# **1219.** *Chemistry of Soil Minerals. Part II.*[1] *Reactions of Phosphates with Kaolin and Faujasite*

By R. M. BARRER and D. J. MARSHALL

Under hydrothermal conditions up to 350° kaolin reacted with phosphates and hydroxides of Na, K, and $NH_4$; and sodium near-faujasite with phosphates of Na and $NH_4$. From both aluminosilicates a range of species was obtained which were largely aluminophosphates, and often new phases. These have been characterised by $X$-ray powder photography. In addition aluminosilicates were readily prepared (potash felspar, albite, kalsilite, kaliophilite, muscovite mica, phosphatic and basic cancrinite, basic sodalite, and the zeolites analcite, Na$P$ and Na$S$). Kaolin was a versatile source of such compounds.

IN the previous Paper[1] it was found that phosphate-rich hydrous aluminosilicate gels crystallise as separate aluminosilicates and aluminophosphates, with no observable isomorphous substitutions. Although reactions of aqueous solutions of phosphates of Na,

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[1] Part I, R. M. Barrer and D. J. Marshall, preceding Paper.

K, $NH_4$, and Mg with several soil minerals have previously been shown to produce a variety of alumino- and ferric phosphates,[2-6] no aluminosilicates were identified. A recent Review[7] has, however, summarised a wide range of hydrothermal transformations of analcite ($Na_2O,Al_2O_3,4SiO_2,2H_2O$) to other aluminosilicates, and of converse transformations yielding analcite. Moreover kaolinites, micas, and other clay minerals have been synthesised in various ways from gels and other products, and are known to yield other species in their turn, under hydrothermal conditions.[7] It was therefore thought of interest to examine the reactions of kaolin, and of the alkali-rich zeolite, synthetic faujasite, with aqueous media predominantly rich in phosphates. The results are now reported.

## EXPERIMENTAL

Pure kaolin was supplied by English Clays, and the synthetic near-faujasite (Sieve X) by Linde Air Products. The hydrothermal reactions of these phases were studied using apparatus already described,[1] and the crystalline products were examined by microscope, electron microscope, *X*-ray diffraction, and in a limited number of cases by chemical analysis.

In experiments at 110° and below, 0·4—0·5 g. of kaolin or of faujasite were added to 6—10 ml. of water. Above this temperature the same weight of mineral was usually added to 6 or 7 ml. of water. In each case the required amount of phosphate or of alkali was added. The reactions at 110° or below were normally effected in sealed glass tubes and those above 110° in stainless steel autoclaves.

*Reactions of Kaolin with Potassium Phosphates and Hydroxide.*—Results of some experiments in which potassium phosphates and hydroxide interact with kaolin are summarised in Table 1. The K-bearing solutions readily yielded such aluminosilicates as potash felspar ($K_2O,Al_2O_3,6SiO_2$), kalsilite ($K_2O,Al_2O_3,2SiO_2$), and kaliophilite ($K_2O,Al_2O_3,2SiO_2$). Kalsilite was a common product from more alkaline media (KOH or $K_3PO_4$ solutions). Over shorter times $K_3PO_4$ solutions yielded kaliophilite sometimes admixed with kalsilite or mica. Potash felspar appeared regularly with acid potassium phosphate.

Among the aluminophosphates or phosphates the commonly occurring species was *H*, of composition $K_2O,2Al_2O_3,2P_2O_5,5H_2O$, and previously characterised by Haseman *et al.*[2] The remaining species *M*, *T*, and *K* could not be identified with phosphates previously crystallised[2, 8-11] but their characteristic *X*-ray spacings are given in Table 2. *M* and *T*, which are probably aluminophosphates, result from low-temperature reactions of long duration, and both on ignition to 900° recrystallised to *K*. The aluminosilicates are thus in general hydrothermal products at higher temperatures, but *H*, *M*, and *T* are products of low-temperature reactions. This distinction suggests that at low temperatures the kaolin lattice decomposed to give aluminium hydroxide and silica of which only the alumina then reacted (with phosphate). Only when the medium is very alkaline or the temperature is high does the silica react.

Recrystallisations involving $KH_2PO_4$ and kaolin resulted in corrosion of the autoclaves, giving additional and mostly iron-bearing products. For example, in one of the runs of Table 1, the crystals were at least partially separated by decantation and hand picking. Five species were apparent: potash felspar; light brown, opaque crystals with well-grown faces (*U*); a few very dark brown crystals with less developed, glossy faces (*V*); small bright green crystals of lath-like habit (*W*); and large, well-grown white crystals, often in spherulitic clusters. The *d*-spacings are given in Table 3. Bracketed coincidences between certain spacings of *U* and *V* suggest that *V* is a mixture of two phases.

Despite the diversity of its reactions the kaolin also showed considerable low-temperature stability toward phosphates. Some situations where kaolin did not recrystallise are: $K_3PO_4$ (8 g., 4 g., 2 g., and 1 g. per 10 ml. $H_2O$) at 150° for 4, 8, and 53 days; $K_3PO_4$ (1 g. in

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[2] J. F. Haseman, E. H. Brown, and C. D. Whitt, *Soil Sci.*, 1950, **70**, 257.

[3] M. C. Ford, *J. Amer. Soc. Agron.*, 1933, **25**, 134.

[4] L. E. Ensinger, *Soil Sci. Soc. Amer. Proc.*, 1948, **13**, 170.

