the ultimate strength of portland cement paste is related to the $Ca(OH)_2$ that fills the originally water-filled space. The pseudomorphs of the original cement grains are often completely embedded in the crystalline $Ca(OH)_2$ matrix (Fig. 2b), thus permitting the crystalline $Ca(OH)_2$ to transmit the applied load within the microstructure.

Electron optical studies reveal primarily the formation and growth of the outer products, and the nature and origin of the inner product is not known. The existence of inner products and formation of pseudomorphs, suggested by light microscope studies (*3*, *6*), have not been regarded as fundamental processes in the hardening of portland cement. Brown (*3*) suggested the term "pseudomorphous hydration" for the growth of the inner product, and indicated that it was responsible for the usefulness of portland cement concrete as a construction material. He pointed out that pseudomorphous hydration takes place without significant changes in the imposed external dimensions.

In explaining why this process was important, Brown stated: "If the cement particles in the mix ever lost significantly their mechanical resistance or rigidity, the external boundaries of the mass could not be expected to remain fixed." Our micrographs give the first clues to the structure of the inner product, and suggest that pseudomorphous hydration should be investigated further.

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7. Specimen preparation for Figs. 1 and 2: Cast 2 June 1964, sealed in butyrate tubes until age 3 days, then mold was stripped, and specimens were immersed in distilled water in covered polystyrene bottles. On 27 June 1964, age 25 days, specimens were scraped of $Ca(OH)_2$ on exterior and were coated with epoxy resin; put under triaxial compression until 19 May 1966, age 2 years, and were stored in desiccator until used.
8. I thank L. Trescony and M. Nemanic for their assistance in carrying out these experiments, and A. Klein for preparing the pure $3\,CaO \cdot SiO_2$. The microscope used for this study was in the Electronics Research Laboratory, University of California; it was purchased under grant GB-6428 from NSF, and is operated under grant GM15536 from NIH.

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Aluminum-Rich Apatite

Abstract. *More than 25 atomic percent of aluminum can susbtitute for other cations in the structure of apatite* $[A_{10}(XO_4)_6Z_2]$. *Such a synthetic product was obtained by expelling volatile constituents* (H_2O *and F*) *from morinite during thermal treatment. Infrared absorption spectra, chemical analysis, and x-ray powder diffraction demonstrate that the aluminum has two coordination numbers, and more than twice as much aluminum substitutes for calcium* (A *position*) *as for phosphorus* (X *position*).

Significant advances in the knowledge of the substitution of vicarious elements in the apatite structure $[A_{10}(XO_4)_6Z_2]$ have taken place in recent years through analysis of both synthetic and natural substances. The incorporation of rare earths, divalent tin, sodium, strontium, and so forth, as substitutes for calcium in the A position with coordination number (CN) 7 to 9 is not particularly surprising, since the charge of the cation X with $CN = 4$ (ordinarily phosphorus) can either increase or decrease. (In ellestadite it does both, that is, the 6 P^{5+} are replaced by 3 S^{6+} + 3 Si^{4+}.)

The case of aluminum is not so readily resolved. Bredig *et al.* (*1*) claimed to have introduced Al into the apatite structure, but their interpretation concerning its CN is not reconciled with suitable data or with adequate structural theory. Pieruccini (*2*) stated that the maximum amount of Al_2O_3 that can be incorporated in the apatite structure is probably 2 percent. Again, there is little basis for deciding whether the Al has $CN = 4$, $CN \geqq 6$, or both.

It might be assumed that Al has two different types of coordination in apatite, that is, that Al can substitute for both Ca and P. The radius of Al^{3+} is very considerably smaller than that of Ca^{2+}, but it is considerably larger than that of P^{5+}. On the basis of $CN = 6$, Ahrens (*3*) has calculated the radii of interest to be (in angstroms) those in the first row of values:

Ca^{2+}	Na^{+}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}
0.99	0.97	0.51	0.42	0.35	0.30
		0.48	0.39	0.33	0.28
1.02	1.00	0.53			

The correction for other CN suggested by Goldschmidt *et al.* (*4*) has been applied by multiplying Ahrens' radii by 0.94 (for $CN = 4$, second row of values) and 1.03 (for $CN = 8$, last row). Comparable radii for Al with different coordination numbers have been observed (*5*).

