# 33. *Synthesis of a Zeolitic Mineral with Chabazite-like Sorptive Properties.*

### By R. M. Barrer.

By heating synthetic and natural analcites with water and excess of barium or potassium chloride or bromide, it was found possible under certain conditions to produce new aluminosilicates as characteristic small rectangular crystals. Similar products were obtained from synthetic or natural leucites, and from gels similar to but not necessarily identical with analcite in the proportions of base : $Al_2O_3 : SiO_2$. In these gels the base could be BaO, CaO, $K_2O$, or $Na_2O$, provided always that the mineralising salt was present in excess. The best proportions of analcite : water : salt for the recrystallisation were studied and it was demonstrated that bromides and chlorides of potassium or barium were specific mineralisers for the reaction, which did not take place with the salts $CaCl_2$, $SrCl_2$, $KNO_3$, $Ba(NO_3)_2$, and KF.

The minerals produced contained large amounts of interstitially incorporated mineralising salt, but all the products were believed to be based on the same or similar aluminosilicate frameworks. This was proved by *X*-ray photographs to be the case for the minerals containing barium chloride and bromide. Analyses of the mineral containing the chloride gave approximately the composition $BaO,Al_2O_3,4SiO_2,xBaCl_2,yH_2O$, where $x$ varied between 0·6 and 0·8 and $y$ between 3 and 2.

The interstitially incorporated salt could be removed by high-temperature extraction with distilled water, with a minimum of alteration of the parent aluminosilicate framework in the case of the mineral containing barium chloride, with a marked tendency to produce a new species when the parent mineral contained barium bromide, and with decomposition when it contained potassium chloride. The unaltered but salt-free aluminosilicate proved to be a zeolitic molecular sieve sorbent having sorptive properties similar to those of chabazite but based upon a different crystalline structure. The sorptive behaviour is studied in the following paper.

ZEOLITES are believed to arise through the mineralising action of solutions on rocks under relatively stagnant and possibly rather alkaline conditions, between 100° and 350° (Lindgren, " Mineral Deposits ", McGraw-Hill Book Co., 1919, 427). These hydrous minerals are endowed with base-exchange properties, and sometimes, when dehydrated, with remarkable gas-absorbing powers and molecular-sieve characteristics. Although they occur in widespread localities they are not usually found in quantity, except in a few instances such as mordenite.

One of the best gas-absorbing zeolites is chabazite $(Ca,Na_2)Al_2Si_4O_{12},6H_2O$, with sorbing power equal to that of active charcoals, and in addition with singularly clear-cut molecular-sieve properties which enable it to effect a great variety of separations of mixtures by selective sorption (Barrer, *J. Soc. Chem. Ind.*, 1945, **64**, 130, 131, 134). This mineral has not so far proved easy to make or there is little doubt that it would find many applications as a selective special purpose sorbent. Its behaviour has led it to be described as a Class 1 molecular sieve, using certain molecules as yardsticks in defining the types of molecule which will or will not be sorbed. Thus it cannot sorb *iso*paraffins (*e.g.*, $CHMe_3$) but sorbs *n*-paraffins ($CH_2Me_2$) slowly, and molecules such as ethane or methane with great rapidity (Barrer, *loc. cit.*; Barrer and Ibbitson, *Trans. Faraday Soc.*, 1944, **40**, 195, 206). Corresponding to these typical molecules it was shown that chloroform, bromoform, *sec.*-propyl alcohol, and other molecules of similar shape and size to *iso*butane were not sorbed; methylene chloride or bromide and other molecules of similar shape and size to propane were slowly sorbed; and molecules like methanol and methyl cyanide similar in shape and size to ethane were rapidly sorbed. The molecular-sieve property arises because the dehydrated lattice of the sorbent is traversed by channels of molecular dimensions too narrow to accommodate some molecules but wide enough to contain others (Barrer, *loc. cit.*).

Many types of mixtures can be resolved by using different classes of molecular-sieve sorbent; *inter alia*, chabazite can separate *n*-paraffins quantitatively from *iso*-paraffins and aromatic hydrocarbons; methyl chloride and methylene dichloride from chloroform and carbon tetrachloride; water, methanol, and ethanol from higher alcohols, or from ketones and ethers; or simple monosubstituted methanes ($CH_3Br$, $CH_3{\cdot}CN$, $CH_3{\cdot}NH_2$, etc.) from similar monosubstituted ethanes, propanes, and so on (Barrer, *loc. cit.*; B.P. Appln. No. 15561/43; *ibid.*, No. 548,905; U.S.P. No. 2,306,610). One can thus see that peculiar interest attaches to syntheses of molecular-sieve sorbents.

