Fossil Coccoliths in Limestone Examined by Electron Microscopy

Abstract. *Examination of polished and etched limestone surfaces (Jurassic from the Alps, Paleocene from Spain) by electron microscopy reveals coccoliths, in varying stages of preservation, in numbers of 100,000 to 1,000,000 per cubic millimeter.*

Coccoliths and related objects are tiny skeletal plates of the Coccolithophorida—pelagic marine flagellate "algae" of the chrysomonadine group. Their diameter ranges from 1 to 30 microns. They are normally composed of calcite, though under certain conditions aragonite and vaterite are precipitated (*1*). They were first discovered in 1836 by Ehrenberg in sedimentary rocks. In 1858 Huxley described their occurence in Recent deep-sea ooze, and in 1902 Lohmann established their organic relationships. Despite their small size the coccoliths have a highly complex structure, much of which is too small to be resolved by the ordinary topical microscope, but which is being revealed by electron microscopy (*1, 2*).

In recent years there has been a revival of paleontological interest in coccolithophore remains. Specimens have been obtained from many unconsolidated and semiconsolidated sediments by dispersing the constituent particles in water and settling out the appropriate size range (*3*). The established record of coccoliths extends back to the Jurassic, and since then there appears to have been considerable evolution in this group, with the appearance and disappearance of various distinctive types. This, coupled with the coccoliths' wide distribution and numerical abundance (up to millions of coccoliths per cubic millimeter of coccolith-rich sediments) suggest that they may have great potential value in stratigraphy. Distribution of fossil coccolithophores also offers promise of providing data on ancient climates and currents.

Nearly all the work to date has been on specimens freed from soft matrix, and next to nothing is known about coccoliths in consolidated rocks: Deflandre (*4*) reports a coccosphere from chert, and Colom (*5*) observed coccoliths in the thin edges of thin sections of Mesozoic limestones. Bramlette (*6*) called attention to their absence in thin sections of limestones from Central Algeria which correlate with coccolith-bearing chalks of southern Algeria. Presumably, these limestones were once similar chalks, but were recrystallized to solid limestone by folding or burial or both. This recrystallization converted the chalks into mosaics of interlocking calcite crystals, in the size range of coccoliths, and presumably the latter were destroyed in the process. Bramlette attributed to the same process the absence of coccoliths in late Jurassic—earliest Cretaceous limestones of the northern Alps, which by virtue of larger fossils (*Calpionella*, Radiolaria, and ammonite aptychi) are revealed as former pelagic oozes.

We have been engaged in studies of Alpine limestones (*7*) and in the ultramicroscopic structure of limestones in general (*8*). Among others we have investigated the already mentioned alpine *Calpionella*-bearing Jurassic limestones, and Paleocene limestones from the Flysch of Spain; in both of these, coccoliths are revealed by electron microscopy (*9*).

On the optical level we have examined these rocks mainly by use of "ultra-thin" sections (ranging in thickness from 10 to 2 μ in place of the standard 30 μ (*10*). For electron microscopy, cubes of limestone are embedded in plugs of epoxy resin, cut, ground by a series of abrasives, and brought to a high polish by brief buffing with gamma-alumina suspension on a Pellon-covered polishing lap. The surface is then lightly etched by 0.1*N* hydrochloric acid. From this surface, chromium-shadowed carbon replicas are prepared (*10*) by standard techniques used in electron microscopy.

Investigation of the Spanish Flysch has been mainly focused on a dull red, somewhat marly though well consolidated limestone from the western end of the beach cove at Zumaya, of Paleocene age. Thin sections reveal pelagic Foraminifera in fine-grained matrix, and ultra-thin sections provide good images of giant coccoliths (*Braarudosphaera*) and discoasters, as well as scattered, nondescript images of normal coccoliths, recognizable chiefly by virtue of their swastica-type extinction cross in cross-polarized light. The bulk of the matrix appears as an irregular mosaic of grains of uncertain origin.

Under the electron microscope the rock takes on a much more definite character—about half of it consists of coccoliths (Fig. 1, left). The remainder includes other fossils, plain calcite grains of indeterminate origin, and clay mineral grains. The rock is thus seen to be a lithified coccolith ooze, containing on the order of a million coccoliths or coccolith fragments per cubic millimeter.

