### 294. *Some Properties of, and a Structural Scheme for, the Harmotome Zeolites.*

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An account is given of dehydration, sorption, and $X$-ray diffraction for several closely-related synthetic aluminosilicates belonging to the harmotome–phillipsite group of zeolites. A structure is proposed for a cubic variety of the synthetic phases, and the relations between this structure and orthorhombic or monoclinic unit cells of harmotome and phillipsite are indicated. The aluminosilicate framework of the cubic structure is formed by placing cubic structural units at each corner and at the centre of each unit cell. These cubic units, which occur also in Linde Sieve A,[1] are formed by union by oxygen bridges of two rings of four $SiO_4$ or $AlO_4$ tetrahedra, giving a cluster of eight such tetrahedra. Each cubic unit is then joined by single oxygen bridges to eight similar units, and thereby a system of intersecting channels with eight-membered rings as "windows" is produced.

HARMOTOME, phillipsite, and wellsite are three closely related natural zeolites, harmotome and phillipsite being of fairly widespread occurrence whereas wellsite is rare. Several synthetic minerals have been observed in the calcium, barium, potassium, and sodium aluminosilicate crystallisation fields which bear marked similarities to these natural minerals.[2-5] A structure is now proposed for a synthetic cubic form of the sodium minerals referred to as Species Na-$P$ in an earlier paper.[2] This structure, with slight modifications, could also fit the symmetry of tetragonal and orthorhombic sodium forms and, although they differ greatly in symmetry from the cubic mineral, it is shown that the natural minerals may have a closely similar aluminosilicate framework. Dehydration, sorption, and ion exchange were also investigated for the synthetic sodium minerals.

### EXPERIMENTAL

The method of mineral synthesis has been described.[2] $X$-Ray powder data were obtained with a 9 cm. Debye–Scherrer camera and a Guinier camera, and single-crystal diffraction patterns for natural harmotome were obtained with a Weissenberg camera and a Unicam single-crystal goniometer. Cu-$K_\alpha$ radiation was used throughout. Dehydration was studied thermogravimetrically by heating to constant weight in a furnace a known weight of the zeolite contained in a Morgan ARR alumina crucible, which was suspended from one of the pans of a modified beam balance by a platinum wire. The standard gas volumetric method was used in sorption work.

Finally, ion-exchanged forms of several of the species, natural or synthetic, were prepared by heating the mineral in sealed Pyrex tubes with the appropriate chlorides in aqueous saturated solution at 100°. In all, three treatments were given lasting for a total of 15 hr. for the synthetic minerals. The natural minerals were treated until the mother liquor gave no trace of calcium or barium.

[1] Reed and Breck, *J. Amer. Chem. Soc.*, 1956, **78**, 5972; Barrer and Meier, *Trans. Faraday Soc.*, 1958, **54**, 1074.
[2] Barrer, Baynham, Bultitude, and Meier, *J.*, 1959, 195.
[3] Barrer and Baynham, *J.*, 1956, 2882.
[4] Barrer, Hinds, and White, *J.*, 1953, 1466.
[5] Barrer, unpublished work.

*Ion-exchange and* X-*Ray Powder Patterns.*—Three zeolitic sodium aluminosilicate phases designated Na-*P* have previously been prepared, all of which belong to the harmotome family of zeolites.[2]  These comprise a cubic phase which may be called Na-*P*1, a tetragonal phase Na-*P*2, and an orthorhombic phase Na-*P*3.   The powder photographs are shown in the Plate. From the cubic variety, Na-*P*1, the Li^{+}-, K^{+}-, Ca^{2+}-, and Ba^{2+}-exchanged forms were prepared. All exhibited slight changes from cubic symmetry, having the strong (211) line split into two, while in the Ca^{2+}- and K^{+}-forms the very strong (310) line was also doubled.   It was however possible to index the forms to cubic pseudo-cells having the values of $a$: Li^{+} $9 \cdot 8_9$, Na^{+} $10 \cdot 0_1$, K^{+} $9 \cdot 8_3$, Ca^{2+} $9 \cdot 9_5$, Ba^{2+} $10 \cdot 0_3$ Å.