Morinite, a rare pegmatite phosphate, has the composition shown in Table 1 (column I). On heating this in air above 400°C, Fisher (*6*) found that it yielded an apatite phase which carried Na, F, and Al. When heated as described in Table 1, this was the only phase produced (as shown by the x-ray diffraction maxima from the powder); it carried 3.45 percent F, as is given in analysis II in Table 1. Because of its very high Al content, it should shed further light on this problem. Fisher (*6*) gives a structural formula which indicates nearly 3 Al atoms substituting for Ca for each Al substituting for P.

In order to obtain a clearer description of the structural model, a few assumptions are necessary: (i) the unit cell contains 26 anions ($O + OH + F = 26$), there being no possible vacancies; (ii) all cationic positions are filled ($Ca + Na + Al + P = 16$); and (iii) there is a charge balance for anions and cations. The basis for assumptions (i) and (iii) has been discussed elsewhere (*7*). The necessity for (ii) arises from the analysis per se; there is already an apparent excess of cations if (i) and (iii) are correct. When the cations are summed to 16 their charges total merely 48, whereas the necessary minimum is 50 for fluorapatite (24 oxygen plus 2 fluorine ions). However, if F were substituted for O in two of the $6(XO_4)$ ions in a fluorapatite, the charges could sum to only 48, still satisfying both electrical and spatial requirements.

Although we are unable to explain the deficiencies in cationic charges assuming 16 cations per unit cell, these 16 cationic structural sites may be accounted for as follows:

10 Ca are represented by 4.5 Ca + 2.3 Na + 3.2 Al;

6 P are represented by 4.5 P + 1.5 Al.

However, inasmuch as Fisher's earlier conclusions seemed to require more thorough justification, a new sample of Black Hills morinite was heated in a Pt foil envelope for 2 days at 535°C and overnight at 650°C; this resulted in a weight loss of 10.35 percent; it was subsequently heated in an open boat for 2 days at 650°C and 2½ days at 700°C; total weight loss was about 17 percent. This sample, on analysis, contained merely 1.86 per-

Table 1. Chemical analyses (recalculated, $\Sigma = 100$ percent). I, Morinite, Hugo Mine, Black Hills, South Dakota. II, Same, but large sample heated in air to 535°C for 46 hours and then to 650°C for overnight. Apatite structure; probable weight loss of about 18 percent. (Analyses I and II by Alex Volborth.) III, Same as I, assuming no H_2O and 1.86 percent F. IV, Same as I, assuming no H_2O and 3.45 percent F; compare with column II.

Constituent	I	II	III	IV
CaO	23.55	28.15	28.27	28.00
Na_2O	6.61	7.91	7.94	7.86
Al_2O_3	22.29	26.07	26.73	26.50
P_2O_5	29.98	35.87	35.98	35.64
F	13.28	3.45	1.86	3.45
H_2O+	9.88			
Sum	105.59	101.45	100.78	101.45
−O for F	5.59	1.45	0.78	1.45
Total	100.00	100.00	100.00	100.00

cent F and < 0.03 percent water (*8*). The cationic contents of this material (column III of Table 1) were considered to be essentially similar to those of the original preparation. Background scattering on the x-ray powder diffraction pattern of the new sample is unusually low, and all lines with $d > 1.40$ Å are attributable to apatite with $a = 9.38$ and $c = 6.89$ Å. No appreciable quantity of glass could have been present or such an excellent pattern would not have been produced. Examined under the polarizing microscope, the heated morinite is a very fine-grained, largely polycrystalline powder. This has exceedingly low birefringence, showing between crossed polars gray and black with a speckled appearance. This type of study does not serve to prove that no glass is present. About 10 percent of the grains are fragments of clear single crystals with index of refraction values to match fluorapatite.

At least two considerable differences are apparent on comparing the infrared absorption spectra (Fig. 1) of this Al-rich apatite (M, M′) with fluorapatite (F, F′) and hydroxyapatite (H). A moderately strong absorption occurs at a mean wavelength of about 11.7 μ (855 cm^{-1}); it is interpreted to be the stretching vibrations of the XO_4 configuration when Al replaces the P atom (*9*). The other difference is a narrow and weak absorption at 15.6 μ (640 cm^{-1}) which is absent for fluorapatite, but resembles an absorption observed at a slightly greater wavelength for hydroxyapatite. It is not believable that this absorption arises from < 0.03 percent of water in view of the requirement of 1.79 percent water for hydroxyapatite. A straightforward interpretation of this absorption does not seem possible, but it is suggested that such a phenomenon could arise from substitution of Al in sites with higher coordination number ($CN \geqq 6$). Such interpretations are reasonably consistent with the results of recent works on Al-containing minerals (*10*).

