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Genesis and Lithification of a Deep Sea Chalk

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ABSTRACT

Lithification of a deep sea Oligocene chalk in the South Atlantic has been accomplished by chemical precipitation of two types of cement: 1. calcite, which occurs as secondary overgrowths and euhedral crystals up to 10 μm in diameter, and 2. spherical aggregates (about 3 μm diameter), insoluble in HCl, which were deposited as a late stage pore filling. Results suggest that Tertiary strata of present day ocean basins are ideal for studying early phases of diagenesis and lithification in carbonate rock.

Introduction

Although lithified chalks are rare in the younger Tertiary sediments of present day ocean basins, a few isolated chalk horizons have been sampled within unconsolidated pelagic ooze sequences during the recent exploratory operations of the Deep Sea Drilling Project. Studies of these chalks may provide keys for interpreting the early lithification and diagenetic histories of more widespread but more highly lithified chalks of Mesozoic age. We report here our preliminary analyses of an Oligocene braarudosphaerid chalk and the discovery of an interstitial cement or pore filling of unusual character which we hold to be responsible in part for the consolidation of this rock.

Results

The chalk was cored at Glomar Challenger Stations 14, 17, 19, 20 and 22 in the South Atlantic (MAXWELL et al 1970a, 1970b) and was sampled by one of us (KJH) aboard ship. It is unusual in several respects: 1. It is restricted geographically to the South Atlantic and in time to rock units of Oligocene age. 2. It is sufficiently lithified to form an acoustical reflector and, as such, was of special interest as a key bed during on site drilling operations. No explanation could be given, however, for its lithification. 3. Although monospecific oozes are extremely rare in the geologic column, this chalk consists almost entirely of isolated skeletal fragments derived from a single species of golden brown algae (*Braarudosphaera rosa* LEVIN and JOERGER 1967; see MAXWELL et al. 1970a, 1970b). The pentalith construction of the coccospheres of this calcareous planktonic species is well known (LEVIN and JOERGER 1967; ROTH 1970; see also GAARDER 1954; FISCHER, HONJO and GARRISON 1967), and each plate of five distinct segments (Fig. 1) is normally found preserved intact in shallow water sediments; however, within our material, most of the pentaliths are themselves disaggregated, so that the sediment consists primarily of wedge-shaped segments. In view of these facts, this peculiar lithified material has been singled out for intensive laboratory study by scanning and transmission electron microscopy, X-ray diffraction, microprobe and oxygen isotope analysis.

Electron microscope analyses of *Braarudosphaera* chalk sample 3/22/4/1 from Station 22 (Rio Grande Rise) reveal that the pentalith segments and the relatively few specimens of other nannofossil species present show some evidence of solution, and this appears to have caused the disaggregation of the pentaliths. In addition, two types of cement are observed: 1. calcite, which is the principal lithifying material in the rock, and 2. an insoluble substance which occurs as a late stage pore filling to form an accessary cement[1]).

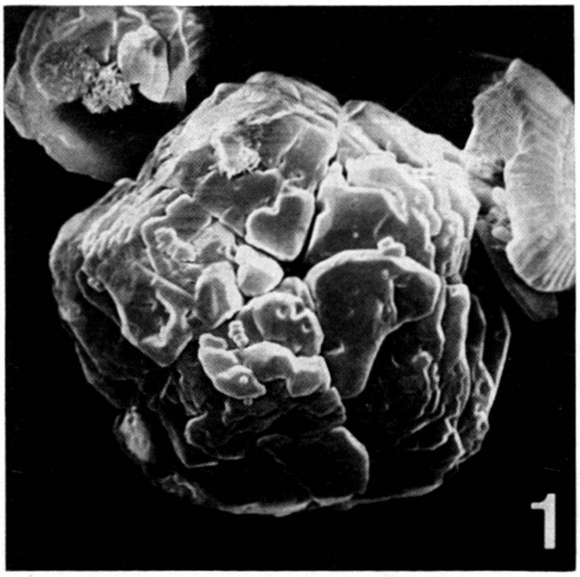

Fig. 1. *Braarudosphaera rosa*, a calcareous nannofossil composed of five wedge-shaped segments which, in a disaggregated state, are the principal constituents of the Oligocene chalk reported here. 2,900 ×

The calcite occurs as secondary overgrowths and as euhedral crytals of a variety of shapes and sizes up to 10 μm in diameter. The latter often envelope biogenic particles, and the large prismatic/rhombohedral crystal in Figure 2 has enveloped a portion of placolith. Similar crystals have been reported in the Jurassic Solenhofen Limestone (LAFFITTE and NOËL 1967, Pl. 8, Fig. 2), and our findings support LAFFITTE and NOËL's contention that the Solenhofen Ls is not inorganic in origin, but represents a lithified nannofossil ooze which has undergone diagenesis.