[5] P. R. Stout, *Soil Sci. Soc. Amer. Amer. Proc.*, 1939, **4**, 177.

[6] P. F. Low and C. A. Black, *Soil Sci. Soc. Amer. Proc.*, 1947, **12**, 180.

[7] *E.g.*, R. M. Barrer and E. A. D. White, *J.*, 1952, 1561.

[8] J. F. Haseman, J. R. Lehr, and J. P. Smith, *Soil Sci. Soc. Amer. Proc.*, 1950, **15**, 76.

[9] J. P. Smith and W. E. Brown, *Amer. Mineralogist*, 1959, **44**, 138.

[10] F. d'Yvoire, *Bull. Soc. Chim. de France*, 1961, 1762, 2277, 2283.

[11] F. d'Yvoire, *Bull. Soc. chim. France*, **1962**, **1224**, **1237**.

10 ml.) at 105° for 140 days; $K_2HPO_4$ (5 g. in 10 ml.) at 105° for 4 and 32 days; $(NH_4)_2HPO_4$ (5 g. in 10 ml.) at 110° for 7 days; $NH_4OH$ (6 ml. of 0·880 $NH_3$ and 6 ml. $H_2O$) at 110° for 17 days; $H_2O$ at 170° for 3 days. However, although new crystalline phases did not appear in the above instances, there was sometimes weakening of the powder reflections of kaolinite, indicating attack on the crystals. Moreover after still longer times recrystallisation was sometimes observed (*e.g.*, species *M* in Table 1).

TABLE 1

Reactions of kaolin with K-bearing solutions

| Product | Solution and composition | Temp. | Time (days) | Remarks |
|---|---|---|---|---|
| Kalsilite | KOH (2·5 g. in 7 ml.) | 350° | 2 | |
| | $K_3PO_4$ (7 g. in 7 ml.) | 350 | 2 | |
| | $K_3PO_4$ (3·3 g. in 8 ml.) | 350 | 2 | |
| | $K_3PO_4$ ( ,, ,, ) | 300 | 2 | |
| | $K_3PO_4$ ( ,, ,, ) | 250 | 7 | |
| | $K_3PO_4$ ( ,, ,, ) | 350 | 7 | |
| | $K_3PO_4$ ( ,, ,, ) | 350 | 7 | After ignition of product |
| | $K_3PO_4$ ( ,, ,, ) | 250 | 2 | ,, ,, ,, |
| Kalsilite and kaliophilite | $K_3PO_4$ (7 g. in 7 ml.) | 350 | 1 | |
| | $K_3PO_4$ ( ,, ,, ) | 300 | 1 | |
| | $K_3PO_4$ ( ,, ,, ) | 250 | 2 | After treatment with dilute HCl |
| Kaliophilite | $K_3PO_4$ (7 g. in 7 ml.) | 200 | 6 | After product treated with dilute HCl |
| Kaliophilite and muscovite mica | $K_3PO_4$ (7 g. in 7 ml.) | 200 | 2 | After product treated with 2N-HCl |
| Potash felspar | $KH_2PO_4$ (2·5 g. in 7 ml.) | 250 | 3 | |
| | $KH_2PO_4$ ( ,, ,, ) | 300 | 3 | |
| | $KH_2PO_4$ (2·8 g. in 7 ml.) | 300 | 7 | |
| | $KH_2PO_4$ (2·5 g. in 7 ml.) | 350 | 3 | Acid washed product (fine fraction) |
| | $KH_2PO_4$ ( ,, ,, ) | 300 | 3 | ,, ,, ( ,, ) |
| | $KH_2PO_4$ ( ,, ,, ) | 250 | 3 | ,, ,, ( ,, ) |
| | $KH_2PO_4$ ( ,, ,, ) | 350 | 3 | ,, ,, (coarse fraction; not felspar only) |
| | $KH_2PO_4$ (3·2 g. in 8 ml.) | 300 | 2 | With several other species (*U*, *V*, *W*, *X*) |
| Phase with some resemblance to felspar | KOH (0·8 g.) + $KH_2PO_4$ (3·5 g.) in 7 ml. | 350 | 1 | |
| | KOH (0·8 g.) + $KH_2PO_4$ (3·5 g.) in 7 ml. | 300 | 1 | |
| | KOH (0·8 g.) + $KH_2PO_4$ (3·5 g.) in 7 ml. | 250 | 1 | |
| Cancrinite (K-rich) | KOH (2 g. in 10 ml.) | 110 | 17 | Other species also present |
| Aluminophosphate *H* | $KH_2PO_4$ (4 g. in 10 ml.) | 105 | 85 | Small spherulites |
| | $KH_2PO_4$ ( ,, ,, ) | 105 | 97 | ,, ,, |
| | $KH_2PO_4$ (2 g. in 10 ml.) | 105 | 97 | ,, ,, |
| | $KH_2PO_4$ (0·2 g. in 10 ml.) | 105 | 140 | Some kaolin still unreacted |
| Species *M* | $K_3PO_4$ (8 g. in 10 ml.) | 105 | 85 | |
| | $K_3PO_4$ (4 g. in 10 ml.) | 105 | 85 | Larger particle fraction |
| Species *T* | $KH_2PO_4$ (8 g. in 10 ml.) | 105 | 85 | Large spherulites |
| | $KH_2PO_4$ ( ,, ,, ) | 105 | 53 | |
| Species *K* | $KH_2PO_4$ (8 g. in 10 ml.) | 105 | 85 | Larger particles heated to 900° |

*Reactions of Kaolin with Sodium Phosphates and Hydroxide.*—Reactions between kaolin and sodium phosphates and hydroxide are summarised in Table 4. Solutions of $Na_3PO_4$ were sufficiently alkaline to produce phosphatic cancrinite very readily in the range 170 to 350°. In addition a zeolite of the chabazite family (Na*S*)[12] appeared at about 100°. Kaolin also reacted with caustic soda to form basic cancrinite or at lower temperatures, basic sodalite. The synthetic zeolite designated Na*P*,[12] which does not appear to have a natural counterpart, and Na*S*, were also readily formed.