In addition to these more specific, tentative conclusions, a further implication arises from the infrared spectra that tends to confirm the conclusion, obtained from the x-ray diffraction data, that essentially all of the constituents are present in a crystalline phase with the apatite structure: namely, that there is no significant amount of glass present. This implication arises from the general similarities among the three spectra, as well as the fairly well-defined differences. Although the band at 11.7 μ in M and M′ of Fig. 1 is rather broad, this is to be expected because of the low symmetry of such tetrahedral groups.

The Al-rich apatite is also deficient in (F + OH) with respect to the two structural sites normally occupied by OH or halogens. This may indicate the existence of oxyapatite (*11*), but there is no direct evidence. Similar difficulties arise in conjunction with the interpretation of Cr-bearing apatites (*12*).

If it is assumed that the sodium is not essential, the compositional (but not structural) substitution can be considered in terms of successive $Ca_2PO_4^+$ units of fluorapatite being replaced by $Al_2AlO_4^+$, leading to a theoretical series each member of which has a charge total of 50. This series has five Al-bearing members, the last of which has no Ca and only one P. However, if they were isotypic with apatite, the members of this series obviously would require their Al atoms to have coordination numbers either larger or smaller than the usual CN = 6. Thus their stable existence is highly improb-

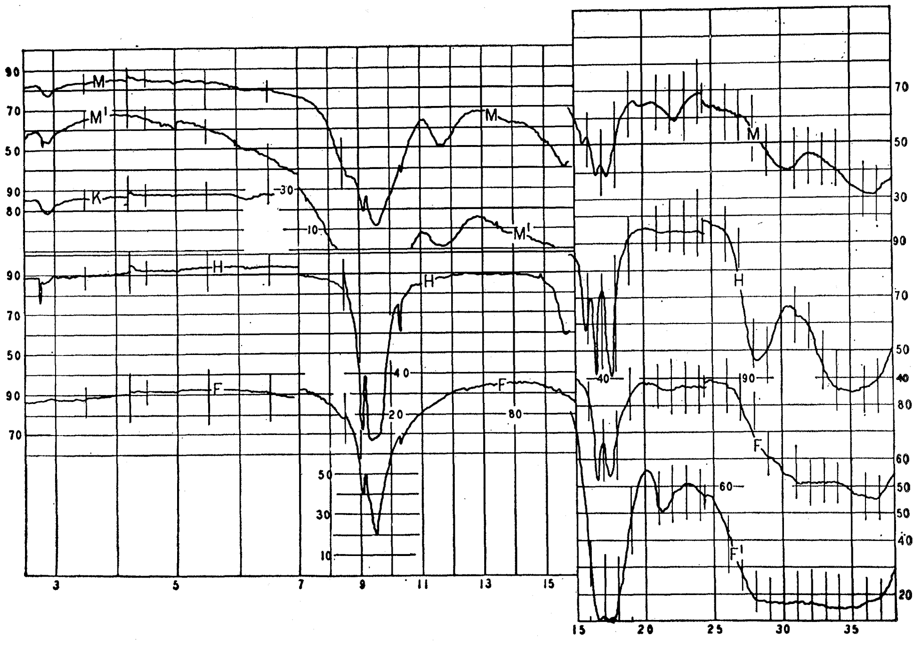

Fig. 1. Infrared spectra of three phosphate specimens (*9*). Abscissa shows wavelengths in microns; ordinate is transmittance (lines spaced at 10 percent intervals). Sampling method: KBr pellet. Reference beam contained KBr pellet for samples F, F′, and H. No reference pellet for M or M′. Perkin-Elmer, model 237, with grating optics for 2.5- to 7.0-μ and 7.0- to 16.0-μ ranges; model 21 with CsBr prism for 15.0- to 38.0-μ range. Filter interchanges at 4.2, 8.4, and 24.3 μ. F, Igneous fluorapatite from Missouri, 0.4 mg/400 mg; F′, same, except 5.0 mg/400 mg; H, synthetic hydroxyapatite, 0.4 mg/400 mg; K, KBr; M, heated morinite (Black Hills), 0.6 mg/400 mg; M′, same, except 5.0 mg/400 mg.

able. Our heated morinite lies between $Ca_8Al_2(PO_4)_5(AlO_4)F_2$ and $Ca_6Al_4(PO_4)_4(AlO_4)_2F_2$ (as far as Al content is concerned) and may contain as much Al as this structure will tolerate.

