1218. *Chemistry of Soil Minerals. Part I. Hydrothermal Crystallisation of Some Alkaline* Al_2O_3–SiO_2–P_2O_5 *Compositions*

By R. M. Barrer and D. J. Marshall

In attempts to make viseite and other mineral-type compounds, in which there is substitution of Si by P, the hydrothermal crystallisation has been studied of some magmas containing lime, lime and soda, or soda with phosphorus and aluminium compounds and silica. From these magmas various phosphates (apatite, crandallite, angelite, and scorzalite) and aluminosilicates (montmorillonite, paragonite, analcite, cancrinite, and albite) were crystallised, together with five unidentified species which were probably aluminophosphates, and quartz and cristobalite. No evidence could be found, however, of isomorphous substitution such as $2SiO_4^{4-} \rightleftharpoons AlO_4^{5-} + PO_4^{3-}$ or $SiO_4^{4-} \rightleftharpoons PO_4^{3-} + X^-$ where X^- is a univalent interstitial anion.

Oxygen compounds of phosphorus are often based on tetrahedral units PO_4^{3-}. Various structural similarities exist between phosphates and silicates.[1] The synthetic aluminophosphates [2-6] are numerous, and may sometimes resemble aluminosilicates. Equal numbers of AlO_4^{5-} and PO_4^{3-} tetrahedra yield a variety of neutral framework structures, both anhydrous and hydrated; among the anhydrous forms of $AlPO_4$ are analogues of quartz, cristobalite and tridymite.[2] In three-dimensional networks where any given tetrahedral AlO_4^{5-} or PO_4^{3-} unit shares each apical oxygen atom with one of four other tetrahedra, the oxide formula for the structure must be

$$(M_2O)_{(n-m)}(Al_2O_3)_n(P_2O_5)_m,xH_2O$$

where m, n, and x may vary. However, in a typical aluminophosphate such as taranakite the composition is [6]

$$2(K,NH_4)_2O,3Al_2O_3,5P_2O_5,26H_2O.$$

Because $(n-m)$ is negative, taranakite cannot be analogous to a tectosilicate. The same can be said of many iron and aluminium phosphates, such as those in ref. 5, Table 3.

McConnell [7] has formally represented certain aluminophosphates, such as kehoeite, as composed of units PO_2^+, AlO_2^-, and $H_3O_2^-$, together with the necessary cations for electrical neutrality. The taranakite composition is then

$$2(K,NH_4)^+[3AlO_2,4H_3O_2,5PO_2]^{2-},7H_2O$$

while kehoeite is

$$(Zn^{2+})_{5\cdot5}(Ca^{2+})_{2\cdot5}[16AlO_2,16H_3O_2,16PO_2]^{16-},32H_2O$$

This compound is isostructural with the zeolite analcite

$$(Na^+)_{16}[16AlO_2,32SiO_2]^{16-},16H_2O$$

which has a three-dimensional giant anion with intracrystalline Na^+ and H_2O.

The structural analogies between crystalline silicas and forms of $AlPO_4$ and between

1 H. Brasseur, *Silicates Industriels*, 1961, **26**, 169.
2 F. d'Yvoire, *Bull. Soc. chim. France*, 1961, 1762, 2277, 2283.
3 F. d'Yvoire, *Bull. Soc. chim. France*, 1962, 1224, 1237.
4 J. F. Haseman, E. H. Brown, and C. D. Whitt, *Soil Sci.*, 1950, **70**, 257.
5 J. F. Haseman, J. R. Lehr, and J. P. Smith, *Soil Sci. Proc.*, 1950, **15**, 76.
6 J. P. Smith and W. E. Brown, *Amer. Mineralogist*, 1959, **44**, 138.
7 D. McConnell, *Mineralog. Mag.*, 1964, **33**, 799.

kehoeite and analcite lead one to enquire how far Si and P can replace each other in phosphates and silicates. In viseite,[8] which is also isostructural with analcite, partial replacements occur giving

$$(Ca^{2+})_{10}(Na^+)_2[20AlO_2,12H_3O_2,6SiO_2,10PO_2]^{22-}16H_2O$$

A further compound in which PO_4^{3-} tetrahedra replace some SiO_4^{4-} is griphite,[9] a phosphate garnet, while in apatite, PO_4^{3-} can be partially replaced by $SiO_4^{4-} + SO_4^{2-}$ (wilkeite and ellestadite[10]). Nevertheless such replacements are rare, and the small amounts of phosphorus present in igneous rocks usually appear as apatites.[11]

In the chemistry of soil minerals, reactions between phosphates and aluminosilicates are of special interest, and may throw light on the replacements $OH^- + PO_4^{3-} \rightleftharpoons M^+ + AlO_4^{5-} \rightleftharpoons SiO_4^{4-}$. The hydrothermal method, which is very fruitful in crystallising aluminosilicates,[12,13] is likely to be useful here. It was proposed therefore to employ this method in a study of crystallisation from magmas containing phosphate, alumina, and silica.