Many attempts were made to synthesise chabazite, but although these led to the preparation of several calciferous aluminosilicates, they were not successful in their primary object. However, the present paper describes the synthesis of a new zeolitic mineral which possesses the same molecular-sieve characteristics as chabazite itself (see following paper). The new mineral does not appear to occur naturally.

## EXPERIMENTAL.

Aluminosilicate gels or minerals were crystallised or recrystallised hydrothermally in stainless-steel autoclaves, capable of sealing the mineralising solutions at temperatures up to 400°, and thus at several hundred atm. pressure of water vapour. These autoclaves were prepared according to a small number of simple designs. The smaller had internal volumes of *ca.* 10 c.c., and the larger of *ca.* 25 c.c. Sealing was effected by soft copper washers which flowed slightly under pressure when the cap of the autoclave was tightly screwed down. Lead washers were also tried, but flowed too readily at temperatures above 220°.

Substances treated with mineralising solutions included analcite ($NaAlSi_2O_6,H_2O$), leucite ($KAlSi_2O_6$), chabazite, bentonite, a variety of aluminosilicate gels specially prepared, and base-exchange gel zeolites sold under the trade names " Doucil ", " Burgess Freeze Formed Zeolite " and " Permutit ". Synthetic gels were prepared by dissolving known weights of previously analysed sodium aluminate (" Alfloc ") in water, and stirring it into a creamy suspension of silicic acid gel of known silica content. The mixture was then evaporated to dryness. The powdered product was in some instances base-exchanged by salts of cations such as $Ca^{++}$, $Ba^{++}$, or $K^+$, to produce powdered gels rich in these cations. As a rule, however, the sodium-rich gels were used as such.

Synthetic as well as natural leucite and analcite were among the crystalline minerals used. Analcite was prepared from gels of approximate compositions $Na_2O,Al_2O_3,4SiO_2,xH_2O$, by hydrothermal crystallisation with distilled water at temperatures which in different preparations ranged from 150° to 300°. The duration of heating was usually about 24 hours, and a temperature of 200—220° was then very effective. Synthetic leucite was obtained from analcite by base exchange of $Na^+$ using $K^+$ in excess, for similar times and at similar temperatures.

*Preparation of a New Group of Minerals.*—The first successful conversion of analcite into a member of the new group of minerals was observed when analcite powder was mixed with about its own volume of barium chloride, water was added equal in amount to the total apparent volume of solids, and the whole heated at 210° for 2 days. In subsequent experiments the salt was varied from 0·5 to 1·5 times the volume of analcite, and the water over a similar range in volumes, without finding any critical conditions. The various mixtures were heated to temperatures ranging from 180° to 270°, being given progressive treatments of from 2 to 6 days. Recrystallisation was observed in all cases, being most extensive in the temperature range 180—220°. The analcite ikositetrahedra were converted into small rectangular crystals (see fig. 1).

Similar experiments to those described above were next carried out, various minerals and gels being used in place of analcite (Table I). All the experiments were successful save those with the minerals chabazite and bentonite, and it is obvious that some latitude is possible in the composition and character of the gel. Further successful series of experiments were conducted with barium bromide in place of barium chloride as mineralising salt (Table II). Potassium chloride and bromide were also employed with success, as can be seen in the figures, the conditions being similar to those used in the experiments with the barium salts, with a recrystallising temperature of 240°.

The reaction depended specifically upon the character of both cation and anion. Thus NaCl, $SrCl_2$, and $CaCl_2$ were ineffective, and show the effect of varying the cation; $KNO_3$, KF, and $Ba(NO_3)_2$ were equally ineffective both with analcite and with a gel of the same composition. Base exchange only was now found, which could be complete in the case of the potassium salts, but was never more than partial with analcite and $Ba(NO_3)_2$. On raising the reaction temperature to 300° base exchange of $2Na^+$ by $Ba^{++}$ in analcite became complete, but instead of recrystallisation a product amorphous to *X*-rays was obtained.*

As appears often to be the case in hydrothermal crystallisation of silicates (Baur, *Z. anorg. Chem.*, 1911, **72**, 119), the crystallites deposited were very small, and when once formed showed little tendency to further growth. Thus crystals derived in an earlier experiment were given a further 15 days' hydrothermal treatment with water and barium chloride, without a sensible increase in size.

