

**725.** *Crystal Structures with a Chabazite Framework. Part V.\* Interpretation of Physicochemical Properties in Terms of the Crystal Structure.*

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The atomic positions obtained from studies of dehydrated-, hydrated-, and chlorinated-Ca-chabazites have been used to extend the interpretations of the physical properties put forward by Kington, Barrer, and others.

The most important conclusions are: (a) atoms of the framework move as much as 0.5 Å during sorption, changing the shape of the apertures greatly; (b) the cations lie in clusters of water molecules in the hydrated form, and during dehydration move to new positions to make contact with the oxygen atoms of the framework; (c) large univalent cations may occupy the eight-membered ring in the dehydrated form; (d) the initial high isosteric heat of sorption may result from linkage of the cations to the sorbed molecules; (e) the symmetry may be reduced from rhombohedral to (perhaps) triclinic in response to Si,Al ordering or as a result of packing requirements for sorbed molecules; (f) compositions of natural specimens tend to lie near one of the two compositions which would give an ordered Si,Al framework and a reasonable number of cations per cell.

Positions are suggested for univalent cations in dehydrated chabazite, and for various molecules sorbed into the cavities. Further crystal structure work is suggested.

WE here attempt to explain the physicochemical properties of chabazite in terms of the crystal structures of the dehydrated,<sup>1</sup> hydrated,<sup>2-3</sup> and chlorinated<sup>4</sup> varieties. Some of the interpretation is not new, for many Papers from Imperial College, London, have described data on chemical properties of chabazite together with interpretation in physicochemical terms. Thus, to some extent, this Paper reviews earlier data. However, when most of the work was carried out at Imperial College the only crystallographic data available for chabazite<sup>5</sup> suggested that it has the sodalite structure in which the channels are constricted by six-membered rings. The difficulties occurring in interpretation of sorption data were resolved with the independent discoveries by Dent Glasser and Smith<sup>6</sup> and Nowacki, Koyama, and Mladeck<sup>7</sup> that chabazite is not based on the sodalite framework, but has cavities separated by eight-membered rings. In addition, the earlier interpretations assumed that the framework and the cations did not change position during sorption while our results show that there are major shifts. In our interpretations, considerable use will be made of data for other zeolites; we hope that the conclusions will be applicable to the whole zeolite group of minerals, particularly to those with large apertures and cavities, which are of industrial value. Uncertainties have seriously hampered the interpretation of the electron density maps for hydrated and chlorinated chabazite, and further uncertainties will appear here. To resolve these problems, proposals for further structure determinations will be made.

*General Properties.*—A typical unit cell content of chabazite is  $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24}\cdot 13\text{H}_2\text{O}$ . Natural specimens usually contain small amounts of sodium and potassium, and 17 recent analyses taken at random yield an average of  $\text{Ca}_{1.53}\text{Na}_{0.54}\text{K}_{0.17}\text{Al}_{3.87}\text{Si}_{8.13}\text{O}_{24}\cdot 12.1\text{H}_2\text{O}$ . Although most specimens have an Si : Al ratio near 2, there are values as high as 3 and

\* Part IV, preceding Paper.

<sup>1</sup> Smith, *Acta Cryst.*, 1962, **15**, 835.

<sup>2</sup> Smith, Rinaldi, and Dent Glasser, *Acta Cryst.*, 1963, **16**, 45.

<sup>3</sup> Smith, Knowles, and Rinaldi, *Acta Cryst.*, 1964, **17**, 374.

<sup>4</sup> Fang and Smith, preceding Paper.

<sup>5</sup> Wyart, *Bull. Soc. franç. Minér. Crist.*, 1933, **56**, 106.

<sup>6</sup> Dent Glasser and Smith, *Nature*, 1958, **181**, 1794.

<sup>7</sup> Nowacki, Koyama, and Mladeck, *Experientia*, 1958, **14**, 396.

as low as 1.6. An earlier collection of analyses by Winchell<sup>8</sup> gave a spread from 3.0 to 1.6. Our chabazite (ref. 1, p. 836) is  $\text{Ca}_{1.8}(\text{Na} + \text{K})_{0.3}\text{Al}_{3.9}\text{Si}_{8.1}\text{O}_{24} \cdot x\text{H}_2\text{O}$  (with  $x$  between 12 and 15), while the ones principally used at Imperial College (Barrer and Sammon,<sup>9</sup> p. 2839; Barrer and Langley,<sup>10</sup> p. 3805) were  $\text{Ca}_{1.59}\text{Na}_{0.37}\text{Al}_{3.49}\text{Si}_{8.50}\text{O}_{24} \cdot 12.4\text{H}_2\text{O}$  and  $\text{Ca}_{1.49}\text{Na}_{0.58}\text{Al}_{3.43}\text{Si}_{8.56}\text{O}_{24} \cdot 11.6\text{H}_2\text{O}$ . Chabazites with a wide range of Si : Al ratios have been synthesized, ranging from 2.3 to 1.15 (Barrer and Baynham,<sup>11</sup> p. 2894). The Si : Al ratio is probably very important with respect to the arrangement of the silicon and aluminium atoms in the framework. For a 2 : 1 ratio it is possible to arrange the atoms in an ordered pattern<sup>4</sup> with 2Al and 4Si in each six-membered ring and with no oxygen atoms bonded to more than one aluminium. Several other ratios, e.g., 1 : 1 and 5 : 1 permit an ordered pattern. Of the natural specimens, there is a tendency for the compositions to lie near the 2 : 1 ratio and this may indicate that the crystals tend to form with an ordered pattern. On the other hand, it may arise from cation control (see later). The biaxial optical properties of many chabazites, and the X-ray data for the hydrated-Ca-chabazite used in this Series are most easily interpreted on the basis of an ordered Si,Al distribution<sup>2,3</sup> though this apparent low symmetry may arise merely from collapse and rotation of the framework to produce a configuration with lower bond energy. Thus feldspar frameworks collapse to give lower symmetry, and for anorthite Megaw, Kempster, and Radoslovich<sup>12</sup> have given a detailed interpretation of the structure on the basis of engineering principles for freely hinged frameworks. Through the kindness of Dr. L. C. V. Rees, I have received several specimens of the ion-exchanged chabazites used at Imperial College. All of them give sharp optical extinction with uniaxial properties. It is reasonable to suggest that the Si : Al ratio of 2.5 of the Imperial College material results in a disordered atomic pattern with the consequent uniaxial optical properties. A test of this idea can be made by determining both the optical properties and the chemical composition of a wide range of chabazites. Preliminary studies with an electron probe micro-analyser have shown that good accuracy (0.5% of total weight of sample) can be obtained for the elements Al, Si, K, Ca, and Fe, thus permitting both chemical analysis and optical study of the same crystal. Previous wet chemical analyses of chabazites may have suffered because of impurity in the chabazite; for example, intergrowths of gmelinite and chabazite occur<sup>13</sup> and complete reliance cannot be placed on the analyses in the literature. The different possible patterns of aluminium and silicon atoms in chabazite may have significant effects on the physical properties of sorbed molecules because of the consequent difference in the electric fields. The disordered pattern would lead to more symmetric fields because of the influence of neighbouring unit cells.