From the tetragonal form, Na-*P*2, the Ca^{2+}- and Ba^{2+}-exchanged forms were also prepared. The powder patterns differed from the corresponding patterns of these forms derived from
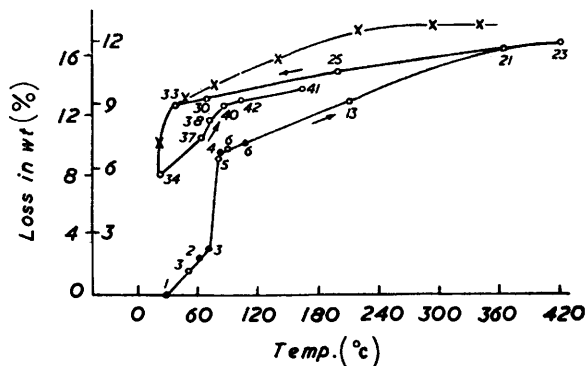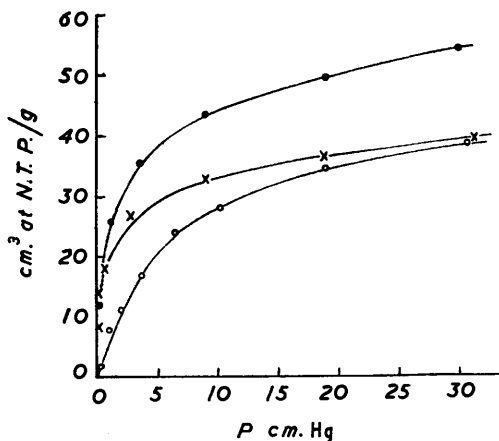


FIG. 1.   *Dehydration curves of* Na-*P on the thermogravimetric balance* (O, ●) *and under vacuum conditions* (×). The inner left-hand scale is the number of water molecules lost per unit cell.



FIG. 2.   *Sorption of ammonia at* 210° *on species exchanged derivatives.*   Na-*P* (O) *and its* Ca- (●) *and* Ba- (×) *forms.*

Na-*P*1.   They showed even more marked similarities to the patterns of natural minerals of the harmotome group than did the same ion-exchanged forms of Na-*P*1, or the parent phases Na-*P*1 and Na-*P*2 (Table 3 and Plate).   These Ca^{2+}- and Ba^{2+}-forms contained respectively 19·9% and 14·7% by weight of water compared with 17·0% for the original sodium form.

Also shown in the Plate for comparison are powder photographs of natural harmotome, its Na^{+}-exchanged form, a new natural zeolite of the harmotome family, found in Co. Down, Ireland, and provisionally named garronite by its discoverer,[6] Dr. G. Walker (Geology Department, Imperial College), and a synthetic phase designated K-*M*.[3]

*Dehydration.*—On dehydration of Na-*P* below 73°, several hours were required before the end points were reached, but between 73° and 83° a marked step was observed in the curve, 3 days being required to reach the end points over this portion of the curve.   Above 83° and below 73° the curve was continuous.   This portion of the curve is represented by points 1 to 23 in Fig. 1 (O), only a few of the observed points being included.   On rehydration, after heating the crystals to ~450°, an apparent hysteresis phenomenon occurred (points] 23 to 34, Fig. 1).

  [6] Walker, personal communication.

*Comparative X-ray powder photographs of a series of zeolites of the harmotome family.*
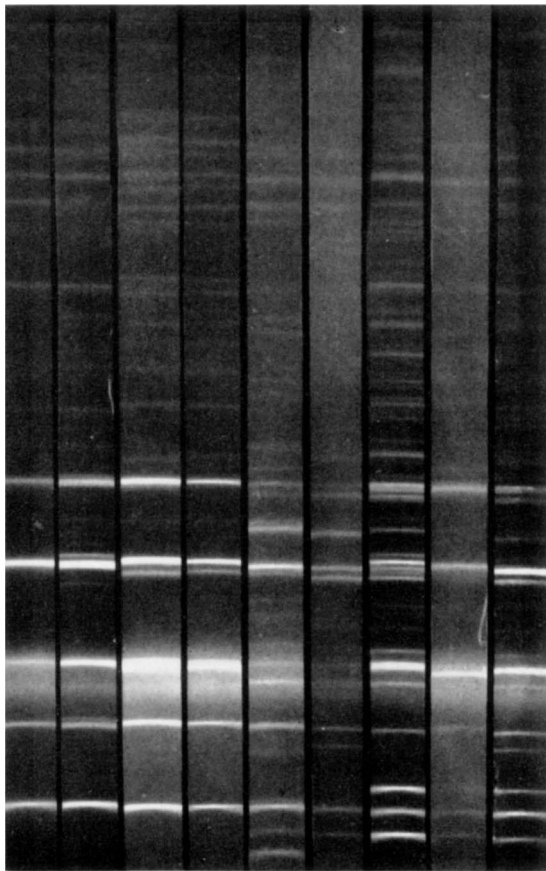
1. Na-*P*1 (cubic).