*The Composition and Nature of the New Species.*—Analysis revealed that the halide ($BaCl_2$, $BaBr_2$, KCl, and KBr) had entered into the composition of the minerals illustrated in Figs. 2—5, almost certainly as an interstitial solid solution. The interstitial character was shown by extracting the minerals in autoclaves with distilled water at about 200°, whereupon large amounts of halide (which could not be extracted simply by refluxing with water at 100°) appeared in the mother-liquor. A number of analyses were then made on small amounts of different preparations of the mineral containing barium chloride † (Table III). In spite of small deviations the " ideal " composition of the mineral was taken to be $(Na_2O,BaO),Al_2O_3,4SiO_2,xBaCl_2,yH_2O$, where the interstitial $BaCl_2$ and $H_2O$ contents may vary somewhat, but where $x$ is not far from 0·66.

*X*-Ray powder photographs were made of the minerals containing barium chloride and bromide. The main spacings are given in Table IV, and, in view of the sorptive properties described in the next paper, some main spacings for chabazite in the same range were also determined. It is clear that the minerals containing these two barium salts are based upon the same space lattice, which is not identical with the chabazite space lattice. When the occluded barium chloride or bromide was removed from the lattice as described on p. 132. giving the products of cols. 3 and 4, the lattice spacings show some shrinkage and variability, but the same aluminosilicate framework is still recognised. The extent of shrinkage is believed to depend upon the severity and extent of the extraction process, which sometimes if too prolonged gave an " amorphous " band, and also resulted in partial recrystallisation. Even the parent mineral containing barium chloride showed spacings with minor variation (col. 1, Table IV) which may be associated with variations in barium chloride content (cf. Table III).

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* Analysis of this material gave $SiO_2$, 43·92; $Al_2O_3$, 20·12; BaO, 27·42; $H_2O$, 6·84%; $Na_2O$, not determined. The molar proportions were respectively 0·732, 0·197, 0·179, and 0·380, *i.e.*, the composition is $0{\cdot}98BaO,1{\cdot}07Al_2O_3,4{\cdot}00SiO_2,2{\cdot}08H_2O$, the constituents still being in analcite proportions.

† The amount of mineral used per analysis ranged from 0·5 to 1·0 g.

TABLE I.

*Typical preparations of the mineral obtained with barium chloride as mineraliser.*

| Aluminosilicate component. | Treatment. | Temp. | Yield of mineral. |
|---|---|---|---|
| Naturally occurring analcite | Five progressive treatments with fresh charges of $H_2O$ and $BaCl_2$, each of 12 hours' duration | 200° | Excellent |
| Naturally occurring analcite | Four progressive treatments as above, each of 1 day | 233 | Good to moderate |
| Synthetic analcite | Six progressive treatments as above, each of 1 day | 210 | Excellent |
| Natural leucite | Four days' continuous heating with one charge of $H_2O$ and $BaCl_2$ | 218 | Appreciable |
| Synthetic leucite | Two days' continuous heating with one charge of $H_2O$ and $BaCl_2$ | 208 | Moderate |
| Synthetic leucite | Two days' continuous heating with one charge of $H_2O$ and $BaCl_2$ | 218 | Fine growth of crystals of new mineral |
| " Burgess Freeze Formed " gel zeolite | Five days' continuous heating with one charge of $H_2O$ and $BaCl_2$ | 208 | Good |
| Ca-base-exchanged " Doucil " gel zeolite | Six days' continuous heating with one charge of $H_2O$ and $BaCl_2$ | 180 | Crystallisation not noted |
| Gel as above | Five days' continuous heating with one charge of $H_2O$ and $BaCl_2$ | 208 | Excellent |
| Potassium aluminosilicate gel, $K_2O,Al_2O_3,4SiO_2,nH_2O$ | Six days' continuous heating with one charge of $H_2O$ and $BaCl_2$ | 180 | Excellent |
| Barium aluminosilicate gel, $BaO,Al_2O_3,4SiO_2,nH_2O$ | Three days' continuous heating with one charge of $H_2O$ and $BaCl_2$ | 235 | Good |
| Gel as above | Treatment as above | 270 | Moderate |
| Gel as above | One day's heating at 210° and two days' heating at 197°, with one charge of $H_2O$ and $BaCl_2$ | — | Good |
| Chabazite | Five days' heating with one charge of $H_2O$ and $BaCl_2$ | 208 | Slight evidence of crystal growth |
| Chabazite | Three days' heating with one charge of $H_2O$ and $BaCl_2$ | 218 | No evidence of crystal growth |
| Bentonite | Seven days' heating with one charge of $H_2O$ and $BaCl_2$ | 200 | No evidence of alteration in bentonite |