The dimensions of the unit cell change relatively little between the different modifications as shown in the Table. Considering the experimental error of 0.5–1.0% there is no detectable difference in  $a$ . The angle  $\alpha$  varies between the different forms. The dehydrated varieties have angles 2–3° smaller than the hydrated forms. Change of cation produces changes of about 0.5° in the hydrated variety. Replacement of the water with chlorine or iodine produces angle changes of about 1°, up for chlorine, and down for iodine. The smallness of the change in cell dimensions is deceptive, for X-ray analyses of the hydrated, dehydrated, and chlorinated forms show movements of 0.5 Å for oxygen atoms of the framework. Tied in with the framework changes are major shifts in the positions of the cations, so it is unwise to rely too much on dimensions obtained for hydrated zeolites when interpreting the sorption properties of zeolites. In addition

<sup>8</sup> Winchell, *Amer. Mineralogist*, 1925, **10**, 88.

<sup>9</sup> Barrer and Sammon, *J.*, 1955, 2838.

<sup>10</sup> Barrer and Langley, *J.*, 1958, 3804, 3811, 3817.

<sup>11</sup> Barrer and Baynham, *J.*, 1956, 2892.

<sup>12</sup> Megaw, Kempster, and Radoslovich, *Acta Cryst.*, 1962, **15**, 1017.

<sup>13</sup> Fischer and O'Daniel, *Naturwiss.*, 1956, **43**, 348.

Cell dimensions of chabazite.

Type	<i>a</i> (Å)	$\alpha$ (degrees)	Ref.
Hydrated Ca .....	9.45	94° 28'	1
Hydrated Ca .....	9.43	94° 27'	9
Hydrated Ca,Na .....	9.35	94° 37'	7
Hydrated Na .....	9.40	94° 6'	1
Hydrated Na .....	9.50	94° 3'	9
Hydrated Ag .....	9.45	94° 18'	2
Hydrated Ba .....	9.47	94° 3'	2
Dehydrated Ca .....	9.37	92° 01'	1
Dehydrated Ca,Na .....	9.30	91° 33'	14
Cl <sub>2</sub> -Ca (about 2 molecules) .....	9.41	95° 21'	1
Cl <sub>2</sub> -Ca (about 3 molecules) .....	9.36	95° 19'	4
I <sub>2</sub> -Ca,Na (2 molecules) .....	9.39	93° 19'	14
Estimated error .....	0.05 to 0.10	3' to 10'	

to the changes of shape of the apertures between the cavities, there might be changes in the positions of the cations which could block the apertures.

The general features of the structure are explained in detail in ref. 1. Briefly, sets of two six-membered rings of tetrahedra are linked to form di-trigonal prisms, which are themselves linked by four-membered rings in a pattern analogous to the close-packing of spheres. The resulting framework contains large, elliptical cavities entered by six windows formed from eight-membered rings. These cavities are 6—7 Å in diameter and about 10 Å in length. Sorption may take place in all three directions through the eight-membered rings whose apertures range in diameter from 3 to 4 Å depending on the type of chabazite. The aperture is almost circular for the hydrated and chlorinated forms, but is elliptical for the dehydrated variety.<sup>1,4</sup>

The properties of the zeolite depend markedly on the exchangeable cations. There must be twice as many univalent cations as bivalent ones to satisfy electrical neutrality, and the number of aluminium atoms must equal the sum of the univalent plus twice the bivalent cations if protons do not enter the structure. Nowaki, Koyama, and Mladeck<sup>7</sup> report a composition of (Na,K)<sub>0.4</sub>Ca<sub>1.65</sub>Al<sub>3.7</sub>Si<sub>8.3</sub>O<sub>12</sub>.11.67H<sub>2</sub>O.0.25NaOH for their specimen. Most chemical analyses show reasonable agreement between Al and (2Ca + Na + K), but it appears that account must be taken of the possible occurrence of cations deviating from the ideal formula. Hoss and Roy (ref. 15, p. 395) found deficiencies of cations when ion-exchange was carried out with the pH below 7. In addition, heating of NH<sub>4</sub>-exchanged zeolites can remove NH<sub>3</sub> thus reducing the large, exchangeable cations (of course, an equivalent number of protons are present). Similar H-zeolites can be formed by ion-exchange with a cation too large to enter the zeolite using a solution whose anion gives an insoluble precipitate with the cation in the zeolite (ref. 16, p. 103).