2. Na-*P*2 (tetragonal).

3. Ca-exchanged Na-*P*2.

4. New naturally occurring zeolite, garronite.[14]

5. Na-*P*3 (orthorhombic).

6. Species K-*M*.[10]

7. Natural harmotome.

8. Ba-exchanged Na-*P*2.

9. Na-exchanged phase from natural harmotome.

This may be due to very slow attainment of equilibrium but no trend with time was noticeable, some readings being taken after 3 hr. and others after 20 hr. About four days elapsed between the readings at 79° and 57° for a gain in weight of 0·1%. After three weeks at room temperature an ~4½% gain in weight had been recorded. On reheating, the curve did not return to its original position (points 34 to 42, Fig. 1). A second sample (●), on dehydration, gave the same step in the curve, this sample being heated to a maximum temperature of 108°. On cooling to room temperature it had regained its original weight within six days.

A smooth curve was obtained on dehydrating a specimen under vacuum (*X*) for 16 hr. at increasing temperatures (see Fig. 1). Almost two-thirds of the water was removed by evacuating the sample at room temperature. After the fully dehydrated sample had been exposed to the atmosphere at room temperature for four weeks, a weight of water had been regained equal only to that removed above room temperature, *i.e.*, about one third.

Heating of samples to 61° and 90° caused a slight decrease in the unit cell from 10·0$_1$ Å to 9·9$_5$ Å with practically no alteration in the diffraction intensities. At 165° and 260° the cell edge showed a decrease in size of ~5½% to 9·4$_6$ Å, with a marked alteration in some of the intensities. Thus (200), (222), and (330) lines became stronger and the (310) and (321) weaker, and there appeared in addition some reflections for which $h + k + l = 2n + 1$. After standing over a saturated ammonium chloride solution for about three weeks the unit cell and diffraction-line intensities had returned to those of the original mineral except for the appearance of a weak (111) reflection. Samples heated to 450° under vacuum appeared to have been destroyed.

*Sorption.*—Since outgassing under vacuum at 450° appeared to have destroyed the material, dehydration for sorption experiments was carried out at between 200° and 300° for 16 hr. The sodium form sorbed no appreciable amount of oxygen at −183° and sorption of ammonia by the sodium, barium, and calcium ionic species was very slow both at room temperature and at 100°, but at 210° apparent equilibrium was reached after 24 hr. The sodium and barium forms sorbed, per g. of original hydrated material, almost 40 c.c. of ammonia at N.T.P. at 30 cm. pressure, and the calcium form ~55 c.c. under the same conditions (Fig. 2). A specimen of natural harmotome from Strontian, Argyllshire, outgassed at 180° for 16 hr. also sorbed no oxygen at −183° and ammonia slowly at room temperature. Per gram of the original hydrated mineral, 27·2 c.c. at N.T.P. of ammonia were sorbed after 14 hr.

*Composition of Potassium and Calcium Derivatives.*—Other synthetic minerals with a similar type of framework structure have been observed in the potassium, calcium, and barium aluminosilicate fields.[3] The potassium analogue was of widespread occurrence, being grown from gels $K_2O,Al_2O_3,nSiO_2,xH_2O$ where $n = 1$—7 over a range of 200° to 300° with excess of potassium hydroxide present, and at slightly lower temperatures from gels $n = 7$—10. This compares with growth of Na-$P$[2] from gels of composition $Na_2O,Al_2O_3,nSiO_2,xH_2O$ where $n = 1$—12 in presence of excess of sodium hydroxide over a range of 60° to 250°. The *X*-ray pattern of the potassium mineral (K-*M*), which was also prepared as an alteration product of leucite by treatment with potassium hydroxide at 200—250°,[4] was very close to the ortho-rhombic sodium form grown at 250° (Plate). The composition of the potassium mineral was always near to $K_2O,Al_2O_3,3SiO_2,3H_2O$.

A synthetic calcium " harmotome " was grown from a gel $CaO,Al_2O_3,4SiO_2,xH_2O$ by treatment for long periods between 200° and 300°.[5] The product contained excess of calcium oxide, possibly as free lime, and analysis gave 1½$CaO,Al_2O_3,3\cdot3SiO_2,1½H_2O$. A barium harmotome-like mineral was grown from a parent gel $BaO,Al_2O_3,3SiO_2$ with excess of $Ba(OH)_2$, pH ~ 10·5, by heating for two days at 220° and then three days at 200°; and from a similar gel with no excess of $Ba(OH)_2$, pH ~ 7·0, by heating for three days at 360°.[5]

A natural mineral very similar to one of the synthetic species is garronite. From its crystal habit it was classified by Dr. G. Walker as probably belonging to the harmotome group of minerals although identical with none of them.[6] The *X*-ray pattern, which can be indexed to the tetragonal system with $a = 10\cdot0_1$ Å and $c = 9\cdot8_7$ Å, is almost exactly the same as that of a calcium-exchanged tetragonal form of species Na-$P$ (cf. Table 3 and Plate). No analysis of garronite is available, but it seems clear that it is also a zeolite of the harmotome group based on a similar aluminosilicate framework to that of the natural and synthetic phases already discussed.