TABLE II.

*Typical preparations of the mineral obtained with barium bromide as mineraliser.*

| Aluminosilicate component. | Treatment. | Temp. | Yield of mineral. |
|---|---|---|---|
| Synthetic analcite | Two progressive treatments with fresh charges of $H_2O$ and $BaBr_2$ of two days and 30 hours respectively | 205° | Excellent |
| Barium aluminosilicate gel, $BaO,Al_2O_3,4SiO_2,nH_2O$ | Treatment as above | 205 | Negligible yield |
| " Burgess Freeze Formed " gel zeolite | Two days' treatment with $H_2O$ and $BaBr_2$ | 205 | Small, as very tiny crystals |
| Gel as above | Treatment as above | 220 | Improved yield |
| " Permutit " gel zeolite | Treatment as above | 205 | Small, as very tiny crystals |
| Gel as above | Treatment as above | 220 | Improved yield |

TABLE III.

*Typical analytical results.*

| | % by weight in analysis no. : | | | | Molar proportions in analysis no. : | | | |
|---|---|---|---|---|---|---|---|---|
| Component. | 1. | 2. | 3. | 4. | 1. | 2. | 3. | 4. |
| $SiO_2$ | 36·91 | 36·8 | 36·8 | 33·85 | 4·00 | 4·00 | 4·00 | 4·00 |
| $Al_2O_3$ | 16·26 | 16·16 | not detd. | 15·29 | 1·04 | 1·03 | — | 1·06 |
| BaO | 20·98 | 18·55 | 19·72 | 20·03 | 0·89 | 0·79 | 0·84 | 0·93 |
| $Na_2O$ | not detd. | not detd. | none | 0·28 | — | — | — | 0·03 |
| $BaCl_2$ | 22·1 | 19·85 | 19·85 | 23·88 | 0·69 | 0·62 | 0·62 | 0·81 |
| $H_2O$ | not detd. | 8·5 | not detd. | 6·06 | — | 3·08 | — | 2·40 |
| $Fe_2O_3$ | 0·2 | trace | trace | not detd. | — | — | — | — |

TABLE IV.

*Some main X-ray diffraction spacings* (A.) *in the new minerals and allied products.*

