Carbonate Mineralogy of Deep-Sea Sediments from the Ionian Sea

by

JENS MÜLLER and FRANK FABRICIUS
Institut für Geologie, Abt. Meeresgeologie und Sedimentforschung, Technische Universität München (Germany)

I. Introduction

The occurrence of carbonate minerals — especially the metastable polymorphs aragonite and magnesian calcite (>4 Mol % $MgCO_3$) — in deep sea sediments, their stability relationships and lithification resp. cementation by them have been the subject of several studies in recent years [FRIEDMAN 1965, MILLIMAN 1966, *and others*]. According to these authors the occurrence of calcite — mostly derived by planktonic foraminifera — is rather a rule and preservation of magnesian calcite and/or aragonite occurrs only under exceptional conditions.

While the organic origin of calcite and aragonite in deep sea sediments are known (calcite by planktonic foraminifera and coccolithophorids and aragonite by pteropod shells), no biogenic source of magnesian calcite in deep-sea sediments has been detected yet. Magnesian calcite is reported as cement and as main constituent of deep-sea limestone crusts and lutites.

II. Previous work

Limestone crusts in the Mediterranean have been described by NATTERER [1894] and BØGGILD [1912]. Their chemistry and mineralogy has been studied by FUCHS [1894], DE WINDT & BERWERTH [1904], NORIN [1956], EMELYANOV [1965] and more recently by FISCHER & GARRISON [1967] and MILLIMAN *et al.* [1969]. According to these authors limestone crusts rich in magnesian calcite have been formed by still unknown lithification processes during late Cenocoic time. Besides, the deposition of magnesian calcite — rich lutites was reported by MILLIMAN *et al.* [1969].

The present study deals with another occurrence of indurated magnesian calcite crusts and magnesian calcite — rich lutite from the Ionian Sea. The piston core No 17 M-14 G was collected during the cruise No 17 of FS *Meteor* in 1969. Sample location was 36° 11,5′N and 19° 45,7′E, (uncorrected) water-depth 3115 m. The length of the core is 123 cm. The core site is in the western part of the "Mediterranean Ridge " in the transition zone between the " cobblestone area " [HERSEY, 1965] and the " Sattel- und Muldenzone " [GIERMANN, 1966].

Magnetic investigation of core 17 M - 14 G gave an age of 2.3×10^6 years by the number of reversals and an extremely low sedimentation rate of 0.54 mm/10^3a [HEYE, 1970]. But the biostratigraphic studies showed a large gap from the Mindel/Riß interstade to the Riß/Würm interstade. The Pliocene/Pleistocene boundary was not detected by microfossils. These studies and a sedimentological survey will be published elsewhere.

III. Methods

Carbonate mineralogy was determined by X-ray diffraction analysis on the whole sample and on different size fractions (63-20 μ, 20-6 μ, 6-2 μ and < 2 μ). The relative percentages of calcite, magnesian calcite and dolomite were computed by techniques described by J. MÜLLER [1969]. The Mol-% $MgCO_3$

Rapp. Comm. int. Mer Médit., **21**, 11, pp. 855-859, 6 fig. (1973).

in the magnesian calcite was determined by the shift of the (211) — calcite peak [GOLDSMITH & GRAF 1958]. The total amount of carbonate and organic carbon was determined with a LECO-analyzer and calculated as $CaCO_3$. Thin sections of the lithic fragments and the unconsolidated sediment were studied under the petrographic microscope and by scanning electron microscope.

IV. Results (Fig. 1 and 2)

In most of the samples studied the carbonate content is within the range of 40-50 %, extreme values are 34 % and 63 % $CaCO_3$. No distinct variation with core depth could be detected. The values of organic carbon (range 0.065 % - 0.144 % C_{org}) show a slight decrease with increasing core depth.

The carbonate content of the lithic fragments is significantly higher (70-80 % $CaCO_3$) than in the surrounding lutite; the values for organic carbon are usually less (0.054-0.111 % C_{org}) than the average content of the lutite.