*Crystal Symmetry and a Suggested Structure for Species* Na-$P$.—As seen from Table 1, there is no obvious relationship between the crystal symmetry and the composition of the several phases, collectively designated as Na-$P$, which varies from an $Al_2O_3 : SiO_2$ ratio of 1 : 3·35 to

one of 1 : 5·26.   The density of sample 4, Table 1, was found to be ~2·08 g./c.c. by successive suspensions in liquid mixtures (methylene iodide–benzene) of known density.   Hence the number of aluminium and silicon atoms per unit cell was found to be 5·3 and 10·4 respectively. Since the unit cell must contain an integral number of oxygen and (Al + Si) atoms,[7] this gives 16(Al + Si) and 32 oxygen atoms per unit cell.   The X-ray powder data [2] are, except for a very weak (410) line, consistent with a body-centred cubic unit cell.
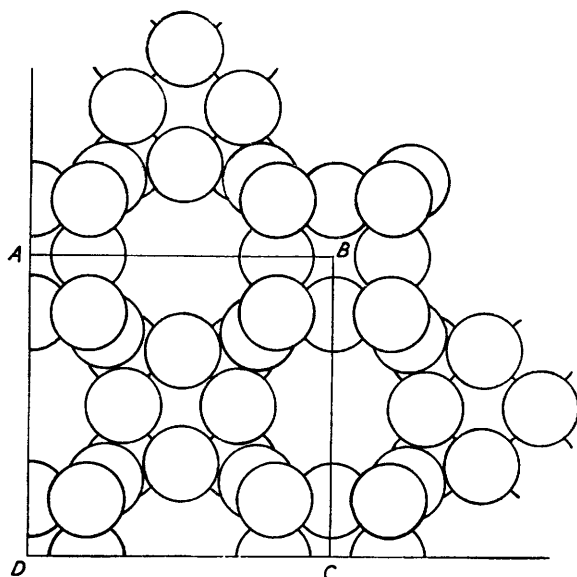


FIG. 3.   *The oxygen-atom framework of the structure of* Na-P1.   *Oxygen atoms above the plane ABCD are not shown, but a number of those below this plane are indicated.*

*Structure.*   It is possible to build a cubic structure of space group $Im3m$ with 16 (Al + Si) and 32 oxygen atoms per unit cell of size $a = 10·0$ Å.   Eight $(SiO_4)^{4-}$ tetrahedra are linked in four-membered rings forming a cube-shaped building unit, which is positioned at the corner and body centre of each unit cell.   Each unit is linked to its eight nearest neighbours by shared

TABLE 1.   *Variation in composition and symmetry of species P.*

| | Composition (%) Oxide ratio | | | Unit cell | | |
| | $Al_2O_3$ | $SiO_2$ | $H_2O$ | | Contents * | |
| Sample | | | | Symmetry | Na | $H_2O$ |
|---|---|---|---|---|---|---|
| 1 | 23·0 | 45·4 | 17·6 | — | 6·0 | 12·9 |
| | 1 | 3·35 | 4·30 | | | |
| 2 † | 21·8 | 47·3 | 17·0 | Tetragonal | 5·6 | 12·2 |
| | 1 | 3·68 | 4·35 | | | |
| 3 | 21·4 | 46·6 | 17·8 | Cubic | 5·6 | 13·9 |
| | 1 | 3·70 | 4·95 | | | |
| 4 | 21·0 | 49·2 | 17·3 | Cubic | 5·3 | 12·5 |
| | 1 | 3·98 | 4·66 | | | |
| 5 | 19·8 | 50·4 | 16·8 | Tetragonal | 5·1 | 12·0 |
| | 1 | 4·32 | 4·75 | | | |
| 6 | 17·4 | 53·8 | 17·5 | Cubic | 4·4 | 12·6 |
| | 1 | 5·26 | 5·72 | | | |

   * In each case Al + Si = 16.
   † Prepared from species Na-$Q$ by treatment with N-sodium hydroxide.[2]

oxygen atoms, the resultant framework being shown in Fig. 3.   The positions of the atoms will be as follows: [8] 24(O) at 24-fold ($h$) positions, $0xx$; 8(O) at 8-fold ($c$) positions, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; 16 (Al + Si) at 16-fold ($f$) positions, $yyy$.

   [7] Bragg, *Z. Krist.*, 1930, **74**, 237.
   [8] International Tables for *X*-Ray Crystallography, p. 344.