*The Dehydrated Structure.*—In ref. 1, it was found that in dehydrated Ca-chabazite a calcium atom occurred at the cell-origin for about two-thirds of the unit cells and thus at the centre of the di-trigonal prism, whereas about one-third of the six-membered rings had a calcium atom lying near their centres. Thus only two-thirds of the two calcium atoms per unit cell were accounted for. Some weak electron density peaks not significantly higher than the random error were consistent with the remaining calcium being distributed statistically over a 12-fold position near the internal surface of the cavity. Later experience with other forms of chabazite showed that estimates of the number of atoms per site were rather inaccurate, and that the above values might be under-estimates, so that all the calcium atoms might be at the centres of the prisms or the six-membered rings. However, if calcium atoms occurred in the same unit cell, both at the corners of the cell and at the centres of the six-membered rings, they would be rather close (2.7 Å) compared with the typical value of 3.3 Å found in silicates. Moreover, there would be

<sup>14</sup> Barrer and Wasilewski, *Trans. Faraday Soc.*, 1961, **57**, 1140, 1153.

<sup>15</sup> Hoss and Roy, *Heidelberger Beiträge zur Mineralogie*, 1960, **7**, 389.

<sup>16</sup> Barrer, *Proc. Chem. Soc.*, 1958, 99.

rather a high local charge concentration. Consequently the best explanation is to suppose that in two-thirds of the unit cells, one atom occurs at the centre of the di-trigonal prisms and one attached to the inside surface of the cavity, while in the other one-third there is an atom at the centre of each of the six-membered rings.

At the moment there is no structural datum on the positions of other cations in dehydrated chabazite. Two obvious factors may change the ion positions: exchange of one bivalent cation for two univalent ones, and substitution by a cation too large to enter the di-trigonal prisms. The site at the origin can only be entered through a six-membered ring whose "free" aperture is about 1.3 Å in radius. As will appear, the exchangeable cations will probably lie in a partial or complete sphere of hydration inside the large cavity, so only those cations which can pass through the six-membered ring can reach the site at the origin, unless the zeolite crystallizes directly with the cation inside the di-trigonal prism. Thus Cs<sup>+</sup> (radius 1.67 Å), Tl<sup>+</sup> (1.47 Å), Rb<sup>+</sup> (1.47), and perhaps Ba<sup>2+</sup> (1.34) and K (1.33) would encounter difficulty. The six-membered rings would be available for all cations, though the larger ones would have to lie displaced away from the ring towards the centre of the large cavity. In addition, there is the problem of placing atoms *both* at the origin and at the six-membered rings. Consequently it is suggested that the Ba<sup>2+</sup>-variety will have all its cations at the two six-membered rings, and that the Sr<sup>2+</sup>-form may have either the Ca- or the Ba-structure. For the Cs, Tl, and Rb varieties in which there will be four cations per cell (for Si : Al = 2), two may locate themselves at the six-membered rings while the other two may either attach themselves to the internal surface of the cavity or occupy the eight-membered rings which form the apertures between the cavities. In dehydrated Ca-chabazite the eight-membered rings are elliptical with a "free area" of 4.4 × 3.1 Å. Thus the larger ions (especially caesium) should be able to bond across the aperture giving reasonable interatomic distances even though the co-ordination number would be low. Occupancy of the apertures would have major effects on the sorption properties, thus permitting a test of this idea. As there are six apertures per cavity, each being shared between two cavities, three cations per unit cell could block all the apertures, while less than this number would not block all the apertures but would seriously hinder sorption.

Barrer and Baynham<sup>11</sup> summarized the earlier observations on the effect of cations on sorption, and have made many observations on chabazites with a wide range of cations and of Si : Al ratios. Unfortunately the interpretation was based on the incorrect sodalite structure, and although the general principles are correct, the details are wrong. They observed that K- and Rb-forms do not sorb oxygen at 90°K, whereas siliceous Li- and Na-chabazites readily do so. In their Fig. 2, it is shown that the sorptive capacity for oxygen, argon, and nitrogen falls off sharply for ion-exchanged Ca,Na-chabazites at a ratio which corresponds to 3 cations per cell (actually 0.4 Ca and 2.6 Na). In their Fig. 5 is shown the sorption of argon at 90°K in a series of Ca-chabazites with different Si : Al ratios. Curves 5 and 6 corresponding to 2.03 and 1.96 atoms per cell show over five times the sorptive capacity of curves 1—4 which correspond to values from 2.54 to 2.79 atoms per cell. For the Na-forms there is moderate sorption of argon when there are 3.92 and 4.06 atoms per cell, but the value drops greatly as the number of atoms goes up to 5.1. (Barrer and Baynham found that the method of exchange had a small effect on the sorptive capacity, and suggested that salt occlusion was occurring.) These observations can be explained (a) by placing many (perhaps all) of the potassium and rubidium atoms in the eight-membered rings; (b) by placing the first two sodium and calcium atoms in the six-rings or in the di-trigonal prisms, and subsequent ones in or near the eight-rings. Three atoms per cell correspond to one-third of the eight-rings being occupied. Thus the sharp reduction of sorption when there are more than three atoms per cell would correspond to sorption being hindered in two directions instead of only one when less than two atoms occur. Strong selectivity between oxygen and argon developed for some of the intermediate forms of chabazite. This might arise either from hindering by cation

sentinels (Barrer's term for blocking atoms) or possibly from change of shape of the apertures such that the large argon atom has difficulty in passing through whereas the smaller oxygen molecule can move freely. The entrance of some of the molecules into the zeolite might change the situation, for with Ca-Cl<sub>2</sub>-chabazite entrance of chlorine molecules changed the positions of the calcium atoms.<sup>4</sup> Thus selectivity could be a function of the amount and type of material previously sorbed (see later).