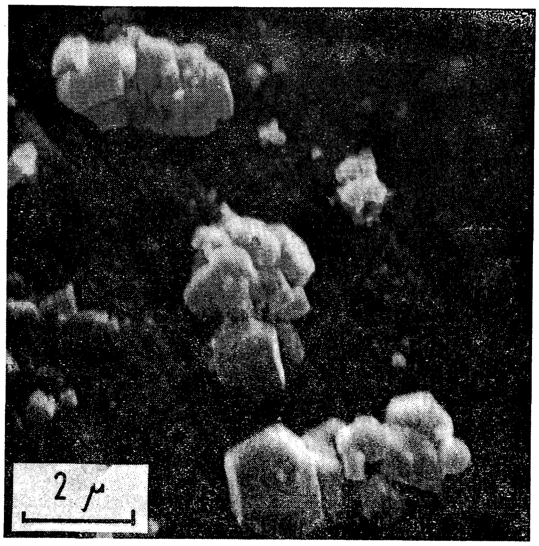


PLATE 1 : electron photomicrographs of magnesian calcite crystals; clay fraction, core depth 25-25.5 cm

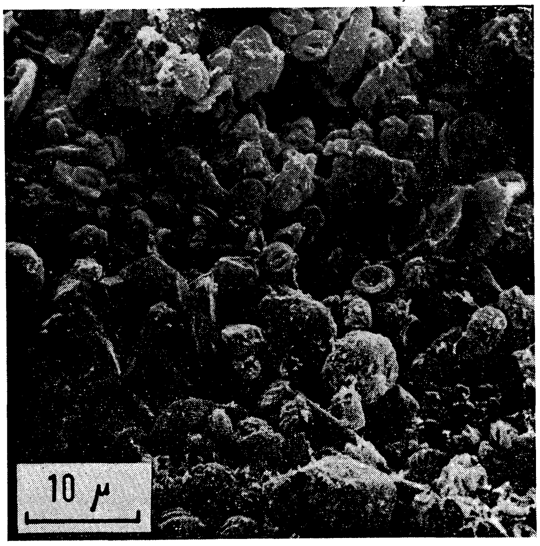


PLATE 2 : abundance of coccolithophorids in a (calcitic) lutite; core depth 85-85.5 cm.

As shown by X-ray analysis quartz, feldspars and micas are present in varying amounts. They probably are of aeolian origin to a good part. No aragonite could be detected. As a rule, the dolomite content increases with decreasing carbonate content, thus showing a distinct relation to the non-carbonate components. Furthermore, the dolomite content of the lithic fragments is the lowest.

Magnesian calcite forms three layers of varying thickness from core depth 5-25 cm, at 65 cm and below 100 cm, corresponding to a lack of calcite which is dominant from 30-60 cm and 70-100 cm. Lithic fragments — almost entirely composed of magnesium calcite — are only present in the layers rich in magnesian calcite. Magnesian calcite resides especially in the fine silt- (6-2 μ) and clay-sized fraction, the latter being free of dolomite.

Magnesium content in the magnesian calcite varies in the range from 8 to 11 Mol-% $MgCO_3$, whereas Mg-content in the magnesian calcite of the lithic fragments is slightly higher (12 Mol-% $MgCO_3$).

The limestone crusts occur — as shown by radiographs — as loose nodular lithic fragments of different shape, size and hardness resp. degree of consolidation. They are mostly flattened, varying in diameter from less than 1 cm to 4 cm.

The investigation of a magnesian calcite rich clay (core depth 25-25.5 cm) by scanning electron microscope revealed aggregates of pseudohexagonal shape with a diameter of about 2 μ, but no organic structures could be found (plate 1); while in the unconsolidated calcitic layer (core depth 85-85.5 cm) about one fifth of the clay fraction are coccolithophorids (plate 2).

The micrit sized matrix of the lithic fragments is characterized by the lack of biogenic structures. Only the tests of planktonic foraminifera and pteropod shells are common. Both show all stages from unaltered to completely destroyed shells : aragonitic shells are more or less dissolved, calcitic tests are partially micritized. Quartz, feldspar and pyrite are present in minor amounts. The chambers of foraminifera are partly filled with micrit, some show the presence of drusy magnesian calcite.