Assuming the tetrahedra to be of regular shape, we would obtain from the symmetry parameters $x = 0.188$ and $y = 0.156$ and an $(Al,Si)-O$ bond length of 1.65 Å, compared with a bond length of 1.66 Å for an aluminosilicate of this composition.[9] The Si–O–Si bond angles within each building unit are 146° but those linking neighbouring units are 180°. Previously-determined silicate structures lead one to expect Si–O–Si angles not greater than 150°. It seems probable then that the oxygen atoms in the eightfold positions are displaced randomly about the triad axes. This problem, in fact, is similar to that met with in β-cristobalite where the oxygen atoms are displaced from the points required by the observed symmetry elements to give Si–O bonds of 1.63 Å and Si–O–Si angles of 146° and not 180°.[10] The oxygen bridges in Species Na-*P* would have to be shifted 0.43 Å from the triad axis to give a bond angle of 150° and length of 1.65 Å.

*Channels.* The framework resulting from such an assembly of structural polyhedra has continuous intersecting channels running parallel to the [100] axes (Fig. 3). Each unit cell has a " cage " or " cavity " centred on the cube faces, each of these cages being shared by two



FIG. 4. (a) and (b): *Projections of the 8-membered rings in species Na-P in plane and elevation.* (c) and (d): *Projections of the 8-membered rings in Na-Q² (Linde Sieve A³), both on the (100) plane.*
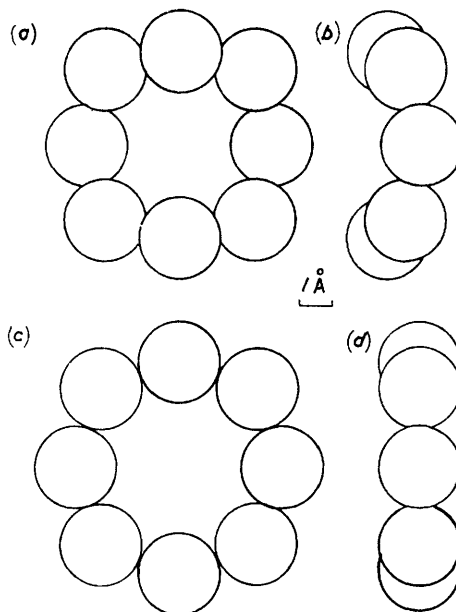
unit cells and another cage centred on the cube edge, these being shared by four unit cells. Thus there are six complete cages per unit cell, which can be regarded as alternate structural building units made up of two parallel four-membered rings linked to each other *via* four pairs of $(Si,Al)O_4$ tetrahedra, thus forming eight-membered rings which determine the narrowest points in the channel system. These are therefore important factors in determining the size of ions and molecules which might be exchanged or occluded. Fig. 4 is a projection on the (100) plane of one of these eight-membered rings for which the " free " diameter is about 3.2 Å. These rings are non-planar which accounts for their having a much smaller free diameter than the eight-membered rings in species Na-*Q*² or Linde Sieve 4A,[1] *i.e.*, 4.2 Å. A projection of the latter ring is also shown in Fig. 4 as are the side views of both types of ring.

Sorption and dehydration on Na-*P* suggest that the minimum " free " diameter must be less than the 3.2 Å which the completely unobstructed rings would give, *i.e.*, the water molecule with a diameter of ~2.76 Å should pass readily through the rings. However, the cationic positions must also be considered in a study of the channel systems.

*Cation positions.* The maximum number of cations observed per unit cell is 6 (Table 1). It is possible to arrange these in at least three different ways, each fulfilling the cubic symmetry elements. They can be placed at the centres of each of the six cages in the positions $\frac{1}{2}00$, $0\frac{1}{2}0$,

[9] Smith, *Acta Cryst.*, 1954, **7**, 479.
[10] Wells, " Structural Inorganic Chemistry," Cambridge Univ. Press, 1945, pp. 568, 569.

$00\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, and $\frac{1}{2}\frac{1}{2}0$ (see p. 1528). For $Na^+$ ions this would leave the channel system with a " free " distance of only $\sim$2·03 Å in certain directions between the cations and the framework, and in other directions a free distance of only $\sim$1·30 Å. A particle diffusing in the channels could however always choose paths which avoid the smaller free distance of $\sim$1·3 Å. Another possible set of positions comprises the six-fold sites $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{4}$, $\frac{3}{4}0\frac{1}{2}$, $\frac{1}{2}\frac{3}{4}0$, $0\frac{1}{2}\frac{3}{4}$. These sites are at the centres of half the eight-membered rings, limiting them to " free " diameters of little more than 1·1 Å, *i.e.*, half the channels are effectively blocked. However, if the cations were in a random distribution in a twelve-fold group, *i.e.*, in the positions $\frac{1}{4}0\frac{1}{2}$, $\frac{1}{4}\frac{1}{4}0$, $0\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}0$, $0\frac{3}{4}\frac{1}{4}$, $\frac{1}{4}0\frac{3}{4}$, in addition to those of the second six-fold positions, all the channels would be effectively blocked. In this case the rate of penetration, for example by ammonia and water, might be governed by the mobility of the cations, *i.e.*, the frequency with which they moved from occupied to vacant sites.