Experimental

The apparatus and methods were similar to those employed in a study of some crystallisation fields of alkaline earth aluminosilicates.[14] Above 120° stainless steel autoclaves served as reaction vessels, while below this temperature sealed glass tubes were used. "Syton" 2X was the source of colloidal silica and aluminates or aluminium hydroxide prepared from Al foil were the sources of alumina. Phosphoric acid, aluminium phosphate, and sodium phosphate, supplied the phosphorus, and mixes with water were prepared with appropriate amounts of ingredients together with bases such as quick lime and caustic soda.

After reaction the solid products were filtered off and thoroughly washed. Different species in one product could sometimes be largely separated by suspension and decantation because of differing particle sizes or densities. The compounds obtained were examined in the optical or electron microscope, and by means of *X*-ray diffraction. Guinier powder cameras were used with Cu-K_α radiation. Where appropriate some samples were analysed, and subjected to thermogravimetry.

Results

It was noted previously that viseite, an analogue of analcite with PO_4^{3-} replacing much SiO_4^{4-}, was one of the few mixed frameworks analogous to the aluminosilicates. It was hoped *inter alia* to prepare viseite, and it was during these attempts that the phosphates and aluminosilicates to be described were synthesised.

Lime-bearing Compositions.—Aqueous mixtures having the dry oxide compositions $5CaO,5Al_2O_3,3SiO_2,3P_2O_5$; $2{\cdot}5CaO,Al_2O_3,2SiO_2,P_2O_5$; and $5CaO,5Al_2O_3,2SiO_2,P_2O_5$ were crystallised under conditions such as those given in Table 1, which presents a selection of the runs made. The phosphorus was introduced as concentrated phosphoric acid. A main feature of Table 1 is, first, the dominance of apatite ($Ca_5[(PO_4)_3{\cdot}OH]$), even in the presence of much alumina and silica. Secondly, no novel mixed phases rich in both P_2O_5 and SiO_2 were observed; rather, known phosphate minerals [crandallite, $CaAl_3(PO_4)_2,(OH)_5{\cdot}H_2O$; and angelite, $2Al_2O_3,P_2O_5,3H_2O$] appeared alongside the clay mineral, montmorillonite. Montmorillonite is relatively poor in bases, so that the lime is bound preferentially by the apatite. This means a relatively low pH in the mother liquor, and accounts for the absence of tectosilicates, which (as aluminosilicates) form preferentially from media rich in available bases.[12,13]

The angelite of Table 1*a* formed as crystals of appreciable size, easily separated from accompanying apatite and montmorillonite. The scorzalite (FeO,Al_2O_3,P_2O_5,H_2O) of Table 1*c* was the result of chemical attack on the autoclave at 450°, and was present as blue crystals in small amounts.

8 D. McConnell, *Amer. Mineralogist*, 1952, **37**, 609.
9 D. McConnell and F. H. Verhoek, *J. Chem. Educ.*, 1963, **40**, 512.
10 D. McConnell, *Amer. Mineralogist*, 1937, **22**, 977.
11 B. Mason and T. Berggren, *Geol. Fōren Stockholm Fōrh*, 1941, **63**, 413.
12 R. M. Barrer, *Trans. Brit. Ceram. Soc.*, 1957, **56**, 155.
13 R. M. Barrer, Trans. VIIth Internat. Ceram. Congress, London, 1960, 379.
14 R. M. Barrer and E. A. D. White, *J.*, 1952, 1561.

Lime–soda-bearing Compositions.—Aqueous magmas having the dry weight compositions $Na_2O,5CaO,10Al_2O_3,3SiO_2,3P_2O_5$ and $Na_2O,5CaO,Al_2O_3,4SiO_2 + Na_3PO_4$ were also crystallised, and some of the results are summarised in Table 1*d* and *e*. In the lime-rich but soda-bearing magma of Table 1*d*, hydroxyapatite was still dominant, and excess of alumina appeared throughout as boehmite (Al_2O_3,H_2O). At 300° and above the montmorillonites of Tables 1*a* to *c* were replaced by another layer structure, paragonite mica $\{(Na,\frac{1}{2}Ca)[Al_3Si_3O_{10}(OH)_2]\}$ which is richer in bases than montmorillonite. This reflects the greater alkalinity of magmas containing soda, which is further emphasised by the appearance of the framework aluminosilicate, phosphatic cancrinite $[3(NaAlSiO_4),xNa_3PO_4,yH_2O]$ after 16 days at 250°.

