low MgO (< 8.3 percent) content. I am aware of only one stony meteorite with a comparable content of Al_2O_3 and CaO. This is the Angra dos Reis meteorite which fell near Rio de Janeiro, Brazil, in 1869 (*14*).

Since the number of silicate spherules recovered from the Tunguska impact area is only a small fraction of the number of metallic spherules (*15*), the silicate spherules should probably be compared to the silicate portion of stony-irons or to the silicate inclusions in iron meteorites. However, the mineralogy of the stony-irons suggests that they also contain more MgO and less CaO and Al_2O_3 than the Tunguska spherules. According to Mason, the composition of silicate inclusions in iron meteorites resembles that of the chondritic meteorites (*16*). Thus, the Tunguska spherules do not seem to resemble silicate inclusions in iron meteorites.

A comparison with microtektites shows that only one of the spherules (sample 753) has a composition similar to that of the microtektites of Australasia or the Ivory Coast; this spherule has an anomalously high K_2O content (Table 1, Fig. 1).

The possibility that the silicate spherules are an industrial contaminant, such as fly ash, or are soil or rock fused by a forest fire cannot be completely disregarded. However, their association with magnetic spherules, whose pattern of distribution suggests that they were produced by the explosion of the Tunguska meteorite, suggests that the silicate spherules are also residue from the Tunguska meteorite. Some authors believe that the Tunguska event was the result of the explosion of a small comet in the atmosphere (*2, 17*). If this is true, then the data reported here may constitute the first analyses of the siliceous residue of a comet.

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7. Five of the Tunguska silicate spherules were obtained from the Committee on Meteorites of the Soviet Academy of Sciences through the assistance of Drs. E. L. Krinov and O. A. Kirova. Four additional silicate spherules from the Tunguska impact area were obtained from Dr. W. A. Cassidy, who had previously obtained them from the same source.
8. The analyses were performed with an electron microprobe x-ray analyzer (Applied Research Laboratories). The measurements were made at 20 kv and 0.03 μa. The methods, standards, and instrument are the same as those used by L. S. Walter [*Geochim. Cosmochim. Acta* **31**, 2043 (1967)]. The analyses given in Table 1 are corrected for background and instrument drift.
9. The chemical composition of commercial slags varies within relatively narrow limits. Analyses of the slags from most American blast-furnaces (based upon examination of hundreds of analyses) fall within the following percentage range: SiO_2, 33 to 42; Al_2O_3, 10 to 16; CaO, 36 to 45; MgO, 3 to 12; S, 1 to 3; FeO, 0.3 to 2; MnO, 0.2 to 1.5 [G. W. Josephson, F. Sillers, Jr., D. G. Runner, *U.S. Bur. Mines Bull. 479* (1949)].
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13. According to Glasstone, it would take an 80-μ particle (with a density of 2.5 g/cm^3) only about 6 hours to fall from an altitude of 36,600 m; the larger silicate spherules (350 μ) would take less than an hour to fall from that height. Thus it is unlikely that the silicate spherules could have been carried very far by winds [S. Glasstone, *The Effects of Nuclear Weapons* (U.S. Atomic Energy Commission, Oak Ridge, Tennessee, 1962)].
14. The percentage chemical composition of the Angra dos Reis meteorite is: SiO_2, 43.94; Al_2O_3, 8.73; FeO, 8.28; Fe_2O_3, 0.31; MgO, 10.05; CaO, 24.51; Na_2O, O.26; K_2O, 0.19; TiO_2, 2.39; and P_2O_5, 0.13 [E. Ludwig and G. Tschermak, *Mineral. Petrogr. Mitt.* **28**, 110 (1909)].
15. According to Kirova and Zaslavskaya (*3*), approximately 1000 to 2000 metallic spherules were recovered from the soil samples collected in the Tunguska impact area as compared to a few dozen silicate spherules of the same diameter.
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19. I am grateful to Dr. B. C. Heezen whose ideas and encouragement led to this investigation. I thank Dr. L. S. Walter and F. Wood for help with the microprobe analyses. Discussions with D. W. Lewis of the National Slag Association and Drs. J. A. O'Keefe, C. C. Schnetzler, B. French, and B. Mason were helpful. J. A. Glass helped prepare the manuscript. I am indebted to Drs. E. L. Krinov and O. A. Kirova for sending me five of the Tunguska silicate samples.