Cation blocking of sorption will only occur for atoms and molecules which do not interact significantly with the cations. Water molecules will link with the cations and move them into the cavities to begin the formation of spheres of hydration (see later). Barrer and Rees<sup>17</sup> and others have studied the effect of partial sorption of polar molecules in changing the sorption of additional non-polar molecules. All observations were made on Na,Ca-chabazites so it was not possible to test whether sentinels in the eight-membered rings could be moved by the polar molecules thus permitting sorption of non-polar molecules not able to enter the dehydrated zeolite. It would be interesting to extend these experiments to potassium, rubidium, and caesium varieties.

The thermal stability of chabazite will depend on the position of the cations in the dehydrated form, for the water molecules are removed before the aluminosilicate framework breaks down. Barrer and Langley (ref. 10 p. 3810) found from differential thermal analysis that the breakdown of the framework for the univalent cationic forms lithium, sodium, potassium, rubidium, and caesium is postponed to successively higher temperatures as the cation increases in radius (there were 3.0 univalent cations per cell in their specimen). This sequence might be related to the increasing ease for which suitable sites can be found for the ions. Thus caesium will fit better than rubidium or potassium in the eight-membered rings. It will be difficult for the three lithium atoms to find suitable sites because of the small radius. However there will be a tendency for the larger cations, because of the lower polarizing effect, to exert a lower destructive force in the framework no matter where they are placed, so the evidence from thermal stability cannot be taken as a confirmation of occupancy of the eight-membered rings by the larger cations. Moreover, the nature of the breakdown products and the kinetic features of the reaction have important effects. Barrer and Langley also studied a series of chabazites with different Al : Si ratios and with different cations, and state that the more aluminous the specimen, and hence the more cations in the cell, the lower the breakdown temperature. However, examination of their Figs. 1—4 shows only moderate justification of this generalization; indeed for calcium the most siliceous specimen with less than 2 atoms per cell breaks down at a lower temperature than more aluminous specimens with between 2 and 2.8 atoms per cell.

Howell,<sup>18</sup> extending the work of Reed and Breck,<sup>19</sup> showed from powder data that in anhydrous Na-type A zeolite the 12 sodium atoms per pseudo-cell are distributed with 8 near the centres of the six-membered rings and 4 arranged statistically near the centres of the eight-membered rings (best agreement is obtained for displacements from the centres of the rings, but the actual positions are somewhat uncertain). No datum has appeared for any other dehydrated molecular sieves. By analogy with Howell's result it might be deduced that for a chabazite with 4 sodium atoms per cell, 2 will go into the six-membered rings and 2 into the eight-membered rings. The effect of cation position on adsorption is clearly shown in the type A zeolite, for study by Breck, Eversole, Milton, Reed, and Thomas<sup>20</sup> of Na,Ca exchanged forms shows that there is a major change of sorption when the 12 sodium atoms are changed to 8Na + 2Ca. It is at this ratio that some of the eight-membered rings become unblocked. For faujasite it may be expected that the sodium and calcium atoms will prefer to go into the six-membered rings. This

<sup>17</sup> Barrer and Rees, *Trans. Faraday Soc.*, 1954, **50**, 852, 989.

<sup>18</sup> Howell, *Acta Cryst.*, 1960, **13**, 737.

<sup>19</sup> Reed and Breck, *J. Amer. Chem. Soc.*, 1956, **78**, 5972.

<sup>20</sup> Breck, Eversole, Milton, Reed, and Thomas, *J. Amer. Chem. Soc.*, 1956, **82**, 1041.

would explain why the cubo-octahedral cages are not accessible to molecules, except perhaps for water which might displace the cations into the cavities to form spheres of hydration (ref. 21, p. 1112).

We conclude that X-ray analysis of a chabazite containing large cations such as rubidium or caesium would be valuable in confirming the suggestion that the eight-membered rings are occupied. In addition a study of the Na-form would be of special interest because the eight-membered rings are small for the sodium ion and it is difficult to find four other sites per cell unless positions near the inside surface of the cavity are occupied: moreover, a comparison could be made with the results for the type A zeolite. However, because of the small electron density of Na, and the possibility of statistical occupancy of sites, such an analysis would require a rather detailed collection of intensities and probably a lengthy structure analysis.

*The Hydrated Structure.*—The most important feature of the hydrated chabazite structure is the relation between the exchangeable cations and the water molecules. W. H. Taylor<sup>22</sup> suggested that in the fibrous zeolites the water molecules are grouped around the cation. Recent structural studies of zeolites have shown that the water molecules indeed do cluster around the cation. Where the cavity is small as in Na-analcime,<sup>23</sup> the cation is in contact with only 2 water molecules but as the cavities grow larger, the cation becomes surrounded by water molecules. Thus in brewsterite,<sup>24</sup> the strontium atom has 5 near water molecules and 4 more distant oxygen atoms as neighbours, while in chabazite the best interpretation of the data<sup>3</sup> is that the 5 nearest neighbours of each calcium atom are water molecules. Other structures in which the cations are linked to the water molecules are gismondine,<sup>25</sup> harmotome,<sup>26</sup> natrolite,<sup>27</sup> and phillipsite.<sup>28</sup> Structure determinations of other zeolites have not yet passed the stage of locating the framework atoms. The X-ray determination of the relation between the water and the exchangeable cations is confirmed by the colours of Co-, Ni-, and Cu-faujasites (ref. 29, p. 134). Thus the hydrated Co-, Ni-, and Cu-forms are, respectively, pink, green, and blue in conformity with the colours of solutions containing these ions. The Co-faujasite is particularly interesting for it is blue when anhydrous, and slowly changes to pink as the water content passes 4 molecules per cation.