*Tetragonal and orthorhombic phases.* Of the forms of species Na-*P* other than the cubic, the tetragonal cell, with $a = 10·0_1$ Å, $c = 9·8_8$ Å, would result from a slight distortion of the lattice, the unit cell corners of the cubic and tetragonal forms being in approximately similar positions. The unit cell corners are thus still at the centres of the cubic structural polyhedra. An ideal
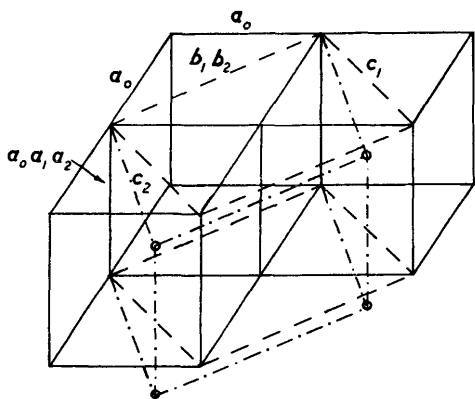


FIG. 5.    *Relationship between cubic, orthorhombic, and monoclinic cells which can be derived according to the structure proposed in the Plate for* Na-*P*.

| | |
|---|---|
| Cubic cell .................................... | $a_0$ |
| Orthorhombic cell ........................... | $a_1 b_1 c_1$ |
| Monoclinic cell ................................ | $a_2 b_2 c_2$ |
| Mid-points of cubic cells .................... | O |

orthorhombic unit cell would be face-centred, but owing to an additional distortion of the framework the centring symmetry vanishes. This lattice is almost identical with that of natural harmotome.

*Relationship between the Natural Zeolites of the Harmotome Group and the Synthetic Species.*— The symmetry of natural harmotome and phillipsite is not entirely certain. They have been reported monoclinic by Wyart and his co-workers [11,12] but one report [13] and also *X*-ray photographs taken in this laboratory support the idea of a B-face-centred orthorhombic structure for both these minerals, with $a = 9·78$, $b = 14·00$, $c = 14·23$ Å and $a = 9·84$, $b = 13·85$, $c = 14·3$ Å, respectively.

Dimensions of monoclinic unit cells for harmotome [11] and phillipsite [12] are presented in Table 2. Also a monoclinic unit cell (Table 2) can be delineated from the cubic cell of Ba-*P*1

TABLE 2.    *Monoclinic cells of harmotome and phillipsite, and the monoclinic cell as calculated from the cubic cell of species* P.

| | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\beta$ | Cell volume (Å³) |
|---|---|---|---|---|---|
| Harmotome .......................... | 10·00 | 14·25 | 8·62 | 54° 20′ | 998 |
| Phillipsite ............................. | 9·80 | 14·10 | 8·66 | 55° 10′ | 981 |
| From cubic form of Na-*P* ......... | 10·01 | 14·15 | 8·67 | 54° 44′ | 1003 |

in the manner shown in Fig. 5. All three are practically identical, and contain the same number of framework atoms (Al, Si, and O) per unit cell, but they differ somewhat in composition. Harmotome, which is rich in barium, is siliceous, with an $Al_2O_3 : SiO_2$ ratio of 1 : 4·66 to 1 : 5·15; [12] whereas phillipsite is rich in calcium and has an $Al_2O_3 : SiO_2$ ratio of 1 : 2·57 to

[11] Sekanina and Wyart, *Bull. Soc. franç. Min.*, 1937, **60**, 139.
[12] Wyart and Chatelain, *Bull. Soc. franç. Min.*, 1938, **61**, 121.
[13] Kalb and Klotsch, *Z. Krist.*, 1944, **105**, 315.