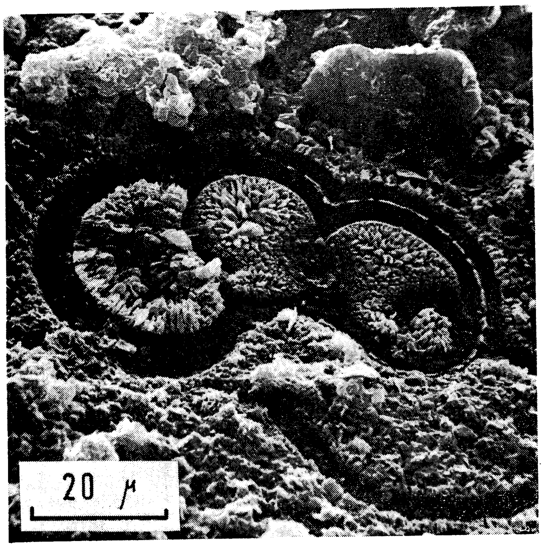


PLATE 3 : drusy magnesian calcite in foraminifera chambers - lithic fragment, core depth 115-118 cm.

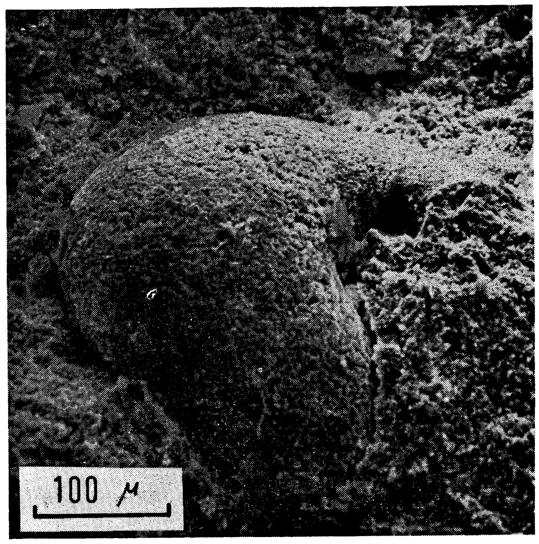


PLATE 4 : almost completely dissolved aragonitic pteropod shell - lithic fragment, core depth 66.5-67.5cm

The above data and observations imply the following statements :

— Dolomite and a part of calcite are detrital; magnesian calcite is thought to be autochthonous, since a biogenic source of magnesian calcite is unknown in the deep sea environment.

— Decrease of organic carbon with increasing core depth and its relatively low content within the lithic fragments indicate diagenetic changes, perhaps decomposition by bacteria.

— The presence of three layers rich in magnesian calcite indicates that both bottom water and the interstitial water are in equilibrium with respect to magnesian calcite.

— The occurrence of lithic fragments rich in magnesian calcite show that lithification processes occur within the magnesian calcite lutite.

— The occurrence of drusy magnesian calcite within the chambers of foraminifera indicates the precipitation from a solution (plate 3).

— Due to the incomplete state of micritisation of calcitic foraminifera tests and different states of dissolution of aragonitic pteropod shells, no decision can be made wether the lithification still endures or wether this represents an interrupted stage of early diagenesis (plate 4).