Other physical properties of zeolites are consistent with contact between the exchangeable cations and the water molecules. Barrer and Langley (ref. 10, p. 3811) found that the larger the cation in the series lithium, sodium, potassium, rubidium, caesium, the lower tends to be the temperature at which substantially all the water is lost. The bivalent cations show a greater retentivity than univalent ions of comparable size. These results can be interpreted in terms of interaction between the cations and the water dipoles, but could also be explained by linkage with the  $\text{AlO}_4$  tetrahedra as proposed by Ducros.<sup>30</sup> Peria<sup>31</sup> found that the activation energies for conductivity of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  in type A zeolites are 0.50 and 1.19 eV which are approximately in the ratio 1 : 2.

The nuclear magnetic resonance and dielectric relaxation studies of the protons in zeolites carried out by Ducros<sup>30</sup> have provided important information on the nature of the water molecules. For chabazite, the nuclear magnetic resonance (n.m.r.) data are interpreted as resulting from interchange about  $10^7$  times per second of water molecules between all the possible sites, each of which is subject to an overall anisotropic electric

<sup>21</sup> Barrer, Bultitude, and Sutherland, *Trans. Faraday Soc.*, 1957, **53**, 1111.

<sup>22</sup> Taylor, *Proc. Roy. Soc.*, 1934, *A*, **145**, 80.

<sup>23</sup> Taylor, *Z. Krist.*, 1930, **74**, 1.

<sup>24</sup> Perrotta and Smith, *Acta Cryst.*, 1964, **17**, 857.

<sup>25</sup> Fischer, *Amer. Mineralogist*, 1963, **48**, 664.

<sup>26</sup> Sadanaga, Marumo, and Takéuchi, *Acta Cryst.*, 1961, **14**, 1153.

<sup>27</sup> Meier, *Z. Krist.*, 1960, **113**, 430.

<sup>28</sup> Steinfink, *Acta Cryst.*, 1962, **15**, 644.

<sup>29</sup> Barrer and Bratt, *J. Phys. Chem. Solids*, 1959, **12**, 130, 146, 154.

<sup>30</sup> Ducros, *Bull. Soc. Franç. Minér. Crist.*, 1960, **83**, 85.

<sup>31</sup> Peria, *Bull. Amer. Phys. Soc.*, 1958, **3**, 230.

field. The transit time is small compared with the residence time and the probability of occupation of the sites of the same type is the same. He similarly describes the properties of the cations and, like Barrer and Bratt,<sup>29</sup> compares the contents of a cavity to that of a concentrated electrolyte. Petch and Bennington<sup>32</sup> have obtained very interesting results by resonance study of the quadrupole moments of aluminium and sodium nuclei in a single crystal of natrolite. It is to be hoped that they will be able to apply this powerful technique to zeolites in which the sodium atoms and water molecules are less firmly bound than in natrolite. Ducros<sup>30</sup> found that n.m.r. studies of protons in faujasite and type A gave only a single sharp line instead of the doublet found in chabazite. Thus the water in the larger cavities gives the same pattern as for the isolated liquid. Although it seems reasonable to suppose that the water molecules near the surfaces of the cavities occupy definite lattice sites, it is questionable whether the ones near the centres of the cavity do so. In addition, it is interesting to speculate on the positions of the cations in these zeolites with large cavities. Analogy with the other zeolites suggests that the cations become surrounded by water molecules, thus requiring a uniform distribution of cations throughout the water molecules. However, in faujasite this would separate the exchangeable cations by long distances from the aluminium ions to which they are electrostatically joined. Possibly a compromise occurs in which cations do bond to the water molecules, but tend to occupy the periphery of the cavities. Unfortunately the largest crystals of Linde A so far reported are 25 microns across, which is rather small for single crystal work. Elegant X-ray studies on powders by Broussard and Shoemaker<sup>33</sup> unfortunately fell short of revealing the positions of the water molecules. They report that Na atoms occur near the six-membered rings, but in view of the similar electron densities for sodium and water, this identification of the observed peak cannot be certain. Similarly the identification of peaks near six-membered rings in the 13X (faujasite-type) molecule sieve is also open to question. Similar positions in Ca-chabazite for which cations and water molecules can be distinguished, are occupied by water molecules. The distances from the peaks to the nearest oxygen atoms in 13X range from 2.7 to 3.7 Å, which are more suitable for a water molecule than an Na ion. However in the 4A and 5A sieves the environment of three oxygen atoms at 2.3<sub>5</sub> and three more at 2.9 Å is more reasonable for a sodium ion than a water molecule, unless very strong hydrogen bonding takes place. Just as for chabazite, it would be of considerable interest to determine positions of cations and water molecules, using cations whose electron density can be distinguished readily from that of water molecules.