$1 : 3.84$ with one exceptional ratio reported as $1 : 4.82.$[12] The $X$-ray powder patterns of these two minerals are very similar, while those of the sodium-exchanged forms, made by repeated treatments with saturated solutions of sodium chloride until no calcium or barium could be detected in the mother liquor, are almost identical and are close to a barium-exchanged form of Na-$P2$ (Table 3 and Plate). Phillipsite, harmotome and Na-$P$ clearly must have similar

TABLE 3. *X-Ray powder patterns.*

| hkl | Garronite Tetragonal $a = 10.0_1$ Å, $c = 9.8_7$ Å Int. | d | Ion-exchanged derivatives Tetragonal form of Species Na-$P$ Ca Int. | d | Ba Int. | d | Na-exchanged natural harmotome Int. | d |
|---|---|---|---|---|---|---|---|---|
| 110 | ms | 7.15 | s | 7.1 | m | 8.2 | m | 8.2 |
| 002 | ms | 4.95 | s | 4.94 | m | 7.2 | ms | 7.1 |
| 211 | s | 4.12 | s | 4.12 | mw | 6.4 | m | 6.3 |
| 112 | m | 4.07 | ms | 4.05 | | | m | 5.3 |
| 310 | m | 3.22 | m | 3.22 | m | 4.95 | m | 5.0 |
| 103 | s | 3.14 | s | 3.12 | m | 4.28 | w | 4.28 |
| 222 | w | 2.88 | m | 2.87 | s | 4.14 | | |
| 321 | vw | 2.68 | | | m | 4.05 | s | 4.08 |
| 213 | s | 2.66 | s | 2.66 | w | 3.88 | w | 3.90 |
| 400 | vw | 2.54 | mw | 2.55 | | | w | 3.65 |
| 303 | w | 2.34 | m | 2.33 | | | w | 3.45 |

| hkl | Garronite Tetragonal $a = 10.0_1$ Å, $c = 9.8_7$ Å Int. | d | Ion-exchanged derivatives Tetragonal form of Species Na-$P$ Ca Int. | d | Ba Int. | d | Na-exchanged natural harmotome Int. | d |
|---|---|---|---|---|---|---|---|---|
| 204 | w | 2.22 | w | 2.20 | w | 3.24 | m | 3.25 |
| 323 | vw | 2.12 | w | 2.12 | | | m | 3.23 |
| 422 | vw | 2.05 | mw | 2.06 | s | 3.12 | s.diff | 3.16 |
| | | | | | | | | 3.15 |
| 224 | vvw | 2.03 | w | 2.02 | | | | |
| 005 | w | 1.970 | mw | 1.975 | | | vw | 3.11 |
| 314 | w | 1.938 | mw | 1.930 | | | w | 3.08 |
| 215 | w | 1.805 | mw | 1.805 | | | mw | 2.94 |
| 440 | mw | 1.770 | mw | 1.770 | vw | 2.90 | vw | 2.91 |
| 522 | vw | 1.745 | mw | 1.735 | | | w | 2.82 |
| 414 | vw | 1.730 | | | w | 2.73 | m.diff | 2.73 |
| | | | | | | | | 2.71 |
| 433 | mw | 1.705 | mw | 1.705 | | | | |
| 600 | vw | 1.665 | w | 1.665 | s | 2.66 | m.diff | 2.67 |
| | | | | | | | | 2.65 |
| 610 | mw | 1.645 | mw | 1.640 | w | 2.64 | | |
| 116 | mw | 1.605 | w | 1.605 | w | 2.57 | w | 2.54 |

aluminosilicate frameworks. The vector relationship, derived from Fig. 5, between the monoclinic, orthorhombic B, and cubic minerals is indicated below, where the suffixes 2, 1, and 0 refer respectively to these lattices:

$$a_2 = a_1 \qquad a_1 = a_0 \qquad a_2 = a_0$$
$$b_2 = b_1 \qquad b_1 = b_0 - c_0 \qquad b_2 = b_0 - c_0$$
$$c_2 = \tfrac{1}{2}(a_1 + c_1) \qquad c_1 = b_0 + c_0 \qquad c_2 = \tfrac{1}{2}(a_0 + b_0 + c_0)$$

*X-Ray Justification for the Structure of* Na-$P1$ *(Cubic).*—Observed intensities for Na-$P1$ were measured photometrically from patterns taken on a Guinier camera, where preferential absorption is minimised by the obliqueness of the incident beam to the slab of powder. Due allowance was made for the absorption by the emulsion of the $X$-ray film.