The presence of phosphate in a typical phosphatic cancrinite was demonstrated by washing the crystals carefully with warm water until all extraneous phosphate was removed. Prolonged washing with hot water was avoided since it converted the cancrinite into an amorphous

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[12] R. M. Barrer, J. W. Baynham, F. W. Bultitude, and W. M. Meier, *J.*, 1959, 195.

TABLE 2

*d*-Spacings of *H*, *M*, *T*, and *K*

| *H* | | *M* | | *T* | | *K* | |
|---|---|---|---|---|---|---|---|
| *d* (Å) | Int | *d* (Å) | Int | *d* (Å) | Int | *d* (Å) | Int |
| 6·87 | s | 15·93 | m | 11·01 | s | 6·99 | vvw |
| 6·63 | w | 7·45 | vvw | 8·52 | mw | 6·30 | w |
| 5·50 | m | 6·35 | vw | 5·82 | w | 6·00 | vw |
| 4·89 | m | 5·06 | mw | 5·61 | mw | 5·67 | ms |
| 4·83 | w | 4·14 | s | 4·49 | vw | 5·19 | vw |
| 4·57 | vw | 4·10 | w | 4·31 | vw | 5·10 | vvw |
| 4·32 | vw | 3·97 | w | 4·26 | vw | 4·13 | w |
| 4·28 | w | 3·87 | vs | 4·24 | vw | 4·09 | m |
| 4·15 | m | 3·67 | ms | 4·06 | m | 3·85 | s |
| 3·94 | vw | 3·58 | mw | 3·96 | w | 3·61 | vvw |
| 3·91 | vw | 3·48 | s | 3·86 | m | 3·58 | w |
| 3·81 | vw | 3·18 | s | 3·76 | m | 3·51 | vvw |
| 3·32 | w | 3·08 | w | 3·70 | vw | 3·45 | mw* |
| 3·22 | s | 3·02 | vw | 3·62 | m | 3·40 | mw* |
| 3·16 | m | 2·92 | ms | 3·46 | m | 3·32 | ms |
| 3·09 | mw | 2·90 | ms | 3·33 | vvw | 3·16 | vvw |
| 3·07 | vvw | 2·87 | m | 3·25 | vs | 3·08 | m |
| 3·04 | vw | 2·64 | m | 3·22 | mw | 3·03 | m |
| 2·92 | w | 2·54 | m | 3·19 | vvw | 3·01 | vvw |
| 2·91 | ms | 2·53 | w | 3·16 | w | 2·97 | m |
| 2·79 | ms | 2·473 | mw | 3·14 | vw | 2·93 | s |
| 2·75 | vw | 2·340 | mw | 3·12 | w | 2·89 | vs |
| 2·69 | vw | 2·318 | mw | 3·09 | w | 2·60 | vvw |
| 2·64 | vw | 2·294 | mw | 3·05 | w | 2·58 | mw |
| 2·59 | ms | 2·162 | vw | 3·01 | w | 2·483 | mw |
| 2·56 | w | 2·128 | m | 2·96 | w | 2·419 | mw |
| 2·55 | m | 2·090 | w | 2·94 | s | 2·372 | m |
| 2·50 | vw | 2·075 | w | 2·83 | s | 2·344 | vvw |
| 2·446 | w | 1·815 | mw | 2·78 | w | 2·309 | w |
| 2·421 | vw | 1·790 | w | 2·74 | vw | 2·286 | vw |
| 2·347 | vvw | 1·721 | vvw | 2·69 | vw | 2·273 | mw |
| 2·326 | vw | 1·687 | mw | 2·66 | vw | 2·260 | w |
| 2·293 | w | 1·609 | mw | 2·64 | mw | 2·153 | mw |
| 2·229 | w | 1·551 | mw | 2·61 | vw | 2·108 | mw |
| 2·217 | vw | 1·538 | w | 2·59 | w | 2·059 | m |
| 2·158 | w | 1·522 | w | 2·55 | w | 2·014 | mw |
| 2·125 | w | 1·500 | vvw | 2·51 | vw | 1·994 | w |
| 2·091 | ms | 1·459 | vw | 2·50 | vw | 1·946 | vw |
| 2·040 | w | 1·378 | vvw | 2·493 | vw | 1·926 | m |
| 2·026 | vw | 1·363 | vvw | 2·473 | vw | 1·888 | vw* |
| 1·972 | vvw | | | 2·460 | vw | 1·876 | vvw |
| 1·961 | vw | | | 2·366 | vw | 1·865 | vvw |
| 1·941 | w | | | 2·332 | vvw | 1·846 | mw |
| 1·908 | vvw | | | 2·270 | vw | 1·805 | w |
| 1·875 | vvw | | | 2·230 | vw | 1·779 | vw |
| 1·834 | ms | | | 2·208 | vw | 1·744 | w |
| 1·802 | vvw | | | 2·184 | vw | 1·733 | w |
| 1·782 | vvw | | | 2·171 | vw | 1·711 | mw |
| 1·768 | mw | | | 2·138 | vvw | 1·695 | vw |
| 1·719 | w | | | 2·112 | w | 1·661 | vvw |
| 1·688 | w | | | 2·093 | w | 1·651 | vvw |
| 1·646 | w | | | 2·084 | vw | 1·632 | w |
| 1·630 | w | | | 2·031 | w | 1·582 | vw |
| 1·619 | m * | | | 1·914 | w | 1·560 | vvw |
| 1·588 | vw | | | 1·882 | w | 1·524 | vvw |
| 1·572 | vvw | | | 1·852 | mw | 1·513 | m |
| 1·522 | m * | | | 1·825 | vvw | 1·486 | vw |
| 1·499 | vw | | | 1·813 | vw | 1·467 | mw |
| 1·462 | vvw | | | 1·784 | vvw | 1·434 | vvw |
| | | | | 1·742 | vvw | 1·353 | vw |
| | | | | 1·728 | vw | | |
| | | | | 1·706 | vw | | |
| | | | | 1·507 | w | | |
| | | | | 1·490 | w | | |