The second cementing material in our sample consists of fine platelets which grow in spherical aggregates about 3 μm in dia (Fig. 3) within the void areas of the chalk. Because the cementation process has not been carried to completion, there is still considerable void space within the rock, and the aggregate material typically shows spherical surfaces of unhindered growth. On fracture surfaces, however, it often shows

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[1]) *Braarudosphaera* chalk samples from stations 14 and 20 have also been analyzed under the electron microscope. In there chalk samples only the calcite cement is present; the pore-filling silicate was not observed.

smooth flat impressions which result from a close contact against larger sedimentary particles (arrow, Fig. 2). This material, therefore, has gone through an active growth stage within the interstices of the sediment, and is an important accessary cement. In transmitted light the aggregates exhibit high refringence and complete extinction under crossed nichols. These features, together with their small size and fibrous construction, give them a slight superficial resemblance to palynomorphs. The aggregates, however, are insoluble in cold HCl, and X-ray analyses of the insoluble residue from the chalk (REX 1970; K. KELTS 1970, personal communication) suggest that they are the mineral clinoptilolite, a silicate belonging to the zeolite group, or an amorphous substance.

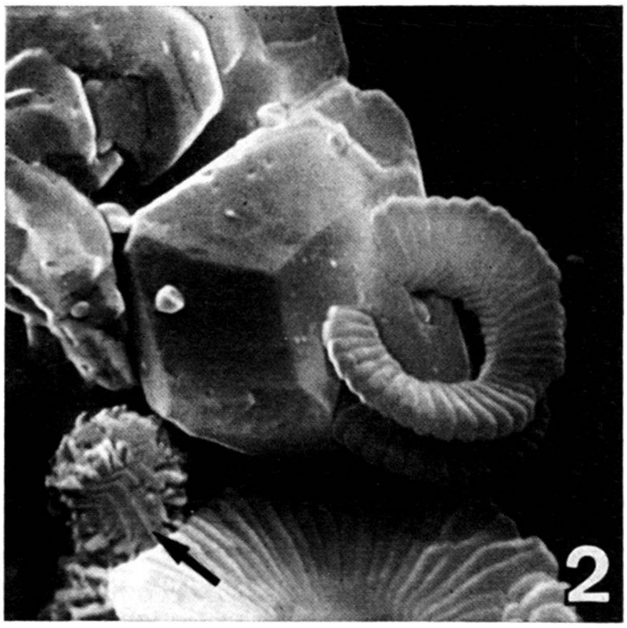

Fig. 2. Euhedral calcite crystal (center) which, through accretion, has overgrown a portion of a placolith. 7,200×

Morphologically, the aggregates are unlike any late Tertiary or Quaternary shallow water cements reported in the literature (example, see HATHAWAY and DEGENS 1969; FRIEDMAN, AMIEL and SCHNEIDERMANN 1970) or any of the fine constituents of unconsolidated shallow water carbonate sediments observed during extensive electron microscope studies (HAY, WISE and STIEGLITZ 1970; STIEGLITZ 1971). The peculiar form and habit of this precipitant are undoubtedly a product of its deep sea environment of deposition. In this respect, the potential importance of interstitial cements of this type as sedimentary environmental indicators should not be overlooked.

X-ray analyses of bulk samples of the chalk indicate that the rock consists of calcium carbonate in the form of low-magnesium calcite (about 1 mole per cent $MgCO_3$). It is not possible to say how much this composition differs from normal skeletal calcite of calcareous phytoplankton because comparative data on modern nannofloras is lacking. Recent studies by GOMBERG and BONATTI (1970), however, suggest that diagenetic alteration of high magnesium calcite to low magnesium calcite can be very rapid in deep sea environment, and this factor should be kept in mind when

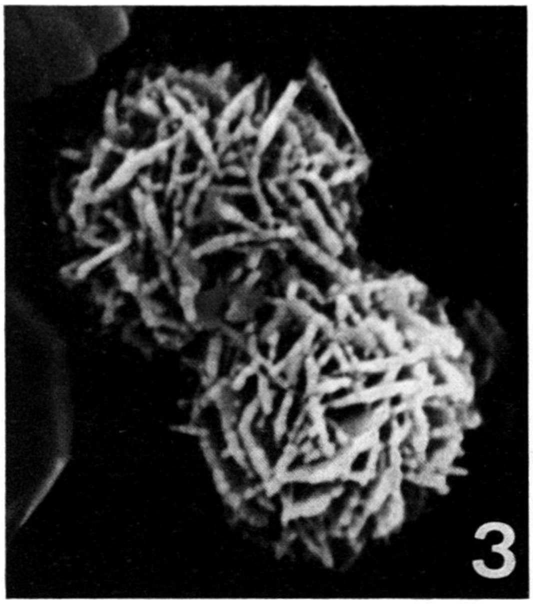

Fig. 3. Spherulitic aggregates composed of small platelets which constitute a second type of cement in the chalk. The flat surface of the aggregate in Figure 2 (arrow) was formed by close contact against a placolith shield. 12,600 ×