Barrer and Sammon<sup>9</sup> have studied the exchange equilibria between aqueous solutions and crystals of chabazite for various ion pairs. Continuous series of solid solutions were obtained, but two of the exchanges indicated preferred intermediate compositions. Thus for  $2\text{Na}^+ \rightleftharpoons \text{Ca}^{2+}$  the equilibrium favours enrichment of the crystal in calcium at the expense of sodium so long as the Na content is above one-quarter; thereafter the situation is reversed. Thus there seems to be a favoured composition. The particular zeolite used by Barrer and Sammon has 1.77 calcium atoms or 3.55 sodium atoms for each 12 oxygen atoms, and three-quarters exchange corresponds to 0.9 calcium and 1.3 sodium atoms for a total of 2.2 per cell. For the  $\text{Na}^+, \text{Cs}^+$  exchange only one-third to three-quarters of the  $\text{Na}^+$  could be exchanged by  $\text{Cs}^+$  in reasonable times, suggesting that about two-thirds of the Na differs in ease of replacement from the other one-third. Unfortunately the favoured composition does not correspond to a whole number of atoms per cell, thus making impossible a simple explanation in terms of filling of sites. The value of 2.2 is only a little greater than the number of sites for calcium atoms in hydrated chabazite.<sup>3</sup> Perhaps after exchange with sodium has filled all these sites (only 1.77 out of 2.0 are occupied for the pure calcium form), a few sodium atoms can go into other sites (possibly near the six-membered rings) but then an electrostatic mis-balance builds up which can

<sup>32</sup> Petch and Pennington, *J. Chem. Phys.*, 1962, **36**, 1216.

<sup>33</sup> Broussard and Shoemaker, *J. Amer. Chem. Soc.*, 1960, **82**, 1041.

only be relieved by occupation of a completely new set of sites. To test this idea it would be interesting to ion-exchange a single crystal while attached to a counter diffractometer and monitor several critical reflections as ion-exchange proceeded. Ames<sup>33a</sup> has examined the cation sieve properties of chabazite and other zeolites. He concluded that the exchange depended on the relation between the cation and the structural water, but that a detailed understanding could come only from a determination by other techniques of the steric relations between the cations and water molecules.

Many data have accumulated on the relation between the water content and type of exchangeable cation. Barrer and Langley (ref. 10, p. 3820) found that for a natural chabazite the number of water molecules per unit cell decreased with increasing cation radius, and that for bivalent cations there were 1—2 more water molecules per cell for a bivalent than for a univalent cation with the same radius. In addition, for synthetic chabazites, the aluminous varieties in general contained fewer molecules than the more siliceous types. These results would be expected on simple packing considerations, though Barrer and Langley, from a detailed analysis, show that the affinity of the ions for the water molecules also is important. Hoss and Roy,<sup>15</sup> in contradiction to Barrer and Langley, did not find that the bivalent cationic forms contained more water than the univalent cationic types. Determination of water content of zeolites is very difficult because of the tenacity with which the last water molecules are held, and because the necessary use of high temperatures can volatilize the alkali atoms thus leading to possible excessive estimates of the water content. Such alkali losses for feldspars and feldspathoids have been clearly shown by following the change of X-ray output as the electron beam heated the sample in an electron probe microanalyser.<sup>34</sup> Water contents reported in chemical analyses of natural zeolites average about 12·5 molecules per cell in reasonable agreement with the value of 13 determined from the structure analysis of Ca-chabazite. It is not possible to determine with certainty whether the low observed value results from only partial occupancy of sites by water molecules or from chemical error, but the loose bonding of the three water molecules at the centres of the eight-membered rings<sup>2,3</sup> might permit only partial occupancy at these sites.

Barrer and Langley<sup>10</sup> found that the integral heats associated with weight loss do not depend in a simple way on the cation radius or on the number of cations per unit cell, and suggest that the cation positions are different for the different exchanged forms, and may also change during dehydration. This conclusion is very reasonable, for packing considerations show the difficulty of placing all the univalent cations inside clusters of water molecules. The best that could happen is that some of the neighbours will be water molecules and some will be oxygen atoms of the framework. Studies of Na-chabazite<sup>1</sup> were inconclusive and complete delineation of the structure will be difficult because of the low electron density of Na. Although the Na-form is of the most interest after the Ca-form because of the geological implications, it seems that the Rb-, Cs-, or K-varieties should be studied first because of the easier technical problems posed by the heavier cations.

Barrer and Langley, Hoss and Roy, and other investigators have found that chabazite loses water continuously with temperature. Nevertheless, it seems likely that water is lost at different rates from the four different types of sites, and that the cations rearrange themselves at various stages of the dehydration. X-Ray study of a partially dehydrated variety would be of interest.

*Sorption.*—The influence on sorption of the size of the aperture, and the effect of sentinels, is quite obvious, though the details are quite complex. Thus, as the molecule increases in size there is a wide range (about 1 Å in diameter) between those which pass freely to those that are excluded. Kington and Laing<sup>34</sup> discussed in detail the sorption of

<sup>33a</sup> Ames, *Amer. Mineralogist*, 1961, **46**, 1120.

<sup>34</sup> Kington and Laing, *Trans. Faraday Soc.*, 1955, **51**, 287.



molecules through apertures; although the calculations of the energy barrier as a function of the aperture size were very valuable, the application failed because they were based on the six-membered rings of the incorrect structure of chabazite. With the new structure having wider eight-membered rings, excellent agreement was obtained between the observed and calculated sorption data.<sup>6,35</sup> In the section on the dehydrated structure, the role of the univalent cations in the eight-membered rings as possible sentinels to non-polar molecules was described, and it was mentioned that a highly polar molecule like water would be able to link up to the cation and move it away, thus freeing the aperture.

The interaction between cations and non-polar molecules must be less than with water. Nevertheless for Ca-Cl<sub>2</sub>-chabazite<sup>4</sup> the calcium atoms are drawn away from the centres of the six-membered rings to make contact with the chlorine molecules. Presumably, weak bonds are being formed as a result of polarization of the chlorine atoms. Consequently it is suggested that calculations of sorption energy of molecules should consider the effect of cation-molecule interactions and of the related change in the configuration of the aluminosilicate framework.