V. Discussion

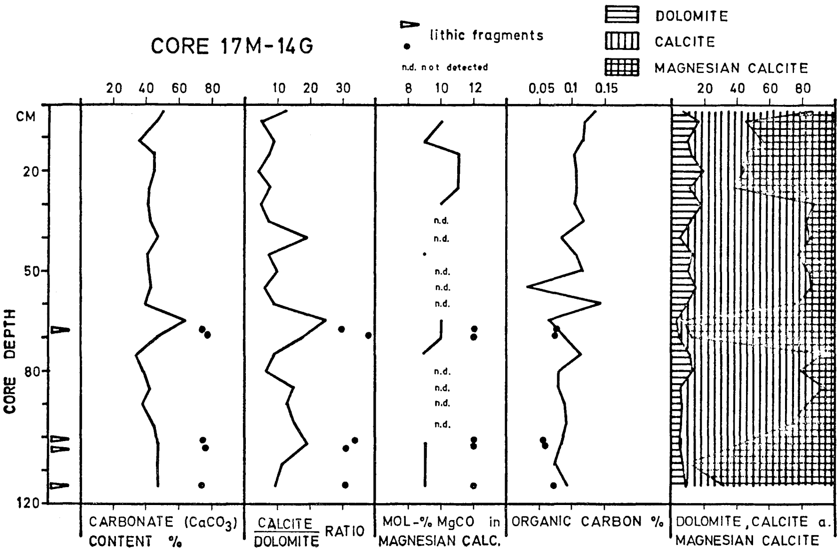
Due to the site of the core the deposition of magnesian calcite derived by shallow water material seems unlikely. Thus, the main — and still unanswered — questions are :

— Is magnesian calcite of synsedimentary origin or has it been precipitated post-depositional by the influx of pore water rich in Mg?

— What is the source of Mg? And what mechanism mobilized Mg in the deep sea environment that made precipitation of magnesian calcite possible?

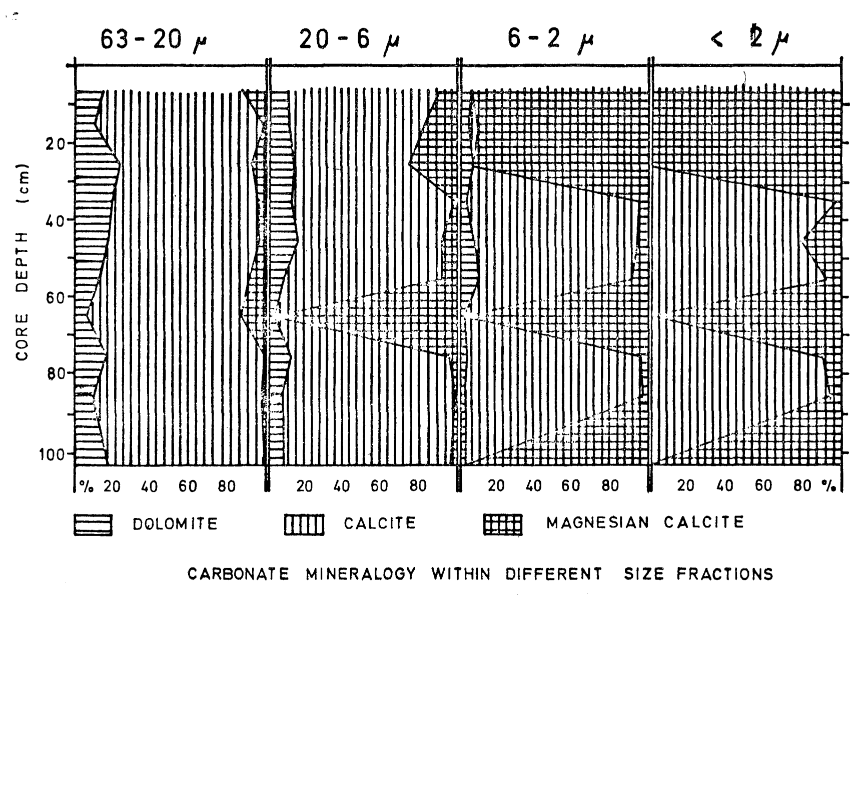
GEVIRTZ & FRIEDMAN [1966] and MILLIMAN *et al.* [1969] studied the deposition of aragonite and magnesian calcite in the Red Sea. They concluded that aragonite has been precipitated during low sea level stages during the Würm glaciation. Magnesian calcite is described partly as inversion product, partly as direct precipitate. MILLIMAN *et al.* (1969) suggested a similar origin of the magnesian calcite lutite and

FIG. 1.



—lithic fragments in sediments of the Sicily Basin. On this base, the above described three magnesian calcite layers could be hypothetically interpreted as precipitations caused by low sea level stages during the Günz-, Mindel- and Würmglaciation. A relatively widespread occurrence of magnesian calcite is shown by preliminary studies of two other cores of the same area. But at present, we have no direct evidence neither to confirm direct precipitation of magnesian calcite nor to deny that magnesian calcite is an inversion product of aragonite.