* Diffuse.

TABLE 3

Products associated with potash felspar of Table 1

| *U* | | *V* | | *W* | | *X* | |
|---|---|---|---|---|---|---|---|
| *d* (Å) | Int | *d* (Å) | Int | *d* (Å) | Int | *d* (Å) | Int |
| 7·89 | mw | 7·55 | w | 13·31 | vw | 6·19 | w |
| 5·22 | s | 7·09 | m | 6·63 | s | 5·89 | ms |
| 5·05 | vvw | 5·55 | w | 5·31 | vvw | 5·04 | vw |
| 4·33 | w | 4·69 | w | 5·13 | vw | 4·24 | ms |
| 4·16 | m | 4·48 | mw | 4·91 | w | 4·20 | vw |
| 3·31 | m | 4·08 | vvw | 4·45 | w | 3·90 | mw |
| 3·26 | ms | 3·70 | w | 4·30 | m | 3·85 | m |
| 3·16 | w | 3·41 | m | 4·23 | ms | 3·79 | w |
| 3·12 | ms | 3·37 | vvw | 4·11 | ms | 3·63 | m |
| 3·04 | m | 2·98 | vvw | 4·00 | m * | 3·57 | m |
| 3·01 | s | 2·91 | ms | 3·81 | vvw | 3·52 | m |
| 2·95 | mw | 2·88 | m | 3·74 | vvw | 3·46 | m |
| 2·80 | w | 2·74 | w | 3·59 | vw | 3·33 | vw |
| 2·77 | vw | 2·64 | vw | 3·47 | m | 3·29 | vvw |
| 2·66 | m | 2·60 | w | 3·35 | w | 3·23 | ms |
| 2·52 | m | 2·496 | mw | 3·16 | m | 3·14 | vs |
| 2·461 | ms | 2·458 | mw | 3·13 | m | 3·09 | mw |
| 2·324 | vvw | 2·421 | mw | 3·08 | m | 2·99 | vs |
| 2·250 | vw | 2·304 | vvw | 3·05 | w | 2·92 | vvw |
| 2·193 | vw | 2·279 | w | 2·99 | ms | 2·84 | ms |
| 2·158 | mw | 2·231 | vw | 2·97 | w | 2·77 | vvw |
| 2·132 | vw | 2·177 | w | 2·82 | m | 2·74 | m |
| 2·027 | m | 2·090 | vvw | 2·77 | vw | 2·67 | w |
| 2·011 | vvw | 2·052 | vvw | 2·74 | w | 2·62 | vvw |
| 1·918 | vw | 2·040 | vvw | 2·70 | vw | 2·58 | w |
| 1·895 | vvw | 1·904 | vvw | 2·66 | w | 2·53 | w |
| 1·874 | w | 1·773 | vvw | 2·61 | vvw | 2·491 | mw |
| 1·846 | vw | 1·652 | vw | 2·58 | vvw | 2·453 | vvw |
| 1·833 | vvw | 1·547 | vw | 2·56 | s | 2·423 | w |
| 1·818 | vw | 1·523 | vw | 2·448 | mw | 2·378 | vvw |
| 1·803 | vw | 1·459 | vw | 2·359 | w | 2·320 | w |
| 1·687 | w | 1·433 | vw | 2·335 | w | 2·303 | w * |
| 1·623 | w | | | 2·284 | w | 2·269 | mw |
| 1·577 | w | | | 2·256 | vvw | 2·249 | w |
| 1·503 | w | | | 2·221 | w | 2·178 | vw |
| 1·474 | vvw | | | 2·182 | vvw | 2·145 | mw |
| 1·458 | vvw | | | 2·155 | vw | 2·122 | w |
| 1·431 | vvw | | | 2·123 | w | 2·077 | m |
| 1·373 | vvw | | | 2·096 | vvw | 2·065 | w |
| | | | | 1·967 | vvw | 2·009 | vw |
| | | | | 1·767 | mw | 1·988 | w |
| | | | | 1·697 | vw | 1·952 | w |
| | | | | 1·569 | vw | 1·875 | vw |
| | | | | 1·536 | mw | 1·857 | w |
| | | | | 1·520 | w | 1·805 | w |
| | | | | 1·435 | w | 1·795 | vvw |
| | | | | | | 1·785 | w |
| | | | | | | 1·731 | m |
| | | | | | | 1·716 | w |
| | | | | | | 1·703 | m |
| | | | | | | 1·687 | vw |
| | | | | | | 1·631 | mw |
| | | | | | | 1·614 | vw |
| | | | | | | 1·599 | vw |
| | | | | | | 1·588 | vw |
| | | | | | | 1·569 | mw |
| | | | | | | 1·523 | vw |
| | | | | | | 1·501 | mw |
| | | | | | | 1·481 | w |
| | | | | | | 1·456 | w |
| | | | | | | 1·427 | m |

* Diffuse.