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10 February 1969

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Portland Cement: Pseudomorphs of Original Cement Grains Observed in Hardened Pastes

Abstract. *Scanning electron micrographs show that a hydration product forms inside the anhydrous cement grains and forms a pseudomorph of the original cement grain. The originally water-filled space between the grains is partially filled with calcium hydroxide crystals that appear to be responsible for the strength of the cement paste.*

The hydration of portland cement occurs by either a dissolution of the cement grains and precipitation of the hydration products, or by a surface chemical reaction on or in the cement grains. Despite controversy over the relative importance of these two modes of hydration (*1*), it is known from optical studies under dilute conditions that both reactions occur simultaneously (*2, 3*) on the inside and the outside of the cement grain. Taplin (*2*) formulated a model consisting of an inner and an outer product to derive equations to represent the hydration of portland cement; however, until recently, no microscopic evidence has been found to support this model for cement pastes with a low ratio of water to cement.

Investigations of hardened cement pastes confirm Taplin's model. The pseudomorphs of the original cement grains are preserved in the hardened cement pastes (Figs. 1 and 2) and there are differences in hydration products deposited within and between the original grain boundaries.

Anhydrous portland cement contains four principal compounds: tricalcium silicate ($3\,CaO \cdot SiO_2$), β-dicalcium silicate, tricalcium aluminate, and a ferrite phase belonging to the $2\,CaCO \cdot Fe_2O_3$–$6\,CaO \cdot 2\,Al_2O_3 \cdot Fe_2O_3$ solid solution series. Small amounts of MgO, CaO, and alkali sulfates also occur in many cements. Portland cement is usually manufactured in a rotary kiln where the material coheres into small rounded lumps (cement clinker) which after cooling are ground to a fine powder.

The reaction of portland cement with water is usually described as a hydration process, although it involves more than the formation of hydrates for each of the four starting compounds. The reaction of $3\,CaO \cdot SiO_2$ and water yields $Ca(OH)_2$, which is easily detected by optical microscopy or x-ray diffraction, and a calcium silicate hydrate (sometimes called cement gel or tobermorite gel). The calcium silicate hydrate is isotropic; its x-ray powder pattern consists of three broad bands. In cement $3\,CaO \cdot SiO_2$ is largely hydrated in 28 days, and hydration approaches completion in 1 year. The

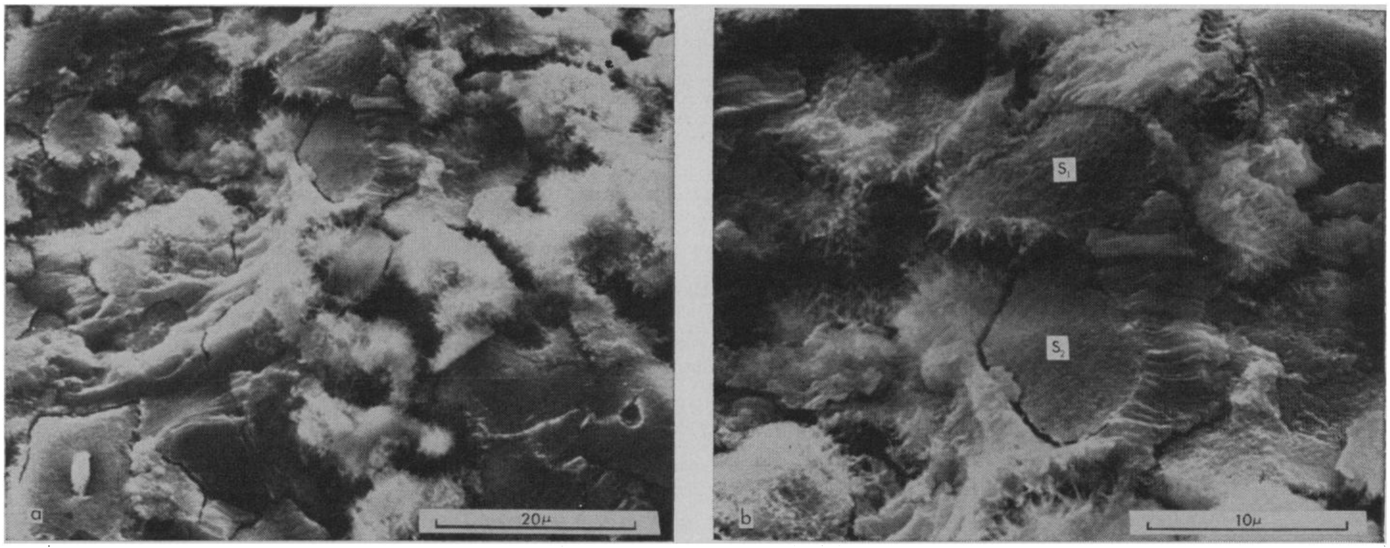

Fig.1. (a) Fracture surface of $3\ CaO \cdot SiO_2$ paste hydrated with a ratio of water to cement of 0.5 (*9*). (b) Higher magnification of a portion of Fig. 1a showing two pseudomorphs (S_1 and S_2) of the original cement grains.

reaction of β-2 $CaO \cdot SiO_2$ with water yields essentially the same calcium silicate hydrate as $3\ CaO \cdot SiO_2$ does, but with less calcium to react, less $Ca(OH)_2$ is formed than in the case of $3\ CaO \cdot SiO_2$.