| Mineral containing $BaCl_2$. | | | Mineral † containing $BaBr_2$. | Mineral originally containing $BaCl_2$ after extraction of $BaCl_2$. | | | Mineral § originally containing $BaBr_2$ after extraction of $BaBr_2$ and some re-crystallisation. | Chabazite ‖ spacings (lines over similar range only). |
|---|---|---|---|---|---|---|---|---|
| (1) * | (2) * | (3) * | | (1) ‡ | (2) ‡ | (3) ‡ | | |
| — | — | 13·10 (s) | 13·57 (v.s.) | — | — | — | 12·67( w) | 18·7 (m.s.) |
| — | — | 9·40 (m) | — | — | — | — | [9·52 (m)] | — |
| — | — | 5·96 (w) | — | 6·16 (v.v.w.) | — | — | [7·65 (m)] | 6·74 (w) |
| — | 4·90 (v.w.) | 5·01 (w) | 4·98 (m) | — | — | — | [6·31 (m)] | 5·52 (m.s.) |
| — | 4·38 (m) | 4·43 (m) | 4·44 (s) | — | — | — | 4·90 (w) | 4·97 (m.s.) |
| — | 4·15 (v.w.) | 4·16 (w) | 4·17 (m) | — | — | — | [4·00 (m)] | 4·30 (v.s.) |
| — | 3·79 (m.w.) | 3·81 (m) | 3·82 (m) | — | — | — | 3·77 (w) | — |
| 3·15 (w) | 3·19 (w) | 3·20 (s) | 3·21 (m) | — | — | 3·15 (w) | 3·26 (w) | 3·86 (m) |
| 2·90 (v.w.) | 3·02 (m) | 3·03 (v.s.) | 3·04 (s to v.s.) | 2·99 (m) | 2·96 (m) | 2·90 (v.w.) | [3·12 (m)] | 3·57 (m.s.) |
| 2·72 (v.w.) | 2·80 (m) | 2·82 (m) | 2·82 (s) | 2·79 (m) | 2·75 (w) | 2·72 (v.w.) | [2·66 (m)] | 3·45 (m.w.) |
| 2·60 (v.w.) | 2·64 (v.v.w.) | 2·64 (w) | — | — | 2·57 (m) | 2·60 (w) | — | 3·19 (w) |
| — | 2·51 (w) | 2·45 (v.w.) | 2·54 (w) | — | — | — | — | 2·91 (v.s.) |
| — | 2·35 (v.w.) | — | — | — | — | — | — | 2·67 (v.w.) |
| — | 2·30 (w) | 2·30 (w) | 2·29 (w) | 2·25 (v.w.) | — | — | 2·33 (v.w.) | 2·60 (m) |
| — | — | 1·90 (v.v.w.) | — | — | — | — | 2·07 (v.w.) | 2·55 (m) |
| — | — | 1·79 (v.v.w.) | — | — | — | — | — | 2·33 (w) |
| — | — | 1·76 (v.v.w.) | — | — | — | — | — | 2·29 (w) |
| | | | | | | | | 2·09 (m) |
| | | | | | | | | 1·92 (v.v.w.) |
| | | | | | | | | 1·86 (w) |
| | | | | | | | | 1·80 (m) |
| | | | | | | | | 1·73 (w) |

* (1) Prepared from synthetic analcite at 210°.
* (2) Prepared from natural analcite at 210°.
* (3) Prepared from natural analcite at 208°.
† Prepared from synthetic analcite at 205°.
‡ (1) Product of col. 1, preparation (2).
‡ (2) Product of col. 1, preparation (1).
‡ (3) Prepared from synthetic analcite and $BaCl_2$,aq. at 235° and subsequently extracted.
§ Prepared from synthetic analcite and $BaBr_2$ at 204°. Lines in square brackets are due to recrystallisation during extraction, giving a new type of crystal.
‖ A natural calcium-rich sample.

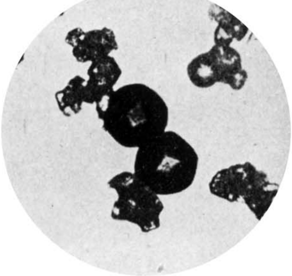

FIG. 1.

*Crystals of ikositetrahedral synthetic analcite amid smaller crystals of new mineral prepared by partial recrystallisation of the parent analcite, using* $BaCl_2$. *Magnification* 200.

FIG. 2.

*Rectangular crystals of the new mineral,* $BaO,Al_2O_3,4SiO_2,0{\cdot}66BaCl_2$, 2—$3H_2O$, *produced by recrystallising analcite, using* $BaCl_2$. *Magnification* 400.

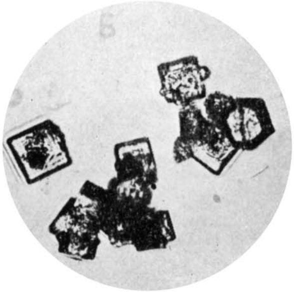

FIG. 3.

*Crystals of similar species grown from synthetic analcite using* $BaBr_2$ *in place of* $BaCl_2$. *Magnification* 400.

FIG. 4.

*Crystals of similar species grown from synthetic leucite using* KCl. *Magnification* 200.

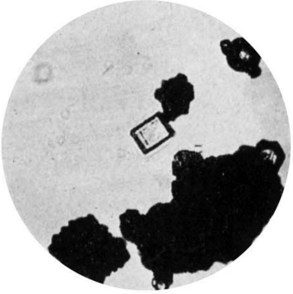

FIG. 5.

*Occasional crystals of similar species to Figs.* 2, 3, *and* 4, *grown from synthetic leucite using* KBr. *Magnification* 200.

