brown particles (*9, 10*). These spherules constitute over 60 percent of the dust particles greater in size than 3 μm near the North American continent and about 5 percent of the particles of this size over the open ocean.

The Northern Hemisphere is about half land and half water. Thus, about half of the fallout will initially enter the hydrosphere. A portion of the land fallout will eventually reach the marine environment by way of the rivers. Expected alterations in the composition of rivers, lakes, and coastal seawaters as a result of fossil fuel combustion may be most difficult to document inasmuch as any such changes must be distinguishable from those that have resulted from industrial or domestic waste disposal or from natural processes.

The above observations emphasize the need for detailed studies of the sedimentary record over the past 100 years or so, with special emphasis on those elements that may be selectively volatilized. Permanent snowfields, lakes, and inshore marine areas can provide datable sedimentary strata, separable into time units, that may furnish information about man's injections into the atmosphere. Furthermore, the atmospheric burdens of such elements in the major wind systems should be investigated to provide information on the long-range transfer processes.

Note added in proof: Joensuu (*16*) has measured the Hg contents of 36 U.S. coals and found an average of 3.3 parts per million, about 300 times the literature value used in Table 1. This figure is most probably a better estimate as a result of the very careful analytical procedures which took into account the ready volatility of Hg. Joensuu's mobilization value of 3.0×10^9 g/year is clearly preferable to the one we derive even though no correction is made for the Hg retained in the bottom ash or incorporated in coke.

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Synthetic Calcareous Pseudomorphs Formed from Siliceous Microstructures

Abstract. *Individuals of the diatom* Coscinodiscus *have been treated hydrothermally in the presence of lime and carbon dioxide with the result that they have been pseudomorphed by calcite. The silica of the original diatoms has been replaced while the intricate reticulations of the alveoli have been preserved down to submicroscopic detail.*

Technical advances in high-temperature, high-pressure systems have made it possible to simulate conditions far beneath the earth's surface, and there are few minerals of the earth's crust that have not been synthesized in the laboratory. The wealth of data on phase equilibria in natural systems has revealed many of the mechanisms involved in the formation of igneous, metamorphic, and sedimentary rocks. However, one of the most interesting types of mineral transformations, about which relatively little is yet known, is the formation of pseudomorphs.

A pseudomorph may be defined as "any substance or structure of definite or characteristic form which is represented or defined by another substance to which the form does not properly belong" (*1*), (A later-formed material B, which has replaced but preserved the structure of an earlier material A, is said to produce a pseudomorph after A.) To be sure, there is a substantial amount of literature on ion exchange in which major chemical changes are being effected with little or no modification of the crystal structure. And there are several very significant papers on topotactic transformations in which the chemical compositions, at least with respect to nonvolatile components, are essentially maintained, while substantial changes are induced in the crystal structures (*2*). In both of these types of transformations the morphology, that is, the external shape, of the starting material may be preserved. However, a great deal remains to be learned about much more drastic transformations such as the silicification of wood, the metallization of organic fossils, and the calcification of siliceous forms. It is with a transformation of the last type that this report is concerned.

My interest in pseudomorphing arose from a desire to explore certain reactions in set, low-alkali mortars containing reactive silica. Reduced to its simplest components, lime liberated by the hydration of anhydrous lime-rich calcium silicates in cement reacts with such silica of the aggregate to produce calcium silicate hydrates with hydraulic properties. Carbon dioxide, which has a great affinity for lime, particularly slaked lime, and for calcium silicate hydrates, plays an important role in the formation of carbonates in many cement and concrete products which are usually cured and used in air.

The strength and corrosion resistance of aged cement structures are also affected to some degree by reactions with carbon dioxide in air. The solubilities of lime and silica individually and together in water are well known (*3*), as is the solubility of calcium carbonate as a function of carbon dioxide pressure (*4*). However, because of other diffusion-controlled mechanisms, these data cannot tell us whether the reactions will take place primarily at the intergranular boundaries or within the lime-rich phases or within the silica-rich phases.