As the proportion of caustic soda was increased and those of lime and alumina reduced, the tectosilicate analcite ($Na_2O,Al_2O_3,4SiO_2,2H_2O$) became dominant, together with the unidentified phase *A*. Apatite is now beginning to be replaced, although near-apatites were observed at 250 and 300°.

TABLE 1

Crystallisation of aqueous suspensions of mixed oxide lime-rich compositions

Temperature (°C)	Time of crystallisation (days)	Crystalline products
(*a*) $5CaO,5Al_2O_3,3SiO_2,3P_2O_5$		
350	5	*Hydroxyapatite* and good *montmorillonite*
300	1	*Hydroxyapatite*, poor *montmorillonite*, and good *angelite*
250	68	Some *hydroxyapatite* and some *crandallite*
(*b*) $2{\cdot}5CaO,Al_2O_3,2SiO_2,P_2O_5$		
350	5	*Hydroxyapatite* and good *montmorillonite*
300	1	*Hydroxyapatite* and poor *montmorillonite*
250	68	Poor *hydroxyapatite* and trace of an unidentified phase
(*c*) $5CaO,5Al_2O_3,2SiO_2,P_2O_5$		
450	2	Some *scorzalite*, *hydroxyapatite*, and some *montmorillonite*
350	3	*Hydroxyapatite* and some *angelite*
300	3	*Hydroxyapatite*, some *angelite*, and little *montmorillonite*
	13	As for 3 days
250	3	*Hydroxyapatite* and *angelite*
	13	As for 3 days
175	13	Very little crystallisation
(*d*) $Na_2O,5CaO,10Al_2O_3,3SiO_2,3P_2O_5$		
450	2	*Hydroxyapatite* and *boehmite*
	7	*Hydroxyapatite*, *boehmite*, and a little *paragonite*
350	7	*Hydroxyapatite*, *boehmite*, and some *paragonite*
	16	As for 7 days
300	7	*Hydroxyapatite*, *boehmite*, and some *paragonite*
	16	As for 7 days
250	7	*Hydroxyapatite* and *boehmite*
	16	*Hydroxyapatite*, *boehmite*, and *cancrinite*
170	7	Little evidence of crystallisation
	16	Trace of *hydroxyapatite*
(*e*) $Na_2O,CaO,Al_2O_3,4SiO_2 + Na_3PO_4$		
300	4	*Analcite*, a near-*apatite* and *species A*
	7	As for 4 days
250	4	*Analcite*, a near-*apatite*, and *species A*
	7	As at 300°
200	5	*Analcite* and *species A*

Soda-bearing Compositions.—Results typical of those obtained with magmas containing soda but no lime are summarised in Table 2. The compositions of Tables 2*a* and 2*b* contained 5 g. of Na_3PO_4 in addition to 0·5 g. of the oxide mixtures in 7 ml. of water. That of Table 2*c* was made by dissolving $AlPO_4$ in H_3PO_4 and neutralising the solution with caustic soda. The required amount of colloidal silica was then added, the pH brought to 9 with NaOH, and the mixture diluted. The compositions of Tables 2*d* and 2*e* were prepared from $AlPO_4$ with appropriate additions of Na_2HPO_4 and colloidal silica in the first instance; and with additions of

Na_3PO_4, colloidal silica and caustic soda in the second. $AlPO_4$ was also used to prepare the mixtures of Table 2*f* and 2*g*.

In mixes where Al_2O_3:SiO_2 = 1 : 4, as in analcite, this zeolite tended to be a dominant phase (Tables 2*a*, *b*, and *f*), even with considerable variations in the proportions of other components. If the proportion of alkali was increased, and the Al_2O_3 : SiO_2 ratio altered to 2 : 4 or 3 : 4, cancrinite became an important phase. Both analcites and cancrinites were very reproducibly formed in large numbers of experiments, of which Table 2 is merely illustrative. A sample of the cancrinite of Table 2*e*, submitted to thermogravimetric analysis, showed a weight loss of 8·5%. Thus, as in basic cancrinites previously made,[14] these crystals contain considerable water.