TABLE 4

Reactions of 0·5 g. kaolin with Na-bearing solutions

| Product | Solution and its composition | Temp. | Time (days) | Remarks |
|---|---|---|---|---|
| Phosphatic cancrinite | $Na_3PO_4$ (4 g. in 7 ml.) | 350° | 3 | All these products were extracted with hot water till only a slight $PO_4$ test was observed |
| | $Na_3PO_4$ ( ,, ,, ) | 300 | 3 | |
| | $Na_3PO_4$ ( ,, ,, ) | 250 | 3 | |
| | $Na_3PO_4$ ( ,, ,, ) | 170 | 3 | |
| | $Na_3PO_4$ ( ,, ,, ) | 350 | 6 | |
| | $Na_3PO_4$ ( ,, ,, ) | 300 | 6 | |
| | $Na_3PO_4$ ( ,, ,, ) | 250 | 6 | |
| | $Na_3PO_4$ ( ,, ,, ) | 170 | 6 | |
| | $Na_3PO_4$ (3·5 g. in 7 ml.) | 250 | 4 | |
| | $Na_3PO_4$ ( ,, ,, ) | 170 | 4 | |
| | $Na_3PO_4$ ( ,, ,, ) | 250 | 7 | |
| | $Na_3PO_4$ ( ,, ,, ) | 170 | 7 | |
| | $Na_3PO_4$ ( ,, ,, ) | 170 | 11 | |
| | $Na_3PO_4$ (4 g. in 7 ml.) | 250 | 33 | |
| | $Na_3PO_4$ ( ,, ,, ) | 170 | 33 | |
| Basic cancrinite | NaOH (mod. concn., 7 ml.) | 350 | 3 | Large crystals, with *sodalite* |
| | NaOH ( ,, ,, ) | 170 | 3 | |
| Basic sodalite | NaOH (mod. concn., 7 ml.) | 170 | 3 | With *cancrinite* |
| | NaOH (2·5 g. in 10 ml.) | 100 | 10 | With *zeolite* Na*S* |
| | NaOH (5 g. in 10 ml.) | 100 | 10 | |
| | Glycerol (10 ml.) $Na_3PO_4$ (5 g.) | 105 | 48 | |
| Zeolite Na*P* | NaOH (0·5 g. in 10 ml.) | 100 | 10 | Tetragonal variety |
| | NaOH ( ,, ,, ) | 100 | 17 | |
| Zeolite Na*S* | $Na_3PO_4$ (4 g. in 10 ml.) | 110 | 17 | With unchanged kaolin |
| | NaOH (2 g. in 10 ml.) | 110 | 17 | |
| | $Na_3PO_4$ (10 g. in 10 ml.) | 100 | 10 | With unchanged kaolin and species *E* |
| | NaOH (3·75 g. in 10 ml.) | 100 | 17 | |
| | $Na_3PO_4$ (10 g. in 10 ml.) | 100 | 24 | With unchanged kaolin and species *E* |
| Albite | $Na_2HPO_4$ (2·5 g. in 7 ml.) | 250 | 3 | Then boiled with aqua regia + 1 vol. $H_2O$ for 15 min. |
| | $Na_2HPO_4$ ( ,, ,, ) | 300 | 3 | Then acid washed and dried at 105° |
| Aluminophosphate *A* | $Na_2HPO_4$ (2·5 g. in 7 ml.) | 350 | 3 | With species *F* |
| | $Na_2HPO_4$ ( ,, ,, ) | 300 | 3 | With species *B* |
| | $Na_2HPO_4$ ( ,, ,, ) | 250 | 3 | With species *B* |
| | $Na_2HPO_4$ ( ,, ,, ) | 170 | 3 | |
| | $Na_2HPO_4$ ( ,, ,, ) | 240 | 13 | Accompanied by other products, one similar to albite |
| | $Na_2HPO_4$ ( ,, ,, ) | 310 | $>6$ | |
| | $Na_2HPO_4$ ( ,, ,, ) | 240 | 17 | |
| | $Na_2HPO_4$ ( ,, ,, ) | 240 | 18 | |
| Species *F* | $Na_2HPO_4$ (2·5 g. in 7 ml.) | 350 | 3 | With species *A* |
| Species *B* | $Na_2HPO_4$ (2·5 g. in 7 ml.) | 300 | 3 | With *A* |
| | $Na_2HPO_4$ ( ,, ,, ) | 250 | 3 | With *A* |
| Species *E* | $Na_3PO_4$ (10 g. in 10 ml.) | 100 | 10 | With Na*S*, and unchanged kaolin |
| | $Na_3PO_4$ ( ,, ,, ) | 100 | 24 | With Na*S*, and unchanged kaolin |