In the experiments reported here, I used a reactive form of silica having an intricate and characteristic morphology—a sample of diatomite from the Miocene deposits of Santa Barbara County, California. The other materials were standard analytical reagent grade chemicals. I carried out the reactions over a wide range of conditions in the water-rich part of the SiO_2-CaO-H_2O-CO_2 system between room temperature and 600°C, using standard hydrothermal techniques (*5*). Silica in the form of the diatomite comprised 4 to 14 percent (by weight) of the sample, and the amount of silica used varied in approximately 2 percent intervals. Ratios of silica to lime between 1 and 7 were used, and the amount of water saturated with carbon dioxide ranged between 80 and 95 percent (by weight) in the total system. Duration of the experiments ranged from 1 to 10 days.

The unaltered diatoms have an easily recognized reticulate morphology, a refractive index which, although somewhat variable, is characteristically low as compared to that of the calcareous phases, and a birefringence which approaches zero. As seen under the microscope, the development of carbonate phases is unmistakable (Fig. 1). Carbonate pseudomorphs after diatoms were observed, consisting generally of one, two, or three relatively large single crystals of calcite. These calcite pseudomorphs often retained the details of the alveoli down to submicroscopic detail. The effect of diatom composition on the pseudomorphing process is not known. Although highly siliceous, the composition of diatom frustules may vary from one individual to another, depending on their environments during growth (*6*). Compositional variations may presumably also have been induced since the burial of the diatoms in Miocene times. Chemical analyses of the diatomite used have shown that it contains at least 83 percent silica and 6 percent R_2O_3 (where R represents primarily Al and Fe, plus Ti, P, V, Zr, and the rare earth elements) (including 4 percent alumina), and that there is a 7 percent loss on ignition (including a 4 percent loss of H_2O between room temperature and 105°C). However, these figures do not indicate the true compositions of individual diatoms.

Among the diatoms, *Coscinodiscus* is the most abundant and apparently the most susceptible to artificial pseudomorphing by calcite. Several stages of replacement can be observed (see Fig. 1), and, on the basis of the variable refractive indices, these evidently contain phases other than the opaline silica of the original frustules and the calcite of the final stage. A poorly crystallized calcium silicate hydrate and tobermorite have been identified by x-ray powder diffraction.

The tendency of the pseudomorphs to consist of single crystals may be attributed to the siliceous structure of the diatom. Cooper (*7*) and Rogall (*8*) have pointed out that the constitution of diatom skeletons resembles that of colloidal silica dispersed in water. We are dealing with a gel-like material and can expect that the mechanisms of replacement are similar to those summarized by Henisch (*9*) for the growth of single crystals of calcite in gels. The unusual feature of the pseudomorphs after *Coscinodiscus* is that the single crystal fills the gel which retains its very intricate shape throughout the process. A similar process with another gel is probably involved in the growth of echinoid shells and spines (*10*). However, in the artificial pseudomorphs of calcite after diatom frustules there is no obviously preferred orientation of