Careful calorimetric measurements of the isosteric heat of sorption of various molecules in chabazite, type A, and faujasite<sup>20,34-38</sup> have shown that the initial heats are high, but drop steeply to minimum values after the sorption of about one-quarter of the molecules. With continued sorption there is a small rise, followed by a drop to the latent heat of condensation as molecules begin to condense on external surfaces of the zeolite. The large initial heat of sorption has been interpreted as the result of an energy heterogeneity of sites such that the first molecules occupy the more energetic ones. Barrer and Wasilewski (ref. 14, p. 1144) conclude that the heterogeneity of the sorption energy increases with the polarizability of the molecule, its dipole moment of quadrupole moment, and also with the polarizing power of the cation. It is tempting to correlate the sites of high energy with the positions of the silicon and aluminium atoms in the framework: however, in view of the contact of the calcium atoms and chlorine molecules described in ref. 4, and the correlation with the polarizing power of the cation, it is more likely that the initial heterogeneity arises from interaction between the molecules and the exchangeable cations (ref. 14, p. 1148). The small increase of sorption energy for medium to high concentrations has been interpreted as the result of interactions between the molecules as several molecules begin to form clusters in the cavities. Kington<sup>38</sup> showed that the amount of this increase does indeed depend on the quadrupole moment of the molecules, in agreement with this suggestion. Moreover, calculations of the magnitude of the effect agree with observed values. A very valuable experiment would be the determination of the structure of chabazite loaded with measured numbers of molecules per cavity. It would then be possible to relate the varying heats of sorption to the observed positions of the molecules, cations, and framework. An apparatus to permit controlled sorption of a single crystal mounted on a counter diffractometer is being designed; if it is successful, the chabazite-iodine complex appears to be the most obvious material to be tackled first, for Barrer and Wasilewski have determined the isosteric heat of sorption, and the heavy iodine atoms should be easily located by X-ray diffraction.

It is interesting to speculate on the position of molecules in chabazite. Kington and MacLeod<sup>35</sup> report that the following numbers of atoms or molecules can enter one cavity (or one unit cell) of chabazite: 5.9 atoms of argon, 6.3 molecules of oxygen, 5.4 of nitrogen, 5.7 of carbon monoxide, and 4.3 of carbon dioxide. Barrer and Wasilewski<sup>14</sup> report sorption of 2 molecules of iodine per cavity. If the molecules obey the symmetry





<sup>35</sup> Kington and MacLeod, *Trans. Faraday Soc.*, 1959, **55**, 1799.

<sup>36</sup> Garden, Kington, and Laing, *Trans. Faraday Soc.*, 1955, **51**, 1558.

<sup>37</sup> Kington, *Trans. Faraday Soc.*, 1956, **52**, 475.

<sup>38</sup> Kington, Proc. Tenth Symposium of the Colston Research Society. Butterworths Scientific Publications, London, 1958, p. 59.

of  $R\bar{3}m$ , there are definite restrictions on the positions and orientations of the sorbed molecules. With the nomenclature of International Tables for X-ray Crystallography, the possible positions in  $R\bar{3}m$  are:

1	<i>a</i>	$\bar{3}m$	0	0	0	(centre of di-trigonal prism)
1	<i>b</i>	$\bar{3}m$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	(centre of cavity)
2	<i>c</i>	$3m$	$\pm x$	<i>x</i>	<i>x</i>	(on body diagonal)
3	<i>e</i>	$2/m$	0	$\frac{1}{2}$	$\frac{1}{2}$	(centre of eight-membered rings)
6	<i>f</i>	2	$\pm x$	<i>x</i>	0	
6	<i>g</i>	2	$\pm x$	<i>x</i>	$\frac{1}{2}$	
6	<i>h</i>	<i>m</i>	$\pm x$	<i>x</i>	<i>z</i>	
12	<i>i</i>	<i>l</i>	$\pm x$	<i>y</i>	<i>z</i>	

The six chlorine peaks<sup>4</sup> were consistent with occupancy of position *h*, though the orientation of the molecules could not be determined. It seemed likely that the actual symmetry was lower than  $R\bar{3}m$  and that the observed peaks were the result of averaging of several peaks from a space group with lower symmetry (perhaps triclinic). Such lower symmetry might result from Si : Al ordering, but could just as well arise from difficulties of packing the large ellipsoidal chlorine molecules into a cavity of rhombohedral symmetry. The ease with which aluminosilicate frameworks can twist into new configurations to satisfy the co-ordination requirements of the interstitial cations is now well documented, and movement of the chabazite framework to accommodate adsorbed molecules might be expected. We suggest the rule: the chabazite framework will tend to the highest geometrical symmetry consistent with the packing requirements of the exchangeable cations and adsorbed molecules. For the spherical atom argon, packing requirements are not so severe as for the larger ellipsoidal chlorine molecules, and it seems reasonable that the 6 argon atoms enter similar positions to those occupied by chlorine and distort the aluminosilicate framework less. This 6-fold position which yields molecules at the corners of a distorted octahedron (actually trigonal antiprism) is very suitable for medium-sized molecules for it permits distances of 3–4 Å between the molecules and the framework oxygen atoms. It is quite likely that the 5.4 molecules of nitrogen and the 5.7 molecules of carbon monoxide also enter this position (some adjustment of the variable parameters *x* and *z* can be expected). There are too many oxygen molecules (6.3) to enter just this position. Perhaps six of the molecules go into the trigonal antiprism while the remainder go into the centre of the prism (*i.e.*, at the centre of the unit cell). It seems certain that the two iodine molecules per cell cannot occupy positions satisfying  $R\bar{3}m$  unless they rotate, or occupy positions on a statistical basis. The only position that would permit oriented molecules obeying  $R\bar{3}m$  would be along the body diagonal in position (*c*), but the iodine molecules are probably too long to fit in these positions as the I–I distance in a molecule is 2.67 Å and the I–O distance should be not less than 3.5 Å. The best fit of the iodine molecules occurs when they lie at an angle to the body diagonal with the two iodine atoms in contact with oxygen atoms of the framework. Such a placement reduces the symmetry to triclinic unless the iodine molecules are disordered.