Inasmuch as the stereochemistry (structure and composition) is controlled primarily by those cations with high charges and low coordination numbers, it is surmised that the sodium plays a subordinate role, merely governing in a minor way the relative distribution of the Al between sites with $CN = 4$ and $CN > 6$. The surprising fact is the absence of any pronounced changes in the spacings and relative intensities of the powder diffraction maxima. This phenomenon suggests that the substitution of Al in both Ca and P sites is probably random, rather than ordered.

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Glycosphingolipids with Lewis Blood Group Activity: Uptake by Human Erythrocytes

Abstract. *The Lewis blood group antigens of the human erythrocyte are acquired from plasma and not synthesized* in situ. *Although assumed previously to be glycoproteins, the Lewis antigens in plasma are glycosphingolipids which are taken up by the erythrocyte membrane from lipoproteins or from aqueous dispersions.*

The Lewis blood group antigens, Le^a and Le^b, are found on erythrocytes, in plasma, and in mucous secretions (*1*). In secretions these antigens occur in the form of glycoproteins whose specific antigenic determinants are oligosaccharide chains attached to a peptide backbone (*2*). The Lewis antigens on erythrocytes are acquired from the plasma and are not synthesized *in situ* (*3, 4*), and it has been assumed, without direct evidence, that the plasma and erythrocyte substances, are also glycoproteins. Hakomori (*5*) has isolated a glycosphingolipid with Le^b activity from erythrocyte stoma, and we now present data indicating that the Lewis antigens in plasma are also glycosphingolipids.

Samples of human plasma were assayed for their content of Le^a and Le^b antigens by hemagglutination inhibition, with the use of goat antiserum to Le^a and Le^b antigens (*6*). The lipoproteins were separated from plasma by ultracentrifugal flotation (*7*) and assayed for Lewis antigens (Table 1). The lipoprotein fractions were strongly antigenic, and the plasma from which lipoprotein had been removed contained little or no antigen. The Lewis antigens were present in both low-density ($d < 1.063$) and high-density ($d = 1.063$ to 1.21) lipoproteins.

Whole plasma and plasma fractions were tested for their ability to transfer the Lewis antigens to Lewis-negative erythrocytes (*3*). After incubation in whole plasma or lipoprotein fractions containing this antigen, Lewis-negative erythrocytes were agglutinated by antiserum to Le^b (Table 2), but after incubation in plasma depleted of lipoproteins such erythrocytes were not agglutinated by antiserum to Le^b. The specificity of this agglutination was demonstrated by specific inhibition with a glycoprotein containing both H and Le^b antigens isolated from ovarian cyst fluid (*6*). Similar results were obtained with plasma and lipoproteins containing Le^a antigen. Erythrocytes can acquire the Le^a and Le^b antigens from plasmas whose antigen content is too low to be detected by hemagglutination inhibition, but Lewis antigens can be demonstrated in these plasmas by concentration of the lipoprotein fraction.

Group O plasmas with Le^a and Le^b activity were pooled separately and low-density lipoproteins ($d < 1.063$) were precipitated with dextran sulfate and $CaCl_2$ (*8*); the precipitate was redissolved in a small volume of 10 percent sodium citrate, *p*H 7.4, and extracted with 19 volumes of chloroform-methanol (2:1). The washed extract (*9*) was applied to a column of silicic acid which was developed with the following solvent systems: chloroform-methanol (9:1), acetone-methanol (9:1), chloroform-methanol (8:2), acetone-methanol (8:2), and chloroform-methanol mixtures containing from 30 to 100 percent methanol. Most of the antigen was eluted with acetone-methanol (8:2), and the eluate was applied to another silicic acid column. This column was developed with increasing proportions of methanol in chloroform, and the antigen was eluted with chloroform-methanol (6:4). The antigen was further purified by preparative thin-layer chromatography on a silica-gel H adsorbent. The active preparations were still impure and contained a mixture of glycosphingolipids but no detectable phospholipids; the antigenic activity was not affected by mild alkaline hydrolysis (*10*). Paper chromatography of an acid hydrolyzate showed the presence of sugars with the mobility of fucose, galactose, glucose, and glucosamine.

After the organic solvent was removed by evaporation, the dried glycolipids were readily dispersed in saline. The resulting optically clear solutions were active in hemagglutination inhibition and in transferring Lewis antigenicity to Lewis-negative red cells (Table 2). After incubation overnight in 1 μg of the crude glycolipid, Lewis-negative cells were intensely agglutinated by