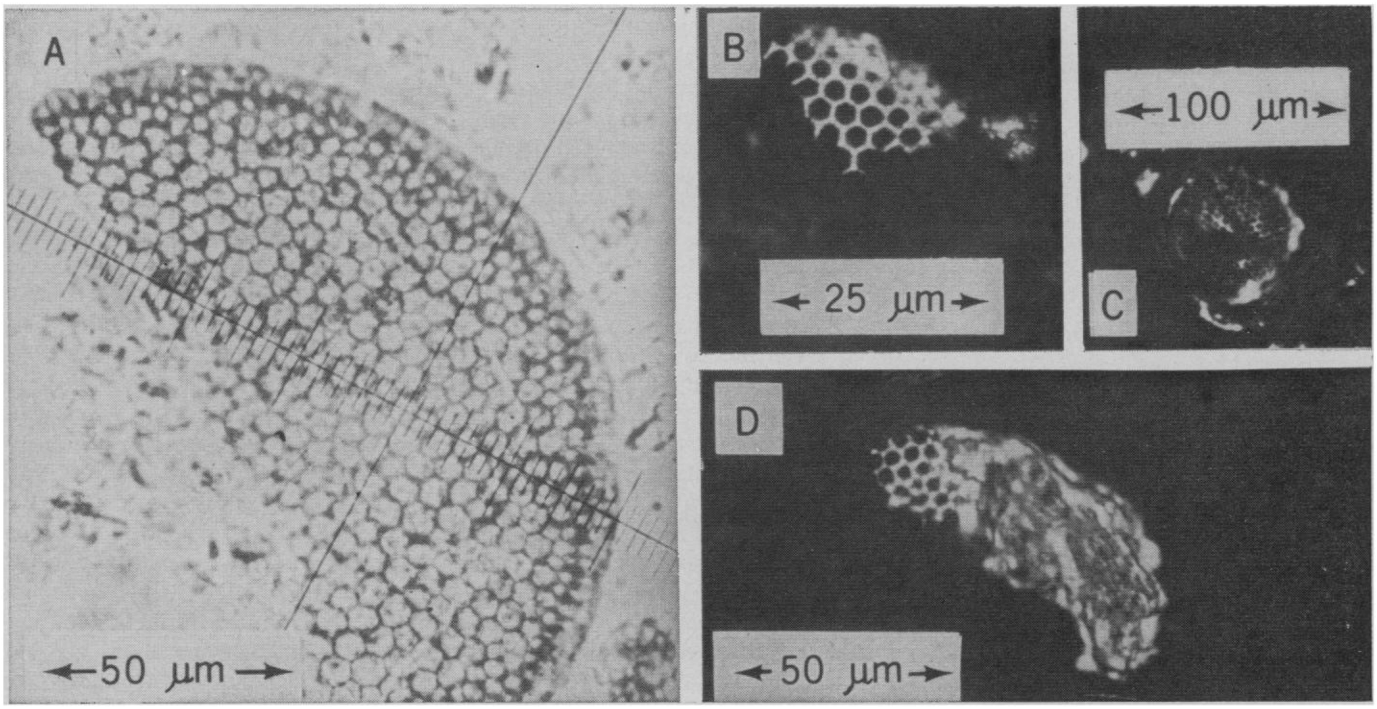

Fig. 1. Carbonated samples of *Coscinodiscus*. (A) Partially carbonated frustule seen under ordinary transmitted light. (B) Calcite single-crystal pseudomorph with detailed morphology of alveoli, seen with crossed Nicol prisms. (C) Partially carbonated frustule seen with crossed Nicol prisms. (D) Calcite single crystal. The crude morphology of the diatom is preserved; fine reticulate detail can be seen at one end (crossed Nicol prisms).

the calcite lattice in relation to the orientation of the diatom.

A few samples of carbonated diatoms were placed in water and subjected to an HCl-H_2O gradient on a microscope slide. As the HCl concentration increased, the "diatoms" effervesced with a violence that fortunately could be controlled to some extent by the gradient. The deterioration could be observed continuously under the microscope. Immediately after the bubbles had ceased to develop and all traces of birefringent material had been destroyed, an ethereal skeleton could be seen as a relic of the fine reticulate structure. This skeleton existed in this form for only a few seconds and then collapsed into a mass that appeared to be structureless. It was evidently unstable in the acid environment that exposed it.

The formation of pseudomorphs preserving the submicrosopic morphological detail of the parent is evidently feasible in the laboratory even when the main components have been completely changed, as from hydrated silica to calcium carbonate. The final composition and crystal structure bear no ion exchange or topotactic relationship to the original material. In the case of the particular pseudomorphing reaction reported here, the siliceous phase itself provides the site for the reactions between lime, silica, and carbon dioxide.

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Aromatic Hydrocarbons in the Murchison Meteorite

Abstract. *Polynuclear aromatic hydrocarbons in the Murchison meteorite have been identified by the combined techniques of gas chromatography and mass spectrometry. The distribution of the aromatic compounds suggests that they are the products of a high-temperature synthesis.*

The formation of complex organic molecules from simple compounds is considered an important cosmochemical process. Evidence for the types of molecules that are important during the early stages of chemical evolution is being obtained from laboratory simulation experiments involving such simple components as methane, carbon monoxide, water, and ammonia (*1*); from radio astronomical observations (*2*); and from analysis of the organic matter indigenous to meteorites (*3*).