TABLE 5

Reactions of 0·5 g. kaolin with $(NH_4)_3PO_4$ solutions

| Product | Composition of phosphate solution | Temp. | Time (days) | Remarks |
|---|---|---|---|---|
| Species *G* | 4 g. in 6 ml. $H_2O$ | 350° | 4 | |
| Species *I* | 4 g. in 6 ml. | 300 | 6 | With another phase soluble in dilute HCl. *I* is insoluble |
| | ,, ,, | 250 | 6 | |
| | ,, ,, | 200 | 6 | |
| Species *J* | 4 g. in 6 ml. | 200 | 2½ | Insoluble in dilute HCl |
| Species *K* | 4 g., and 1 g. catechol, in 7 ml. | 250 | 4 | After ignition of product |

product. Analysis of the washed phosphatic cancrinite gave 3·92% of phosphorus, and the weight loss on ignition was 6·0%. If it is assumed that this loss is due to water and that $Na^+$ is the only cation present, these results agree with the formula

$$6(NaAlSiO_4)1{\cdot}47Na_3PO_4,3{\cdot}9H_2O$$

It is interesting that from $Na_3PO_4$ solutions cancrinites, but not sodalites, appeared, in accordance with results of Guth [13] at 250°. Here aluminosilicate gels in presence of multivalent anions yielded only cancrinites; sodalite formed when $OH^-$ or $F^-$ were present. In phosphatic cancrinite the phosphate is present as an intercalated guest species, not as a substitute for Al or Si.

The only phosphate observed when $Na_3PO_4$ solutions reacted with kaolin was *E*. That this is a phosphate or aluminophosphate is indicated because it appeared only when phosphate but not when sodium hydroxide was the mineralising solution. In each case the zeolite Na*S* was also formed.

If the solution contained $Na_2HPO_4$ the reaction pattern changed. Zeolites and felspathoids now failed to appear; only albite ($Na_2O,Al_2O_3,6SiO_2$) was obtained at the higher temperatures (250 and 300°). On the other hand several phases *A*, *B*, and *C* were obtained which had been synthesised previously from phosphate-bearing, hydrous aluminosilicate gels.[1] The *X*-ray diffraction spacings of *E* are recorded in Table 6.

TABLE 6

*d*-Spacings of *E*, *G*, *I*, *J*, and *L*

| *E* | | *G* | | *I* | | *J* | | *L* | |
|---|---|---|---|---|---|---|---|---|---|
| *d* (Å) | Int | *d* (Å) | Int | *d* (Å) | Int | *d* (Å) | Int | *d* (Å) | Int |
| [4·12] * | ms | 8·88 | s | 5·65 | ms | 5·13 | s | 11·44 | m |
| 3·97 | vw | 4·78 | w | 4·11 | w | 4·46 | vvw | 8·30 | vw |
| 3·18 | ms | 4·23 | m | 2·98 | s | 3·34 | vw | 7·90 | mw |
| 2·86 | vvw | 3·39 | mw | 2·96 | m | 3·07 | mw | 6·15 | vw |
| 2·84 | vw | 2·83 | s | 2·497 | w | 2·96 | m | 5·94 | vw |
| 2·69 | m | 2·417 | w | 2·468 | mw | 2·56 | m | 5·74 | w |
| 2·60 | m | 2·349 | w | 2·154 | w | 1·937 | vvw | 5·42 | mw |
| 2·120 | vw | 2·296 | w | 2·127 | w | 1·707 | vw | 5·30 | mw |
| 1·972 | vw | 2·135 | vw | 2·010 | vw | 1·529 | vvw | 5·10 | s |
| 1·402 | m | 1·897 | vvw | 1·975 | w | 1·494 | vvw | 4·52 | ms |
| [1·301] | m | | | 1·877 | w | 1·418 | vvw | 4·34 | w |
| | | | | 1·856 | w | | | 3·82 | w |
| | | | | 1·802 | mw | | | 3·74 | mw |
| | | | | 1·669 | ms | | | 3·29 | w |
| | | | | 1·514 | mw | | | 3·26 | w |
| | | | | 1·480 | w | | | 3·20 | vvw |
| | | | | 1·374 | vvw | | | 3·17 | vw |
| | | | | 1·366 | vw | | | 3·06 | s |
| | | | | 1·355 | vvw | | | 2·95 | m |
| | | | | | | | | 2·92 | w |
| | | | | | | | | 2·56 | mw |
| | | | | | | | | 2·004 | w |
| | | | | | | | | 1·938 | vvw |
| | | | | | | | | 1·706 | w |
| | | | | | | | | 1·599 | vw |
| | | | | | | | | 1·529 | w |
| | | | | | | | | 1·418 | vvw |
| | | | | | | | | 1·365 | vvw |

* Spacings in brackets may belong to another species.

*Reactions of Kaolin with Ammonium Phosphate Solutions.*—In all the experiments conducted between 200 and 350°, of which representative examples are summarised in Table 5, the kaolin completely reacted and bulky products were obtained. *G* and *I* were the result of attack by ammonium phosphate upon the autoclaves, since they appeared also in absence of kaolin. They are therefore iron phosphates or ammonium iron phosphates. *G* appeared as pale green, very thin flakes readily soluble in dilute hydrochloric acid. *I* consisted of well-formed, deep green, chunky crystals. An additional species, also formed by direct attack on the autoclaves, occurred in minor amounts as clear, yellow prismatic or cuboid crystals.