Most of the coccoliths are large enough to be seen under the optical microscope, but they cannot actually be recognized under that instrument for a number of reasons. Even the extremely thin sections prepared by us are several times as thick as the focal depth of an objective of 1.32 numerical aperture (about ½ μ). This thickness, combined with the high birefringence of calcite, and the multitude of variously oriented grains, produces images of very poor optical quality. The distinctive extinction cross of coccoliths is visible only in essentially complete specimens, oriented parallel to the plane of the section. The microstructure

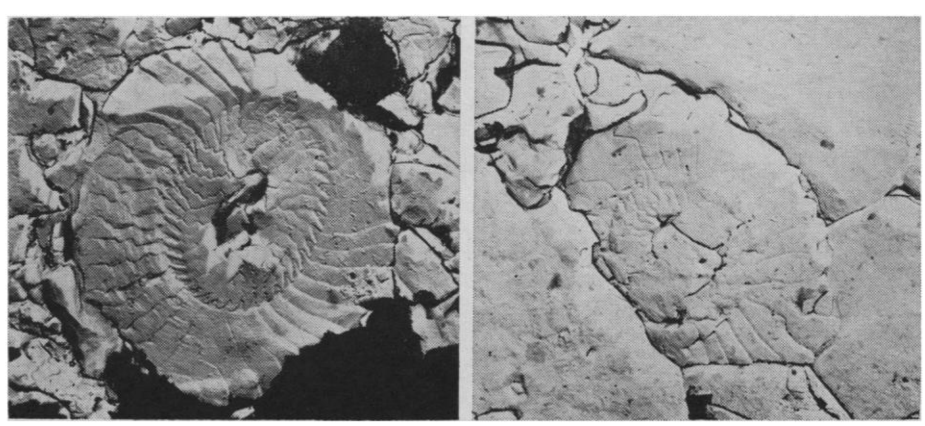

Fig. 1. (Left) Coccolith showing well-preserved structure. Paleocene Flysch, Zumaya, Spain; × 7500. (Right) Coccolith of type *a* showing progressive loss of plate boundaries, presumably due to recrystallization, and loss of periphery by solution welding. Late Jurassic, Alps; × 7500.

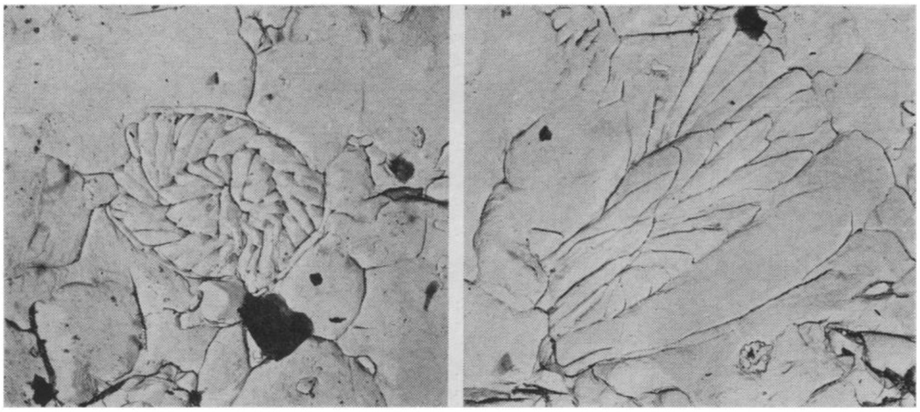

Fig. 2. (Left) Coccolith of type *b*, showing well defined but somewhat dislocated plates, and a peculiar marginal rim. Late Jurassic, Alps; × 5500. (Right) Problematicum, type *d*, probably longitudinal section of *c*. Late Jurassic, Alps; × 7500.

of imbricate plates, by which coccoliths are recognized in electron microscopy, is not revealed in thin section under the microscope.

The great majority of coccoliths present a fragmental appearance. How much of this is due to actual fragmentation is uncertain at this stage of investivation. The following factors must be considered: (i) Coccoliths have complex shapes; in these surfaces, sections of all possible orientations, many of them tangential, are to be expected. (ii) The processes of polishing and etching are likely to destroy the thin edges of tangential sections, thus producing outlines which appear to truncate structural elements of the coccolith. (iii) The surfaces of coccoliths may have been modified by solution while the particle was descending from the surficial waters to the sea floor, a process which, according to Stokes' law, may take months. (iv) The surfaces of coccoliths were modified after burial, by solution welding: Loosely sedimented particles have points of contact—when they are buried and loaded, these points bear the load of overlying sediment, whereas the free surfaces are exposed to hydrostatic pressure only (provided the sediment is permeable). As a consequence, the load-bearing points undergo solution and grain contacts are thus broadened into surfaces, while precipitation may occur in the pore spaces. Presumably, this is one of the main processes whereby oozes and chalks are transformed into consolidated limestone. The effects of solution welding are shown by coccoliths fitted together along surfaces, which tend to truncate internal structure, and in the embayment of coccolith margins by adjacent grains. Only further work can tell the extent to which actual fragmentation is also involved.