Kington and MacLeod<sup>35</sup> gave a diagram showing six molecules lying at the corners of a trigonal prism but this violates the symmetry of  $R\bar{3}m$  and does not give as neat a packing as the trigonal antiprism.

From measurement of the sorption properties and calculation of various models, Kington and Barrer concluded that the molecules tend towards a definite orientation in which they “stick” to the oxygen atoms of the walls of the cavities. This seems very reasonable from crystal-chemical considerations, but it is hoped that it will be possible actually to locate by X-ray diffraction both atoms of diatomic molecules so that this can be tested. Unfortunately the studies of Ca-Cl<sub>2</sub>-chabazite,<sup>4</sup> although suggesting some orientation of the molecules, did not yield an unambiguous interpretation. Use of molecules as bromine and iodine (whose greater electron density would ease analysis) and dihalogenoethane (whose greater halogen separation should give well separated halogen

peaks) appear to offer more prospect of success than a more detailed analysis of the Ca-Cl<sub>2</sub>-chabazite. From these proposed studies it may be possible to return to Ca-Cl<sub>2</sub>-chabazite, and complete the reconnaissance.

*Geological Factors.*—A major question concerning the natural occurrence of zeolites deals with the problem of why zeolites prefer certain cations to others. In those zeolites with small cavities in the aluminosilicate framework the co-ordination requirements are quite strict and it is reasonably easy to see, for example, why natrolite with its ordered Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub> framework shows essentially no variation from complete occupancy of the two cation sites by sodium. However in a zeolite with large cavities, such as chabazite, the spatial restrictions are relatively lax and considerable variation of composition can be expected, and does occur. Nevertheless, even with such zeolites there is a definite tendency for a particular composition range to occur. One problem in identification of the factors which control composition of natural zeolites is that ion-exchange may change it after formation. Another is that many zeolites are formed at 100—300° under considerable hydrostatic pressure, and nearly all experimental observations of zeolites are made under pressures of one atmosphere or less. Perhaps the dehydrated structure is nearer to that pertaining at the time of growth than the hydrated structure, for at relatively high temperatures the water content may be low. Moreover there are geochemical factors to be considered such as the actual availabilities of the exchangeable cations. Thus strontium and barium are relatively rare, while sodium, calcium, and potassium are abundant. The availabilities will differ for the various rock types in which zeolites occur. In addition, there is competition for ions between the different minerals which cannot be evaluated without detailed measurements. Furthermore, the occurrence of many zeolites may be governed by rate factors rather than by equilibrium relations. Clearly any attempts to relate observed compositions with crystal structure data must be made cautiously.

The dominant cations found in natural zeolites are the small sodium and calcium ions. Let us assume that only calcium and sodium ions are available. In both the hydrated and dehydrated forms of chabazite there are not more than two suitable sites for these small exchangeable cations. In the hydrated form there is only room to form two clusters of water molecules around the cations. Other positions, such as the centres of the six-membered rings, are possible but do not permit linkage to water molecules in the same way as the positions actually found for hydrated Ca-chabazite. For the dehydrated form, it is difficult to place more than two small cations in the unit cell because the eight-membered rings are too large.

The actual number of the sodium, potassium, and calcium atoms in the two sites must be related to the Al:Si ratio by the charge relation  $(\text{Na} + \text{K}) + 2\text{Ca} = \text{Al}$ . The most likely control of the Si:Al ratio would be ordering in the tetrahedral sites. If only simple patterns are considered for chabazite, ratios of 1:1, 2:1, and 5:1 are the most reasonable. The three values require, respectively, 3Ca or 6(Na,K), 2Ca or 4(Na,K), and 1Ca or 2(Na,K). The first is incompatible with the requirement of two cation sites while the other two are consistent, yielding ideal compositions, respectively, of Ca<sub>2</sub>Al<sub>4</sub>Si<sub>8</sub>O<sub>24</sub> and Na<sub>2</sub>Al<sub>2</sub>Si<sub>10</sub>O<sub>24</sub>. There are no particular reasons for preferring one to the other. The actual observed compositions are variable with an average near Ca<sub>1.53</sub>Na<sub>0.54</sub>K<sub>0.17</sub>Al<sub>3.87</sub>Si<sub>8.13</sub>O<sub>24</sub>·12·1H<sub>2</sub>O (see earlier). Thus there is an excess of silicon over the 2:1 ratio and an excess of cations over the value of 2. The excess of cations over 2 could be explained by ion exchange of Ca→2Na,K subsequent to formation, but the Si:Al ratio must have been determined at the time of growth because of the difficulty of moving Si,Al atoms in framework silicates. It is clear that the composition of a zeolite like chabazite although in moderate agreement with one of the theoretical possibilities cannot be interpreted in detail. Readers are referred to the extensive series of Papers by Barrer, Kington, and their associates for detailed calculations (using a statistical thermodynamic approach) of zeolite properties.

3770 *Davis and Mann: The Synthesis and Stereochemistry of*

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