When kaolin was present, *J* (Table 5) was an additional product. The catechol referred to was intended to complex the silica. Catechol (1 g. in 7 ml.) did not, however, fully decompose kaolin after 4 days at 250°, nor produce recrystallisation, but was itself largely decomposed.

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[13] J. L. Guth, Thesis. Univ. of Strasbourg, June 1964.

TABLE 7

Reactions of 0·5 to 0·4 g. of Na-near-faujasite with Na- and $NH_4$-bearing solutions

| Product | Solution and its composition | Temp. | Time (days) | Remarks |
|---|---|---|---|---|
| Analcite | Water only | 250° | 3 | No other product |
| | $Na_3PO_4$ (7 ml. sat. solution) | 250 | 6 | In all cases with species *A* |
| | $Na_3PO_4$ (4 g. in 6 ml.) | 300 | 2 | |
| | $Na_3PO_4$ ( ,, ,, ) | 250 | 2 | |
| | $Na_3PO_4$ ( ,, ,, ) | 200 | 2 | |
| | $Na_3PO_4$ ( ,, ,, ) | 300 | 7 | |
| | $Na_3PO_4$ ( ,, ,, ) | 250 | 7 | |
| | $Na_3PO_4$ ( ,, ,, ) | 200 | 7 | |
| Albite | $Na_3PO_4$ (4 g. in 6 ml.) | 350 | 2 | With *A* |
| Aluminophosphate *A* | $Na_3PO_4$ (4 g. in 6 ml.) | 350 | 2 | With albite |
| | $Na_3PO_4$ (7 ml. sat. solution) | 250 | 6 | In all cases with analcite |
| | $Na_3PO_4$ (4 g. in 6 ml.) | 300 | 2 | |
| | $Na_3PO_4$ ( ,, ,, ) | 250 | 2 | |
| | $Na_3PO_4$ ( ,, ,, ) | 200 | 2 | |
| | $Na_3PO_4$ ( ,, ,, ) | 300 | 7 | |
| | $Na_3PO_4$ ( ,, ,, ) | 250 | 7 | |
| | $Na_3PO_4$ ( ,, ,, ) | 200 | 7 | |
| Species *F* | $Na_3PO_4$ (4 g. in 6 ml.) | 450 | 7 | With *N* |
| Species *N* | $Na_3PO_4$ (4 g. in 6 ml.) | 450 | 1 | |
| | $Na_3PO_4$ ( ,, ,, ) | 450 | 7 | With *F* |
| | $Na_3PO_4$ ( ,, ,, ) | 350 | 7 | With *R* |
| Species *R* | $Na_3PO_4$ (4 g. in 6 ml.) | 350 | 7 | With *N* |
| Species *P* | $(NH_4)_3PO_4$ (5 g. in 7 ml.) | 350 | 1½ | Product after treatment with dilute HCl |
| | $(NH_4)_2HPO_4$ (4 g. in 7 ml.) | 350 | 1½ | |
| Species *J* | $(NH_4)_3PO_4$ (5 g. in 7 ml.) | 300 | 1½ | Product after treatment with dilute HCl |
| | $(NH_4)_3PO_4$ ( ,, ,, ) | 250 | 1½ | |
| | $(NH_4)_3PO_4$ ( ,, ,, ) | 200 | 5 | With *G* and *R* |
| | $(NH_4)_2HPO_4$ (4 g. in 7 ml.) | 300 | 1½ | |
| Species *G* | $(NH_4)_3PO_4$ (5 g. in 7 ml.) | 200 | 5 | With *J* and *R* |
| | $(NH_4)_2HPO_4$ (4 g. in 7 ml.) | 200 | 5 | With *R* |
| Species *Q* | $(NH_4)_2HPO_4$ (4 g. in 7 ml.) | 250 | 5 | Product after treatment with mod. concn. HCl |

After solvent extraction of the product, and ignition of the residue to red heat to complete removal of organic material, the final product was species *K*. It was also formed by ignition of *M* and *T* (Table 1). In an additional experiment a 1 : 1 molar mixture of aluminium hydroxide and silica gel was treated at 110° for 106 days with $(NH_4)_3PO_4$ (4 g. in 10 ml. water). The product, *L*, was not typical of any of the previous phosphates.

Though kaolin evidently reacts with $(NH_4)_3PO_4$ rather readily, no aluminosilicates were recognised among the products. The main *d*-spacings of *G*, *I*, *J*, and *L* are recorded in Table 6.

*Reactions of* Na-*near-faujasite with* Na- *and* $NH_4$-*phosphate Solutions.*—Reactions of the alkali-rich, porous aluminosilicate, synthetic Na-faujasite, were examined to a more limited extent than for kaolin, and as a contrast with kaolin which is non-porous and contains no alkali.

With $Na_3PO_4$ solutions between 200 and 300° faujasite readily recrystallised to the more compact zeolite, analcite, and at 350° to albite, whereas kaolin equally readily formed phosphatic cancrinite over this whole range of temperatures. Analcite and albite were the only two aluminosilicates observed, and each was always accompanied by the aluminophosphate *A*. From 350° upwards albite and *A* were both replaced by the phases *F*, *R*, and *N*. Phases *F* and *A* were also formed by reaction with kaolin (Table 3) and from phosphatic alumina-silica gels.[1]

Just as was the case with kaolin, reaction of faujasite with $(NH_4)_3PO_4$ and $(NH_4)_2HPO_4$ did not yield any identifiable aluminosilicates. However, the formation of phases *G*, *J*, *P*, and *Q* was observed. Of these *G* was the product of reaction with the autoclave alone, and *J* was also obtained with kaolin. The *d*-spacings of the species *N*, *R*, *P*, and *Q* are given in Table 8.