Species *A* was still found as a minor product in the soda-bearing magmas of Table 2*b*, in presence of excess of phosphate and considerable alkali. Three new phases, *C*, *D*, and *F*, which are probably aluminophosphates, appeared among the products, *C* and *D* always being found together. A requirement for their appearance is a high alumina : silica ratio (4 : 1 and 1 : 1). The species *A*, *B*, *C*, *D*, and *F* were characterised by means of *X*-ray powder

TABLE 2

Crystallisation of aqueous suspensions of soda-containing mixed oxide compositions

Temperature (°c)	Time of crystallisation (days)	Crystalline products
(*a*) $Na_2O,Al_2O_3,4SiO_2$ + excess of Na_3PO_4		
300	2	*Analcite*
	4	*Analcite*
250	2	*Analcite*
	4	*Analcite*
(*b*) $2Na_2O,Al_2O_3,4SiO_2$ + excess Na_3PO_4		
300	$\frac{1}{2}$	*Analcite* and some *species A*
	2	*Analcite*, trace of *species A*, *species B*
250	2	*Analcite*, moderate *species A*; trace *albite*
200	4	*Analcite*, moderate *species A*; trace *albite*
(*c*) $Na_2O,4Al_2O_3,SiO_2$ + Na_3PO_4		
440	4	*Species A*, some *albite*, and *species F*
	11	*Species C* and *albite* (both poorly crystalline)
340	4	*Species C* and *species D*
	11	*Species C*, *species D*, and " *quartz* "
300	4	*Species C*
	11	*Species C* and *D* and " *cristobalite* "
250	4	*Species C* and *D*
	11	*Species C* and *D*
200	4	*Species C* and *D*
(*d*) $3Na_2HPO_4,2AlPO_4,2SiO_2$		
340	2	*Species C* and *D*
200	2	*Species C* and *D*
(*e*) $3Na_3PO_4,2AlPO_4,2SiO_2,6NaOH$		
340	2	*Species A* and *cancrinite*
300	2	*Cancrinite*
250	2	*Cancrinite*
(*f*) $4Na_2O,AlPO_4,2SiO_2$		
340	1	*Analcite*
300	2	*Analcite*
250	2	*Analcite*
(*g*) $4Na_2O,AlPO_4,2SiO_2,Al_2O_3$		
340	1	*Analcite* and *cancrinite*
300	2	*Analcite* and *cancrinite*
250	2	*Analcite* and *cancrinite*

photographs. *d*-Spacings and visual intensities are recorded in Table 3. The compound *A* melted to a glass at about 950°. Partial analysis was made of a sample containing some albite. Assuming that the albite had its usual formula, a possible composition for *A* is $3Na_2O,Al_2O_3,3P_2O_5,H_2O$.

Discussion

The analcites prepared from phosphate-rich sodiferous magmas gave *X*-ray powder patterns indistinguishable in intensity or *d*-spacings from those of analcites crystallised in absence of phosphate, a number of which were also synthesised in additional experiments. According to McConnell[8] the R.I. of the phosphatic defect-rich analcite, viseite, is 1·53; that of ordinary analcites is 1·48—1·49. The R.I.'s of ten of the analcites of this work were measured and all lay in the range 1·48—1·49, showing that no measurable substitution of $OH^- + PO_4^{3-}$ for SiO_4^{4-} had occurred. The hydrothermal conditions used are thus not suitable for forming viseite, and the requirements for this synthesis remain unknown.

The " quartz " and " cristobalite " structures referred to in Table 2 may be dimorphs of $AlPO_4$ or of SiO_2, or they may be of intermediate compositions. In a subsidiary group of experiments quartz-like $AlPO_4$ was readily synthesised hydrothermally from alumina and phosphoric acid at 450°, and from aqueous mixes of dry oxide composition