Fracture surfaces of well-hydrated samples of pure triclinic $3\ CaO \cdot SiO_2$ were studied through a scanning electron microscope. The samples were prepared with a ratio of water to cement of 0.5, in containers sealed for as long as 4 years. Fresh fracture surfaces were exposed and prepared for the microscope by vacuum coating with gold. The fracture surface shown in Fig. 1a intersects an open pore at the center and the upper left and right. At higher magnification (Fig. 1b) two pseudomorphs of the original cement grains (Fig. 1b, S_1 and S_2) are evident. Anhydrous samples of the same $3\ CaO \cdot SiO_2$ show a faceted polycrystalline surface in contrast with the almost planar surface on both S_1 and S_2. The remaining pseudomorphs (about 20, shown in Fig. 1a) share the same planar, almost featureless fracture surface as S_1 and S_2.

The inner product, to use Taplin's notation, is responsible for the formation of the pseudomorphs of the original cement grains. The outer product must fill the originally water-filled space if the paste is to be strong and durable. The outer product can show considerable variation from place to place (Fig. 1, a and b). The grain marked S_2 in Fig. 1b has a dense outer product on its right-hand side, very much like the material on the upper side of S_1, in contrast to the needlelike outer products projecting into the pores shown on the lower left hand side of S_1. Examination of many micrographs revealed that the outer product can vary from an almost pure $Ca(OH)_2$ to a calcium silicate hydrate based on a two-phase structure of SiO_2 and $Ca(OH)_2$. The latter model of the calcium silicate hydrate has been suggested (*4*).

Regions larger than the original cement grains are occupied by single crystals of $Ca(OH)_2$ (Fig. 2). The single crystal nature of the center of Fig. 2a is evident from the parallel cleavage traces on the fracture surface, and it is identified as $Ca(OH)_2$ by its size and fracture pattern. These micrographs support the hypothesis (*5*) that

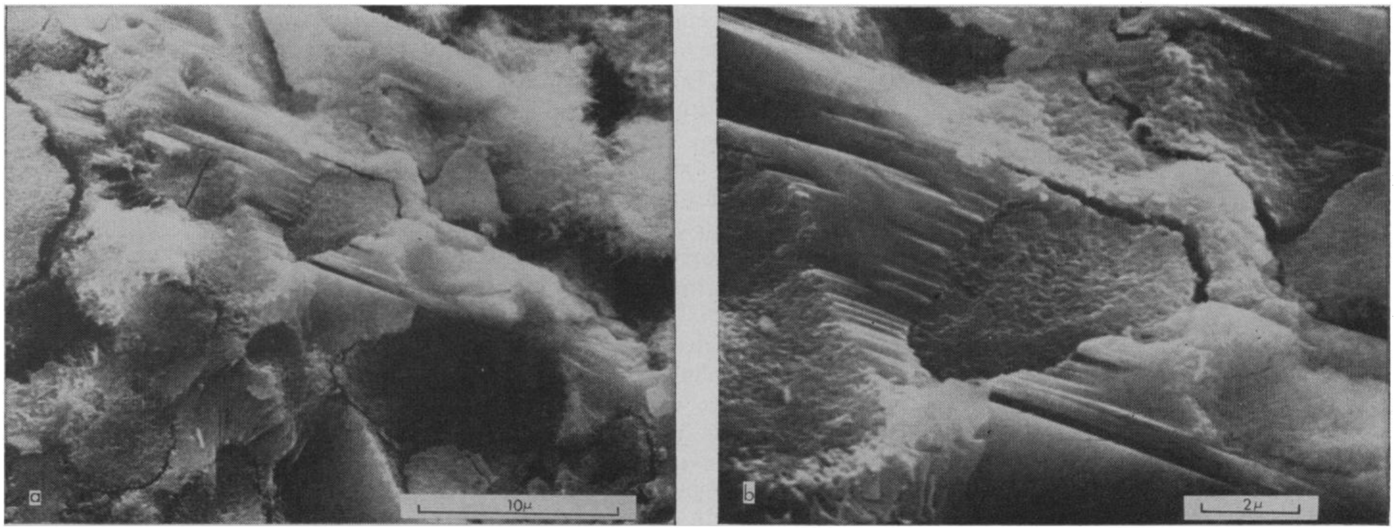

Fig. 2. (a) Another region of the fracture surface of Fig. 1 showing a large $Ca(OH)_2$ crystal. (b) A pseudomorph of one of the original cement grains embedded in the $Ca(OH)_2$ crystal.

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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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.

17 December 1968; revised 24 February 1969

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-