In a number of low-temperature systems the Na-faujasite (0·4 g.) remained unchanged, except for ion exchange: $Na_4P_2O_7$ (0·7 g. in 6 ml.) for 1 and 3 days at 65°; $Na_2KPO_4$ (0·8 g. in 6 ml.) for 1 and 3 days at 65°; $Na_3PO_4$ (4 g. in 6 ml.) for 7 days at 65 and 110°; $(NH_4)_3PO_4$ (3 g. in 7 ml.) for 9 days at 65 and 110°; $(NH_4)_2HPO_4$ (4 g. in 7 ml.) for 9 days at 65 and 110°. The

TABLE 8

*d*-Spacings of species *N*, *R*, *P*, and *Q*

| *N* | | *R* | | *P* | | *Q* | |
|---|---|---|---|---|---|---|---|
| *d* (Å) | Int | *d* (Å) | Int | *d* (Å) | Int | *d* (Å) | Int |
| 8·40 | mw | 8·22 | vvw | 7·87 | w | 9·50 | ms |
| 7·22 | mw | 7·20 | ms | 6·21 | w | 6·04 | ms |
| 5·27 | w | 5·38 | s | 5·42 | vw | 5·44 | vw |
| 4·79 | s | 5·05 | vw | 5·18 | s | 5·38 | ms † |
| [4·05] * | w | 4·93 | mw | 4·23 | w | 5·15 | w † |
| [3·73] | w | 4·53 | mw | 4·14 | vw | 4·47 | vw |
| [3·60] | s | 4·29 | mw | 4·07 | w | 3·24 | mw |
| 2·64 | s | 4·06 | m | 3·44 | w | 3·19 | w |
| 2·60 | s | 3·68 | vw | 3·30 | vw | 3·09 | s |
| 2·52 | s | 3·52 | vw | 3·26 | vw | 3·02 | w |
| 2·259 | vvw | 3·27 | mw | 3·13 | vw | 2·72 | s |
| 2·213 | vw | 3·20 | vs | 3·06 | w | 2·68 | w |
| [2·112] | w | 2·92 | m | 3·02 | s | 2·63 | m |
| [2·049] | w | 2·74 | m | 2·95 | vw | 2·108 | w |
| [1·922] | w | 2·68 | vw | 2·91 | vw | 2·034 | vvw |
| 1·736 | vw | 2·56 | vw | 2·85 | w | 2·013 | vw |
| 1·523 | ms | 2·53 | vw | 2·68 | s | 1·821 | vw |
| 1·485 | ms | 2·383 | w | 2·58 | w | 1·665 | vw |
| 1·465 | w | 2·191 | vvw | 2·51 | ms | 1·591 | vw |
| | | 2·053 | vvw | 2·117 | w | 1·569 | w |
| | | 2·023 | vvw | 2·086 | mw | 1·545 | w |
| | | 1·883 | vw † | 2·037 | w | 1·469 | vw |
| | | 1·788 | vw | 1·794 | vvw | 1·327 | vvw |
| | | 1·764 | vw | 1·772 | vvw | | |
| | | 1·712 | vw | 1·727 | vw | | |
| | | 1·679 | vvw | 1·578 | vw | | |
| | | 1·596 | w | 1·475 | vw | | |
| | | 1·527 | vw | | | | |
| | | 1·456 | vvw | | | | |
| | | 1·429 | vvw | | | | |
| | | 1·399 | vvw | | | | |
| | | 1·372 | vw | | | | |
| | | 1·322 | mw | | | | |
| | | 1·260 | vw | | | | |

* It is not certain whether the bracketed *d*-spacings are those of *N* or of another species.
† Diffuse.

stability of faujasite under ion-exchanging conditions is in line with previous experiments.[14] However, like kaolin, faujasite can be transformed by phosphates into a range of products.

## DISCUSSION

When kaolin is first heated to 230—530° and is then admixed with suitable amounts of caustic soda, hydrous silica, and water, the mixtures have been variously crystallised to synthetic near-faujasites (Linde Sieves X and Y), to the synthetic zeolites Na*A* and Na*P*, and to basic sodalite.[15,16] All these reactions were carried out between room temperature and about 100°. In extension and to some degree in contrast with this work, we have found that at 100 and 110° one can prepare Na*P*, and basic sodalite, and also the zeolite Na*S*, without prior heat treatment of the kaolin and without additions of extra silica. Some of these zeolites have molecular sieve, catalytic, and selective ion-exchange properties of special interest.

The many phosphates or aluminophosphates which were formed were in surprisingly few instances identifiable with previously prepared phosphorus compounds, whether these were obtained by reaction with soil minerals, or by precipitation reactions of mixed salts. Evidently large numbers of phosphates, aluminophosphates, and iron aluminium phosphates can be prepared. In this and previous [1] work some of these phases were of frequent occurrence (for example, *A*, *F*, and *H* and to a lesser degree *B* and *J*).

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[16] U.S.P. 3,119,659/1964.