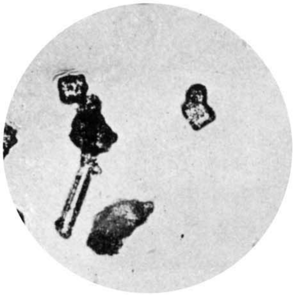

FIG. 6.

*The crystals of rectangular contour are similar to those in Fig.* 2, *but with the* $BaCl_2$ *removed by hydrothermal extraction. The typical elongated crystal is also produced by a partial recrystallisation of the barium mineral of Fig.* 2 *during hydrothermal extraction of the chloride. Magnification* 400.

Although the spacings in col. 4 show a slight similarity between chabazite and the new mineral, this similarity is at best only qualitative. There is some resemblance in the crystalline forms : chabazite occurs characteristically as rhombs with an angle of nearly 90°, whereas Figs. 2—5 show the new mineral to consist of nearly rectangular blocks. These crystals were very nearly isotropic, or at most very feebly birefringent.

*Limiting Conditions for Recrystallising Analcite.*—Systematic variation in the composition of the reaction mixture was undertaken to define more closely the critical conditions for obtaining the new minerals from analcite (Table V). The volume within the autoclaves was about 25 c.c., so that as the

TABLE V.

*Yield in relation to composition of reaction mixture and other factors.*

Mineral containing $BaCl_2$.

| | Composition. | Conditions. | Yield. |
|---|---|---|---|
| (1) | Analcite 5·23 g.<br>$BaCl_2$ 7·78 g.<br>$H_2O$ 5 c.c. | 44 Hrs. at 197° | Excellent. Very small amount unaltered analcite |
| (2) | Analcite 5·23 g.<br>$BaCl_2$ 7·78 g.<br>$H_2O$ 10 c.c. | As above | Good. Crystals larger than in (1), but amount of unaltered analcite larger |
| (3) | Analcite 5·23 g.<br>$BaCl_2$ 7·78 g.<br>$H_2O$ 15 c.c. | As above | Moderate yield. Unaltered analcite increasing in amount |
| (4) | Analcite 3·67 g.<br>$BaCl_2$ 5·50 g.<br>$H_2O$ 18 c.c. | Three days at 173° | No observable yield of new mineral |
| (5) | Analcite 3·36 g.<br>$BaCl_2$ 5·00 g.<br>$H_2O$ 18 c.c. | Two days at 197° | As in (4) |
| (6) | Analcite 3·36 g.<br>$BaCl_2$ 5·00 g.<br>$H_2O$ 13·2 c.c. | As in (5) | Rare crystals of new mineral. Mainly analcite |
| (7) | Analcite 3·36 g.<br>$BaCl_2$ 5·55 g.<br>$H_2O$ 13·2 c.c. | As in (5) | As in (6) |

Mineral containing $BaBr_2$.

| | Composition. | Conditions. | Yield. |
|---|---|---|---|
| (1) | Analcite 3·36 g.<br>$BaBr_2$ 5·00 g.<br>$H_2O$ 15 c.c. | Two days at 194° | Only analcite present |
| (2) | Analcite 3·36 g.<br>$BaBr_2$ 8·00 g.<br>$H_2O$ 15 c.c. | 42 Hrs. at 194° | Small yield new mineral. Some crystals projecting from analcite matrices |
| (3) | Analcite 3·36 g.<br>$BaBr_2$ 10·0 g.<br>$H_2O$ 15 c.c. | Two days at 194° | Some quite well-formed crystals, but much analcite |
| (4) | Analcite 3·36 g.<br>$BaBr_2$ 12·00 g.<br>$H_2O$ 15 c.c. | Two days at 194° | Fair yield, but still considerable analcite |
| (5) | Analcite 3·36 g.<br>$BaBr_2$ 14·00 g.<br>$H_2O$ 15 c.c. | As in (4) | As in (4) |
| (6) | Analcite 3·36 g.<br>$BaBr_2$ 10·00 g.<br>$H_2O$ 8 c.c. | As in (4) | Increased yield of new mineral |
| (7) | Analcite 3·36 g.<br>$BaBr_2$ 10·00 g.<br>$H_2O$ 6 c.c. | As in (4) | As in (6) |
| (8) | Analcite 3·36 g.<br>$BaBr_2$ 10·00 g.<br>$H_2O$ 8 c.c. | Two days at 204° | Extensive recrystallisation, but still some analcite |
| (9) | Analcite 3·36 g.<br>$BaBr_2$ 10·00 g.<br>$H_2O$ 8 c.c. | Two days at 209° | As in (8) |
| (10) | Analcite 3·36 g.<br>$BaBr_2$ 10·00 g.<br>$H_2O$ 15 c.c. | Three days at 225° | Excellent yield. Small amount of analcite only |

TABLE V—*continued*.

