value:	109.5°
(b) (Na, Ca) and O <sub>w</sub> coordination			
(Na, Ca)-O <sub>1</sub>	2.53 (1)		
(Na, Ca)-O <sub>w1</sub>	2.45 (1)	∠O <sub>w1</sub> -(Na, Ca)-O <sub>1</sub>	164.8° (0.7°)
O <sub>w1</sub> -O <sub>w1</sub>	2.96 (2)	∠O <sub>w1</sub> -(Na, Ca)-O <sub>w1</sub>	74.4° (0.6°)
O <sub>1</sub> -O <sub>1</sub>	3.77 (1)	∠O <sub>1</sub> -(Na, Ca)-O <sub>1</sub>	96.4° (0.4°)
O <sub>w1</sub> -O <sub>1</sub>	3.63 (1)	∠O <sub>w1</sub> -(Na, Ca)-O <sub>1</sub>	93.7° (0.5°)
O <sub>w1</sub> -O <sub>3</sub>	3.04 (1)	∠O <sub>w1</sub> -O <sub>w1</sub> -O <sub>3</sub>	110.7° (0.3°)
(Na, Ca)-(Na, Ca)	3.86 (2)		
O <sub>w2</sub> -O <sub>3</sub>	3.26 (4)		

per sodalite cage. Possible hydrogen bonds are O<sub>w1</sub>-O<sub>w1</sub>=2.96 Å and O<sub>w1</sub>-O<sub>3</sub>=3.04 Å, which enclose an angle of 110.7°. Six symmetrically equivalent angles of this kind are around each O<sub>w1</sub>. The one of these angles which is energetically most favorable (largest distances from the cations to the hydrogen atoms) will probably contain the hydrogen bonds. When there are three cations in the sodalite cage one of these hydrogen bonds would have to be in an edge common to two coordination octahedra: a most unlikely arrangement. Szymanski *et al.* (1960) report that the infrared spectrum of faujasite with a water content of

less than 15% of the saturation value (this means with less than 5 molecules  $\text{H}_2\text{O}$  per sodalite cage) exhibits bands at  $3550$  and between  $1700$  and  $1600\text{ cm}^{-1}$ ; they attribute them to OH groups. However, these bands are also typical of hydrogen bonded water: in  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  there are bands at  $3550$  and  $1650\text{ cm}^{-1}$  (Gamo, 1961). It is possible

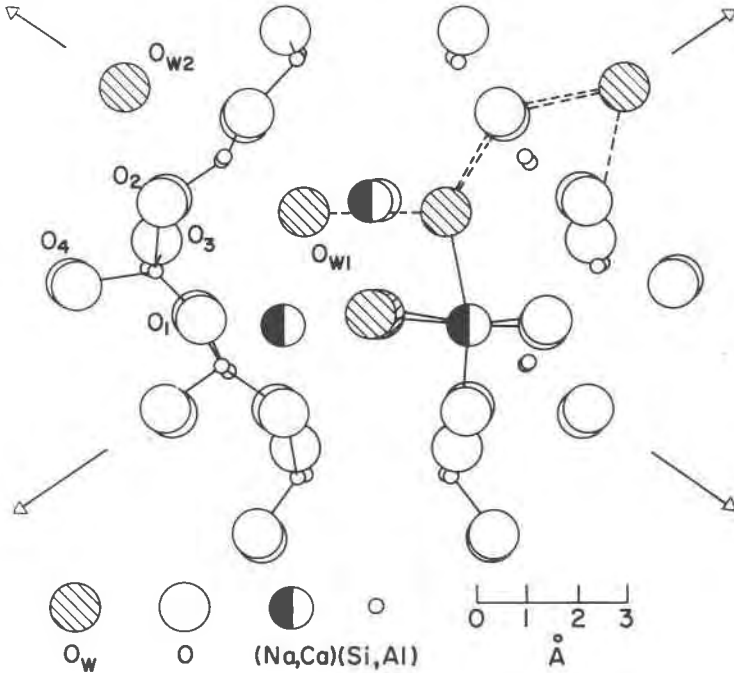


FIG. 1. View of part of a cubeoctahedral cage in faujasite. Only four of the eight  $(\text{Si}, \text{Al})_6\text{O}_6$  rings which are in one cubeoctahedral cage are shown. The plane of the paper corresponds to a mirror plane in the structure. Atoms which occur on both sides of the mirror plane are slightly displaced with respect to each other, in order to show them both. The directions of the 3-fold axes are indicated. A part of the bonding distances are drawn as solid lines. Some of the distances from the water oxygens to their nearest oxygen neighbours are shown by broken lines.