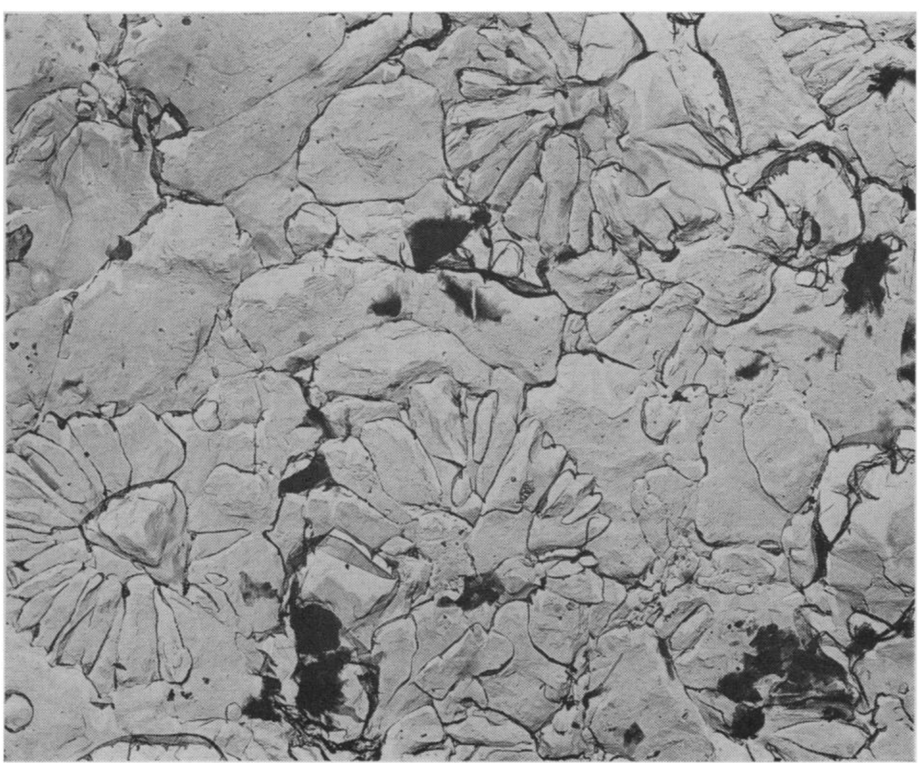

Fig. 3. Problematicum, type *c*. Late Jurassic, Alps; × 8500.

The Aptychus or Oberalm limestone represents the latest Jurassic (Tithonian) in the Northern Limestone Alps. It is a varied sequence of carbonate rocks with some flysch-like aspects. A common rock type in the Unken valley (Kammerköhr range, Salzburg, Austria) is a fine-grained *Calpionella*- and radiolarian-bearing limestone. The groundmass of this rock, as seen in thin sections, is an interlocking mosaic of calcite grains on the order of 10 μ in diameter. No coccoliths are recognizable.

The electron microscope reveals four types of coccolith-like objects, in varying stages of preservation. These are reasonably abundant, but do not constitute more than 10 to 20 percent of the rock. The remainder consists mainly of calcite grains which show no signs of organic derivation, and are clearly the products of recrystallization and cementation. Some of them may have been derived from coccoliths.

Type *a* is a coccolith (Fig. 1, right). Inability to find it in thin sections, and the rather subdued nature of the plate boundaries suggest that these coccoliths have recrystallized to single grains of calcite. The retention of plate boundaries within such a single crystal suggests that these plate boundaries are organic films, which have remained as inclusions and flaws. Solution welding is suggested by the truncated margin.

Type *b* is also coccolith-like, in consisting of two oppositely imbricate rows of plates (Fig. 2, left). The geometry differs from type *a*, as does the preservation: Type *b* is most resistant to recrystallization, retaining sharp plate boundaries. In somewhat crushed specimens adjacent plates have been somewhat displaced, suggesting that plate boundaries were physically weak but chemically discrete. This is further evidence of the existence of organic membranes.

Type *c* (Fig. 3) is represented by simple rosettes of radiating calcite blades. It is resistant to recrystallization, and may or may not represent a coccolithophore. Type *d* (Fig. 2, right) shows longitudinally oriented blades of calcite, and presumably represents type *c* in longitudinal section.