interpreting the trace element data. The oxygen isotope analysis for our material (LLOYD and HSÜ 1971) indicates a paleotemperature of crystallization of 6° Centrigrade (assuming that isotope equilibrium has been achieved). This figure, however, is below the life tolerance limits of most modern calcareous phytoplankton (MCINTYRE and BE 1967), and no live representatives of modern *Braarudosphaera* have been sampled from sub-polar waters lying beyond the 10 °C isotherm. The low temperature readings for our sample probably reflect isotopic re-equilibration during the diagenetic alteration of the original skeletal material. In addition, solution and reprecipitation of calcite within this rock have been significant, and the calcareous cement was apparently formed in equilibrium with sea bottom temperatures which, during the Oligocene, should not have been much higher than the present day value of 4 °C. Both the paleotemperature reading and the trace element analysis, therefore, are considered to be indicative of conditions on the sea bottom rather than at the surface where the skeletal calcite was originally formed by planktonic organisms.

Discussion

The Tertiary braarudosphaerid chalk reported here has had an unusual depositional and diagenetic history, but one which should provide important new data on the little understood problems of deep sea diagenesis and lithification. Certainly it would be more difficult to follow the early phases of these processes in older, more tightly consolidated chalks and limestones. At most of the drilling sites, several laminae of chalk were encountered within an otherwise normal sequence of unconsolidated Oligocene ooze (MAXWELL et al. 1970b). Although the chalk is nearly monospecific, it does not have an unusually high terreginous content which, in the South Atlantic, is a reliable index of degree of dissolution (MAXWELL et al. 1970a). Selective solution of species other than *B. rosa*, therefore, cannot be invoked to explain the monospecificity of the deposit. Extensive selective solution would have produced high insoluble residue contents and would have required inordinantly long periods of time to concentrate the pentaliths if production rates remained constant. Unusual conditions, therefore, must have been responsible for unusually high production rates of *B. rosa*²) and the rarity of other species. We postulate that special environmental conditions which came into play only periodically over the South Atlantic during Oligocene time caused the accumulation of the unusually thick laminae (up to 90 cm) of concentrated braarudosphaerid ooze in its highly disaggregated state. These conditions are thought to be related to the Antarctic current system or temporary climatic cooling. Reduced surface water temperatures would tend to exclude many tropical and semitropical phytoflagellate species from the planktonic flora. Cold bottom temperatures would promote in situ dissolution of the more soluble calcareous nannofossils at the sediment/water interface. The massive, compact construction of the braarudosphaerid pentaliths, however, would make them relatively resistant to solution, although not sufficiently so to prevent their disaggregation into isolated segments.

During the cold intervals (times of *Braarudosphaera* deposition), the organic calcite which formed at surface water temperatures would be in a non-steady state on the sea bottom, and much of the calcium carbonate derived from its dissolution would be held in solution by the cold interstitial fluids. The warming which would accompany a return to normal conditions would cause supersaturation of the interstitial fluids and the inorganic precipitation of calcite cement. It is also possible that circulating supersaturated bottom waters could have supplied additional quantities of calcium carbonate for the precipitation of cement. Until recently, it was generally thought the inorganic precipitation of calcite and the lithification of carbonate sediments could not occur on the sea floor at bathyal depths; however, the compelling evidence presented by FISCHER and GARRISON (1967) indicates that these processes do occur on the sea bottom. This gives us additional reason to believe that our material was indurated shortly after deposition while still in the vicinity of the sediment-water interface.

The origin of the clinoptilolite in the insoluble residue is not certain. REX (1970) reported the occurrence of this species of zeolite in several other samples of the Rio Grande Rise. We suspect that its origin may be related to the particular paleo-oceanographical milieu of the Rise.

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²) The possibility of high production rates of *B. rosa* in the open marine environment was suggested by MAXWELL et al. (1970b) and is favored by us because abundant populations of modern *Braarudosphaera* in open ocean water have been reported by GAARDER (1954).

Note added in proof: Our electron micrographs show that the insoluble residue of the chalk sample consits largely of the spherical aggregates and a platy mineral; the X-ray pattern indicates the presence of both clinoptilolite and an amorphous substance (amorphous silica ?), as well as traces of various detrital minerals. Comparison with the newly published electron micrograph by Gibson and Towe (Science, v. 172, p. 153) identifies the platy mineral as clinoptilolite; the aggregate would then be the amorphous material. This interpretation is in accord with our observation that the spherical aggregates show signs of having been compacted, or squashed (Figure 2, arrow), as one would expect from spherules of silica gels prior to their hardening. Research is currently underway to determine the exact mineralogy and chemical composition of the insoluble residues and to interprete their genetic significance.

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