that in the partly dehydrated faujasite studied by Szymanski *et al.* (1960) the bands were caused by the hydrogen bonded water in the sodalite cages; at higher  $\text{H}_2\text{O}$  saturations they were covered by the spectrum of the other water molecules in the structure. The  $(\text{Si}, \text{Al})\text{-O}_1$  distance is significantly larger than the other three  $(\text{Si}, \text{Al})\text{-O}$  distances which are equal within the limits of error. This lengthening is probably caused by the fact that  $\text{O}_1$  is also coordinated to  $(\text{Na}, \text{Ca})$ . It is interesting to note that the position occupied in hydrated faujasite by the exchangeable

cation is next (at a distance of 3.0 Å) to the position 16(c) inside the hexagonal prism which is occupied by a calcium atom in dehydrated Ca-faujasite (Dodge, 1963). It seems that upon dehydration the cations migrate into this position since it is then the only one which provides a full coordination polyhedron for the cation. The same effect has been observed in chabazite (Smith, 1962; Smith, Rinaldi and Glasser, 1963).

The arrangement within the sodalite cage is well established; the position called  $O_{w2}$ , however, is by no means so certain since its electron density is rather low. Using the oxygen form factor curve the occupancy was calculated to be one third. Because of the large distance  $O_{w2}-O_3$  of 3.26 Å it is believed to be a water molecule.

The positions  $O_{w1}$  and  $O_{w2}$  are occupied by 43 water molecules out of 260; in the (Na, Ca) location are placed 17 out of approximately 43 Na and Ca per unit cell. Thus 84% of the water molecules and 60% of the cations which must be present in the structure are still not accounted for. Subtracting the 17 cations and 32 water molecules per unit cell which are in the sodalite cages there remain 28 to 29 water molecules and 3 to 4 cations per large cage to be accommodated. A little more than one water molecule is in location  $O_{w2}$  in the large cage. The smoothness of the last difference synthesis indicates that the remaining atoms do not occupy fixed positions or at least occupy them only statistically with very small occupancy factors. In fact there is overwhelming evidence from a number of different measurements which suggests that most of the water molecules and exchangeable cations in faujasite float freely through the aluminosilicate framework. Each large cage has a free volume of  $\sim 1000$  Å<sup>3</sup> for the 28 to 29 H<sub>2</sub>O and the 3 to 4 cations; in liquid water there are 33 H<sub>2</sub>O molecules per 1000 Å<sup>3</sup>. That the water molecules and cations in faujasite behave similarly to an electrolyte solution and are disordered and even highly mobile is illustrated by the following points:

- 1) The infrared spectrum of fully hydrated faujasite shows the stretch and deformation frequencies of H<sub>2</sub>O in the same positions as in liquid water (Szymanski *et al.*, 1960).
- 2) The heat of sorption of water in faujasite is comparable to the heat of vaporization of liquid water and of electrolyte solutions (Barrer and Bratt, 1959).
- 3) A self-diffusion experiment (Barrer *et al.*, 1956) with a Na-faujasite in NaCl solution marked with <sup>24</sup>Na showed that within 1 minute 50% of the sodium was exchanged (in analcite this takes 120 minutes).
- 4) The conductivity and the activation energy for cations in hydrated faujasite is essentially the same as for aqueous solutions of these cations (Freeman and Stamires, 1961).
- 5) Low angle x-ray scattering has been observed for faujasites and is interpreted as an effect of the cation disorder in the crystal (Howell, 1960).
- 6) Faujasite changes its cell constants upon exchange of cations very little (by 0.5), that indicates that there are no strong interactions between the framework and the cations (Barrer *et al.*, 1956). For comparison: the cell constants of analcite change by several per cent upon ion-exchange (Barrer *et al.* 1953).

All the above mentioned experiments have been performed on synthetic faujasites, so called X and Y zeolites. However, it seems safe to assume that natural faujasite has very similar properties since the structures are essentially the same, as could be verified by a re-evaluation of Broussard and Shoemaker's (1960) powder data. Broussard and Shoemaker assumed two different cation positions in their hydrated NaX sieve: Na<sub>1</sub> in the 16 fold position 0,0,0, inside the hexagonal prism, Na<sub>2</sub> in a 32 fold position with  $x=0.241$  (near the position called O<sub>w2</sub> in Table 2). A least square refinement of their model yielded  $R=0.40$  (for F<sup>2</sup> and including unobserved F<sub>0</sub><sup>2</sup> with zero) and gave unrealistic values for the temperature factors of the oxygens of the framework (B from  $-1.7$  to  $8.0 \text{ \AA}^2$ ). A refinement starting with the values of Table 2 gave  $R=0.37$  and oxygen temperature factors with B between  $2.7$  and  $4.3 \text{ \AA}^2$ . The best agreement ( $R=0.34$ ) was achieved on inclusion of both the Na positions of Broussard and Shoemaker and the cation position and O<sub>w1</sub> from this work. The occupancy factors of all these positions were varied (while the isotropic temperature factors were kept constant at  $B=3.0 \text{ \AA}^2$ ) and found to be between  $0.3$  and  $0.8$ , therefore, only 70% of the Na present in NaX is located.

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