The sections of coccoliths which appear on our electron photomicrographs are not directly comparable to the surface views obtained from free specimens. This is likely to be a taxonomic obstacle. Nevertheless, the structures seen in these sections are elaborate and distinctive, and the method clearly affords a means of extending research on coccolithophorids into the consolidated limestone facies. Furthermore, it furnishes an approach to the study of fine-grained limestone fabrics as a whole.

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8. Supported by the Petroleum Research Fund of the American Chemical Society, under contract PRF-1114-A2.
9. We used the Hitachi HU-11 and HS-6 electron microscopes.
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Large Electron Pulses in Hydrocarbons

Abstract. *When gamma rays pass through purified, degassed, liquid hydrocarbons held in an electric field, large current pulses are observed, indicating electron multiplication. This seems to indicate that free electrons are stable in these liquids and that their mean free paths may be much greater than had been thought.*

We have observed large electric pulses in diodes filled with liquid hydrocarbons, under static voltages of 600 to 3000 and fields of 750 to 7500 v/cm, when subjected to Co^{60} gamma-irradiation from a 0.3 mc source at 8 rad/hr. The pulses were observed on an oscilloscope; their length was of the order of 3×10^{-5} second. The pulse amplitude varied among pulses at any applied potential; the maximum pulse amplitude increased with applied potential. At 3000 v, the largest observed pulses registered as a 20-v potential drop across the 10^{6}-ohm oscilloscope resistor, indicating a total charge transfer of more than 10^{-10} coulombs. This is much more than the charge separation of approximately 10^{-14} coulombs (maximum) produced in the electron tracks resulting from the passage of a single Co^{60} gamma-ray through the liquid. The number of pulses is less (by a factor of about 10^{3}) than the calculated number of gamma-rays absorbed in the liquid.

These pulses are larger by a factor of 10^{5} than those observed by Blanc, Mathieu, and Boyer (*1*) at much higher fields (60,000 v/cm).

The apparatus consisted of two parallel disc electrodes immersed in the hydrocarbon in an all-glass cell. Pumping reduced the cell pressure to the vapor pressure of the hydrocarbon. The circuit included only the cell, a 3kv power supply (direct current), and the oscilloscope. The source of gamma-irradiation was held outside the cell, either on the central plane or on the axis. The electrodes were not protected from the radiation. No variation with source position was observed. The materials were: (i) *n*-octacosane (Eastman), purified by more than 100 passages in a two-coil Fisher zone refiner; (ii) commercial *n*-octacosane, conditioned by several cycles of heating to 150°C under pumping; and (iii) *n*-hexane, purified by passage through an Aerograph A90P gas-liquid partition chromatograph. Of these, material i gave the largest pulses. Total radiation doses delivered to any sample never exceeded 100 rad, so that radiolysis may be neglected.

Static conductivity of material (i) at 65°C was 5.5×10^{-14} (ohm–cm)$^{-1}$ at applied fields of 1250 to 1875 v/cm in the absence of radiation. Below the value of the pulse threshold, gamma-irradiation at 8 rad/hr increased the conductivity by less than 5 percent. Above the threshold, the pulses prevented meaningful resistivity measurements.

In order to guard against spurious effects, several cells of two designs were used. Electrodes were similar (Al) or dissimilar (Pt gauze and Al), horizontal or vertical, and of different size and spacing. In one experiment, all metal parts were immersed in the liquid to eliminate gas-phase electron multiplication. In the several experiments materials i and ii were generally held at 61° to 90°C and material iii at −78°C. The large pulses were seen in all these cases.

The observed amplification appears to be due to cascading. This implies that most of the charge carriers (presumably electrons) attain kinetic energies which allow them to create new electron-hole pairs. To observe this phenomenon at fields as low as 750 v/cm, it is necessary to postulate that electrons are not trapped as a rule, that their mobilities are high ($>$ 10 cm^{2} v^{-1} sec^{-1}), and that they lose only a small fraction of their energy at each collision even when their kinetic energy is substantial ($>$ 1 ev). This contrasts sharply with the behavior of electrons in less pure hydrocarbon liquids (*2*) which attach to molecules, giving ions which have mobilities of about 10^{-3} cm^{2} v^{-1} sec^{-1} and do not rise above thermal energies.

Preliminary and inconclusive electron mobility measurements have indicated mobility values of 20 to 200 cm^{2} v^{-1} sec^{-1}, in agreement with this explanation. We should expect that, in a material free from electron-trapping sites (trap-free material), electron mobilities could approach the values of 900 to 3900 cm^{2} v^{-1} sec^{-1} observed in diamond (*3*).

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