Mineral containing KCl.

| Composition. | | Conditions. | Yield. |
|---|---|---|---|
| (1) Analcite | 6·07 g. | 44 hrs. at 235° | Rare crystals of new mineral |
| KCl | 11·52 g. | | |
| $H_2O$ | 7 c.c. | | |
| (2) Analcite | 6·07 g. | As above | As above |
| KCl | 9·98 g. | | |
| $H_2O$ | 7 c.c. | | |
| (3) Analcite | 6·07 g. | As above | Increased yield of new mineral |
| KCl | 7·98 g. | | |
| $H_2O$ | 7 c.c. | | |
| (4) Analcite | 6·07 g. | As above | Yield as in (3) |
| KCl | 5·00 g. | | |
| $H_2O$ | 7 c.c. | | |
| (5) Analcite | 6·07 g. | Two days at 235° | Rare crystals of new mineral |
| KCl | 4·00 g. | | |
| $H_2O$ | 7 c.c. | | |

temperature was always well below the critical temperature of water, liquid water was always present to act as mineraliser. It appears that formation of the minerals containing barium chloride or bromide was favoured by low water : barium salt ratio for a fixed amount of analcite (Table V), while good yields were observed in the temperature range 180—220° (Tables II and V). The influence of temperature upon the yield in the reaction between analcite and aqueous barium bromide is well shown in Table V. The reaction between analcite and aqueous potassium chloride was less complete and the optimum salt : water ratio is similar to this ratio for synthesising the barium chloride-containing mineral.

*Removal of Halide from the New Minerals.*—The ease with which $BaCl_2$, $BaBr_2$, and KCl could be extracted from the minerals suggested that the halide was in interstitial solid solution within the aluminosilicate framework, which was the same, at least for the minerals containing barium halides (Table IV). In further test of this the barium chloride-rich minerals were progressively extracted by heating with distilled water in the autoclaves. The first mother-liquors gave very heavy precipitates with silver nitrate, but as the extraction continued the quantity of halide diminished until it was negligible. Several specimens of the extracted mineral were examined by *X*-ray diffraction, and revealed a slightly contracted form of the parent structure (Table IV, col. 3). The original small rectangular crystals were, however, somewhat pitted, and occasional crystals of another shape were also observed (Fig. 6). The yield of extracted mineral may then have been about 70% of the unextracted mineral. The conditions of extraction are recorded in Table VI.

TABLE VI.

*Extraction of barium chloride from mineral containing it.*

| No. of extractions for removing salt | Volume ratio of water to mineral | Temp. and duration of each extraction. |
|---|---|---|
| 10 | 15 : 1 | 24 Hrs. at 210° |
| 10 | 15 : 1 | As above |
| 10 | 6 : 1 | 2 Days in range 200—270° |
| 6 | 15 : 1 | 2 Days at 270° |
| 7 | 15 : 1 | 36 Hrs. at 208° |

A similar extraction of the barium bromide-rich mineral resulted in a much greater proportion of recrystallisation to crystals of the form shown in Fig. 6, and the yield of barium bromide-free parent mineral was correspondingly decreased. Spacings attributed to the recrystallisation product are indicated in Table IV, col. 4, and are enclosed in square brackets, the corresponding *X*-ray diffraction rings being spotty owing to the larger size of the crystallites, instead of being uniformly dark as for the original and the extracted parent mineral. It was thought that these new crystals might have been harmotome, but a comparison with *X*-ray diffraction spacings derived from a photograph of natural harmotome showed no particular correspondence. The mineral containing potassium chloride was also extracted four times by distilled water at 235°. Extraction proceeded rather more slowly than did the removal of barium chloride and bromide, and the tendency of the aluminosilicate to disintegrate led to the abandonment of this experiment.

The minerals thus freed of barium chloride and bromide were hydrated and zeolitic in character, so that when outgassed they copiously sorbed certain gases and vapours and showed the molecular-sieve characteristics described in the following paper.

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