TABLE 3

d-Spacings of some unidentified crystals

Species *A*		Species *B*		Species *C*		Species *D*		Species *F*	
d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
7·68	m	4·27	vw	7·59	m	4·60	mw	4·50	vw
7·38	m	4·02	vw	6·98	mw	4·11	vw	4·40	w
5·83	w	3·98	ms	6·40	vw	4·05	vw	3·69	m
5·30	w	3·88	mw	4·83	vs	3·69	ms	2·73	s
4·80	vs	3·82	ms	3·52	mw	3·40	ms	2·71	s
3·59	s	3·68	ms	3·19	ms	3·34	w	1·879	mw
2·65	vs	3·50	ms	3·14	s	3·04	ms	1·849	m
2·57	s	2·89	vw	2·58	vs	2·96	vw	1·735	m
2·55	vs	2·87	vvw	2·481	vs	2·80	vw	1·700	m
2·427	w	2·83	vvs	1·948	m	2·73	ms	1·504	w
2·396	w	2·76	w	1·762	s	2·54	vw	1·448	w
2·268	mw	2·68	vs	1·287	m	2·431	m	1·424	mw
2·219	mw	2·409	ms			2·359	mw	1·414	mw
1·736	ms	2·209	vvw			2·303	ms		
1·520	m	2·193	vvw			2·226	w		
1·489	ms	2·171	m			2·191	vvw		
1·449	m	2·121	vw			2·171	w		
1·319	w	2·099	vw			2·155	vw		
1·282	mw	2·078	vw			2·069	ms		
1·257	w	2·059	vw			2·051	m		
		2·023	vw			2·003	mw		
		2·009	vw			1·920	w		
		1·983	s			1·894	m		
		1·960	vvw			1·861	mw		
		1·942	vvw			1·818	vvw		
		1·933	mw			1·799	vvw		
		1·759	mw			1·747	mw		
		1·637	vw			1·699	vvw		
		1·606	ms			1·687	vw		
		1·584	ms			1·661	w		
		1·465	ms			1·633	vw		
						1·568	s		
						1·539	mw		
						1·523	mw		
						1·499	s		
						1·478	m		
						1·464	vw		
						1·444	w		

$SrCl_2,Al_2O_3,P_2O_5,2SiO_2$ at the same temperature. The latter mixture, and likewise $SrCl_2,SrO,Al_2O_3,P_2O_5,2SiO_2$, also yielded strontium near-apatites in runs of 5 days at 450°. It was not possible to establish chemically whether any substitution $AlO_4^{5-} + PO_4^{3-} \rightleftharpoons 2SiO_4^{4-}$ occurred in the quartz-like $AlPO_4$ because of contamination of these crystals by other solids. However, the R.I. of the " quartz " was $>1{\cdot}5519$, which is nearer to that of true quartz ($\varepsilon = 1{\cdot}544$, $\omega = 1{\cdot}553$) than of quartz-like $AlPO_4$ ($\varepsilon = 1{\cdot}530$, $\omega = 1{\cdot}524$).

The *X*-ray pattern was also that of true quartz rather than that of quartz-like $AlPO_4$, so that substitution of Al + P for 2Si must be very restricted if it occurs at all. The R.I. of the " cristobalite " was $\leqslant 1{\cdot}488$, again very close to that of silica cristobalite.*

The third possibility of isomorphous substitution arises among the apatites. The series apatite–wilkeite–ellestadite shows increasing substitution of $SO_4^{2-} + SiO_4^{4-}$ for $2PO_4^{3-}$.[10] However, comparison of the *d*-spacings of several of the hydroxyapatites of this work with those of ellestadite and of fluorapatite did not allow any clear distinction to be made. Ellestadite was perhaps a little closer to our hydroxyapatites than was fluorapatite, but even this was not true of all spacings. Nor could the presence of Si in the hydroxyapatites be established by chemical analysis, because of their contamination by other solids.

Although from known compounds Si–O–Si, Al–O–Si, and Al–O–P bonds are all strong, yielding stable structures based on the tetrahedral units XO_4 (X=Si, Al, or P), the evidence is that Si–O–P bonds of similar strength do not form with Si and P in tetrahedral co-ordination. The present work suggests that magmas containing phosphate, alumina and silica can give separate aluminophosphates and aluminosilicates but not silicophosphates. It was thought that, by introducing sufficient alumina, phosphorus might appear in sequences such as Al–O–P–O–Al–O–Si in which direct P–O–Si bonds are avoided. However, Table 1 shows that in these circumstances the excess of alumina crystallised out separately as boehmite (Al_2O_3,H_2O).

True analogues of aluminosilicates would be silicophosphates of formula

$$(X^-)_n[nP_2O_5,mSiO_2]^{n+}$$

where X^- is a univalent ion such as OH^- or F^-. If hydrated porous frameworks analogous to zeolites could be synthesised they should be crystalline anion exchangers. On the other hand substitutions of the type $2SiO_4^{4-} \rightleftharpoons AlO_4^{5-} + PO_4^{3-}$ in $AlPO_4$ should lead to uncharged frameworks. Although we have not demonstrated either of the above possibilities, they appear to merit further study.

This work was sponsored by the Agricultural Research Council. One of us (D. J. M.) acknowledges a Senior Research Assistantship.

PHYSICAL CHEMISTRY LABORATORIES, CHEMISTRY DEPARTMENT,
IMPERIAL COLLEGE, LONDON S.W.7. [*Received, April* 26*th*, 1965.]

* We are indebted to Mr. L. W. R. Dicks of this department for observations on the R.I.