Theoretical intensities have been calculated for several slightly modified atomic arrangements, based on the structure given on p. 1523, of which only those giving best agreement with the observed intensities are mentioned (Table 4). First, $F_c^2 m$ values were calculated for the

TABLE 4. *Observed and calculated relative* X-ray *intensities for the cubic species of harmotome. The results with * and without † Na$^+$ cations are given.*

| hkl | $F_o^2 m$ | $F_c^2 m$ * | $F_c^2 m$ † | hkl | $F_o^2 m$ | $F_c^2 m$ * | $F_c^2 m$ † | hkl | $F_o^2 m$ | $F_c^2 m$ * | $F_c^2 m$ † |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 110 | 60 | 51 | 20 | 321 | 300 | 140 | 53 | 510, 431 | 105 | 66 | 22 |
| 200 | 40 | 53 | 8 | 400 | 16 | 11 | 33 | 521 | 0 | 1 | 11 |
| 211 | 35 | 1 | 9 | 411, 330 | 19 | 100 | 85 | 440 | 207 | 207 | 247 |
| 220 | 0 | 10 | 3 | 420 | 0 | 1 | 40 | 530, 433 | 200 | 227 | 227 |
| 310 | 645 | 493 | 445 | 332 | 0 | 62 | 24 | 600, 442 | 215 | 227 | 215 |
| 222 | 0 | 35 | 2 | 422 | 44 | 4 | 50 | | | | |

aluminosilicate framework of p. 1523 and compared with observed $F_o^2 m$ values ($F_o^2 m = I_0/lp$ where $m$, $l$, and $p$ denote multiplicity and Lorentz and polarisation factors respectively). This gave fair agreement which was improved both by allowing for a displacement of 8 oxygen atoms away from the triad axis, and by addition of water molecules at the 12-fold [[$\tfrac{1}{2}\tfrac{1}{2}0$]]

positions. At this stage, without inclusion of $Na^+$ ions, a reliability factor of $R = \sum|F_o{}^2m - F_c{}^2m|/\sum F_o{}^2m$ gave a value of 0·36, when 17 rings were taken into account. Placing the 6 $Na^+$ ions at $[[\frac{1}{2}00]]$ or nearby worsened the reliability factor to over 0·45.

A Fourier synthesis was also carried out but, on account of the coincidence of diffractions such as 510 and 431 in the powder pattern, only innermost rings could be used. The necessary signs for the observed structure amplitudes were taken from the calculation above and a Fourier projection on the (001) plane, and Fourier sections of the $(100)_0$, $(100)_{\frac{1}{4}}$ and $(110)_0$ planes were evaluated. Individual atoms were not resolved but the general form of the framework was verified, including regions of matter about the 12-fold $[[\frac{1}{4}\frac{1}{4}0]]$ positions. These being assumed to represent the water molecules, no evidence of the six sodium ions could be seen.

## DISCUSSION

The structure which has been suggested for the various synthetic phases and natural minerals of the harmotome group of zeolites may be considered in relation to the discontinuity in the dehydration curve obtained for Na-P, which is similar to those noted in the dehydration of the fibrous zeolites, scolecite, and natrolite.[14] In addition, Na-P gives a differential thermal analysis curve with a very sharp peak [15] of a type found also with the fibrous zeolites.[16] From Fig. 1 it is seen that the step occurs when two molecules of water have been removed per unit cell, and the height of the step corresponds to the removal of another four molecules. Loss of remaining water, nearly half the total, follows a smooth dehydration curve. Each cavity in the structure probably contains one univalent cation and two water molecules, and the step has occurred by the time about half this water has been evolved. Partial dehydration is accompanied by a substantial contraction of the unit cell ($\sim 5\frac{1}{2}\%$).

The contraction, and the similarities to the fibrous zeolites, can be explained as follows. In the harmotome structure as in the fibrous zeolites one can recognise secondary building units in the form of tightly bonded clusters of (Al,Si)$O_4$ tetrahedra (*e.g.*, the cubic anionic units shown in Fig. 3). These are joined by single oxygen bridges to other like units in the harmotome minerals, so that the structure can suffer distortion and shrinkage by diminution in bond angle of these Si–O–(Si,Al) bonds. Only in the fully hydrated form is the structure nearly completely distended. A rather similar situation occurs in the fibrous zeolites. Although tightly bonded clusters of tetrahedra are rather rigidly linked in the direction of the fibre axis, they are more weakly linked by single bonds in the two directions normal to this axis.[17] Hence the unit cell could undergo some shrinkage particularly in these directions during dehydration. Where the lattice alteration is large enough the change is accompanied by a discontinuous discharge of zeolitic water and a step in the dehydration isobar.

In contrast to the situation described above in robust three-dimensional network zeolites such as the chabazite–gmelinite family, the faujasite group, or Linde Sieve A, all the structural polyhedra are not only tightly linked clusters of tetrahedra but they are also linked to other polyhedra by multiple oxygen bridges, leading to frameworks which show minimal lattice changes during dehydration.

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[14] Milligan and Weiser, *J. Phys. Chem.*, 1937, **41**, 1029.
[15] Barrer and Langley, unpublished work.
[16] Koizumi, *Min. J.* (*Min. Soc., Japan*), 1953, **1**, 36.
[17] Taylor, Meek, and Jackson, *Z. Krist.*, 1933, **84**, 373.