Aromatic hydrocarbons may be an important class of primitive organic molecules: they are the major product formed from simple gases such as methane and carbon monoxide at high temperatures (*4, 5*), and they may be present in interstellar space (*6*). A variety of aromatic hydrocarbons have been reported to be present in carbonaceous chondrites (*3*), but lack of precise identification coupled with the ever-present question of contamination renders the significance of much of this work somewhat equivocal. The recently fallen Murchison meteorite provides a new opportunity to characterize these compounds, since our preliminary analysis indicates that the organic matter in it is indigenous and relatively free from terrestrial contamination (*7*). We have now found in this meteorite 14 polynuclear aromatic hydrocarbons whose identity has been established by gas chromatography and mass spectrometry. We have further established the molecular weight of nine additional compounds by mass spectrometry.

Two pulverized meteorite samples were extracted with a mixture of benzene and methanol (9 : 1, by volume) and the recovered extracts (I and II) chromatographed on columns of silica gel, as previously described (*7*). The benzene fraction from one sample, referred to here as in the preliminary report (*7*) as sample II, was evaporated

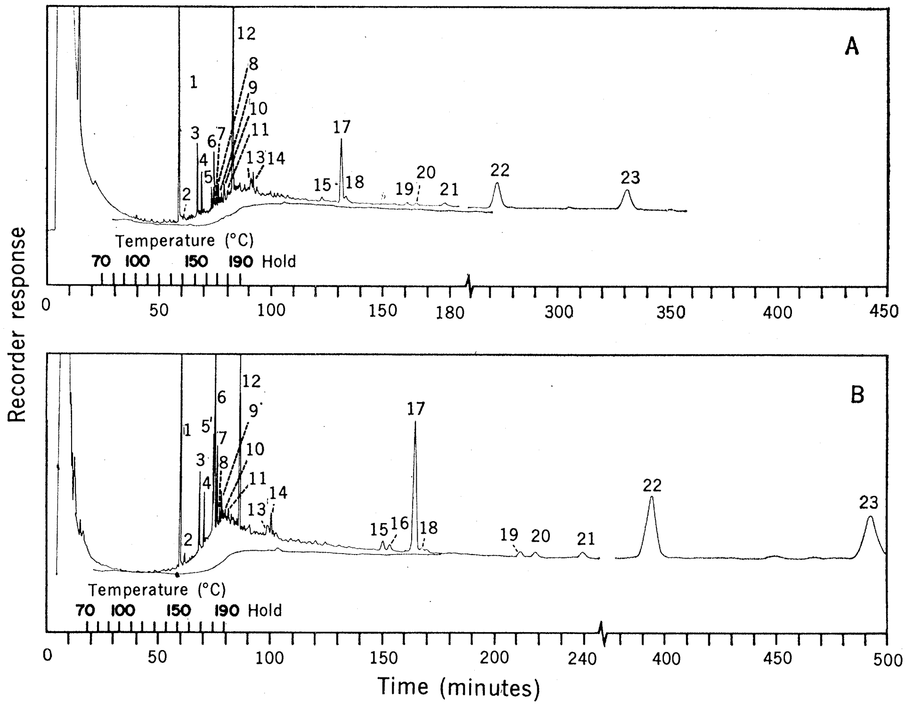

Fig. 1. Gas chromatograms of the aromatic hydrocarbons isolated from the Murchison meteorite sample I (A) and sample II (B). Analytical conditions were as follows: 15.2-m support-coated open tubular polyphenyl ether column (Perkin-Elmer Corp.) in a flame-ionization gas chromatograph (Perkin-Elmer 880); helium flow rate, 3 ml/min; attenuation, × 50. Differences in retention times between the two chromatograms may be due to a slight oxidation of the column when it was unintentionally exposed to air for a period of time while being transferred from the Perkin-Elmer to the Loenco gas chromatograph.