FIG. 2.



References

BØGGILD (O.B.), 1912. — The deposits of the sea bottom. — *Rep. Dan. oceanogr. Exped. Mediter.*, **1**, 3, pp. 257-269.

DE WINDT (J.) & BERWERTH (F.), 1904. — Untersuchung von Grundproben der I., II. und IV. Reise von S. M. « POLA » in den Jahren 1890, 1892 und 1893. — Ber. Comm. Erforschung östl. Mittelmeeres Denkschr. Akad. Wiss. Wien, **74**, pp. 285-294.

EMELYANOV (E.M.), 1965. — Karbonatnost sovremennych donnykh otlozhenii Sredizemnogo morya; pp. 71-83, *in : Osnovnge cherty geologicheskogo stroeniya gidrologicheskogo rezhima ibiologii Sredizmnogo morya.* Moscow, Publ. House. Nauka.

FISCHER (A.G.) & GARRISON (R.E.), 1967. — Carbonate lithification on the sea floor. — *J. Geol.*, **75**, p. 488-496.

FRIEDMAN (G.M.), 1965. — Occurrence and stability relationships of aragonite, high-magnesium calcite and low-magnesium calcite under deep-sea conditions. *Bull. geol. Soc. Amer.*, **76**, pp. 1191-1196.

FUCHS (T.), 1894. — Über einige von der österreichischen Tiefsee-Expedition S.M. Schiffes « POLA » in bedeutenden Tiefen gedredschten Cylindrites-ähnlichen Körper — Ber. Comm. Erforschung östlichen Mittelmeeres Denkschr. Akad. Wiss. Wien, Math.-naturw. Kl., **61**, pp. 11-22.

GEVIRTZ (J.L.) & FRIEDMAN (G.M.), 1966. — Deep-sea carbonate sediments of the Red Sea and their implications on marine lithification — *J. sediment. Petrol.*, **36**, pp. 143-151.

GIERMANN (K.), 1966. — Gedanken zur ostmediterranen Schwelle. — *Bull. Inst. oceanogr. Monaco*, **66**, pp. 1-16.

GOLDSMITH (J.R.) & GRAF (D.L.), 1958. — Relation between lattice constants and composition of the Ca-Mg carbonates. — *Amer. Min.*, **43**, pp. 84-101.

HERSEY (J.B.), 1965. — Sedimentary basins of the Mediterranean Sea — Proc. VII. Symposium Colston Research Society : **17**, pp. 75-91.

HEYE (D.), 1970. — Magnetische Untersuchungen an Sedimentkernen des Mittelmeeres. — Meteor-Forschungsergebnisse, Reihe C, Heft 3, pp. 85-88.

MILLIMAN (J.D.), 1966. — Submarine lithification of carbonate sediments. — *Science*, **153**, pp. 994-997.

MILLIMAN (J.D.), ROSS (D.A.) & KU (T.L.), 1969. — Precipitation and lithification of deep-sea carbonates in the Red Sea. — *J. sediment, Petrol.*, **39**, pp. 724-736.

MÜLLER (J.), 1969. — Mineralogisch-sedimentpetrographische Untersuchungen an Karbonatsedimenten aus dem Schelfbereich um Fuerteventura und Lanzarote (Kanarische Inseln). — Dissertation Universität Heidelberg, 99 p.

NATTERER (K.), 1894. — Chemische Untersuchungen im östlichen Mittelmeer, i. Reise S. M. Schiffes « POLA » im Jahre 1890 — Denkschr. Akad. Wiss. Wien, Math.-naturw. Kl., **65**, p. 445-572.

NORIN (E.), 1956. — The sediments of the central Tyrrhenian Sea. — *Rep. Swed. Deep-Sea Exped.*, **8**, pp. 1-136.

Acknowledgements

We wish to express our thanks to the *Deutsche Forschungsgemeinschaft*, who financed this research and to P. RÖLZ and W. SIGL for their help during laboratory work.