

# YALE PEABODY MUSEUM

P.O. BOX 208118 | NEW HAVEN CT 06520-8118 USA | PEABODY.YALE. EDU

## JOURNAL OF MARINE RESEARCH

The *Journal of Marine Research*, one of the oldest journals in American marine science, published important peer-reviewed original research on a broad array of topics in physical, biological, and chemical oceanography vital to the academic oceanographic community in the long and rich tradition of the Sears Foundation for Marine Research at Yale University.

An archive of all issues from 1937 to 2021 (Volume 1–79) are available through EliScholar, a digital platform for scholarly publishing provided by Yale University Library at <https://elischolar.library.yale.edu/>.

Requests for permission to clear rights for use of this content should be directed to the authors, their estates, or other representatives. The *Journal of Marine Research* has no contact information beyond the affiliations listed in the published articles. We ask that you provide attribution to the *Journal of Marine Research*.

Yale University provides access to these materials for educational and research purposes only. Copyright or other proprietary rights to content contained in this document may be held by individuals or entities other than, or in addition to, Yale University. You are solely responsible for determining the ownership of the copyright, and for obtaining permission for your intended use. Yale University makes no warranty that your distribution, reproduction, or other use of these materials will not infringe the rights of third parties.



This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License.  
<https://creativecommons.org/licenses/by-nc-sa/4.0/>



# *Analyses of Coccolith Ooze from the Deep Tropical Atlantic*<sup>1</sup>

Geoffrey Thompson and Vaughan T. Bowen

*Woods Hole Oceanographic Institution  
Woods Hole, Massachusetts*

---

## ABSTRACT

Analyses of samples from a 200-cm core of coccolith ooze from the deep tropical Atlantic (00°07' S, 17°34' W) show it to be uniformly composed of low-magnesium calcite. The levels of most trace elements were found to be low for pelagic marine carbonate sediments.

*Introduction.* The skeletal plates (coccoliths) of planktonic algae of the family Coccolithophoridae (Parke and Dixon 1964, McIntyre and Bé 1967) are major components of pelagic carbonate sediments and sometimes exceed the mass represented by Foraminifera (Arrhenius 1963). During geological history, the balance of Foraminifera versus coccoliths appears to have varied in an ecologically significant way (Arrhenius 1963); it has been suggested (Bramlette 1958) that the Coccolithophoridae considerably predate the Foraminifera as major biological agents in transferring calcium from seawater to sediments. In view of this, it is unfortunate that so little information is available on the chemistry of coccolithophorid skeletons or of coccolith oozes. Recently we obtained a relatively long core of relatively pure coccolith ooze; it is our purpose here to describe its composition.

*Sample Location and Description.* The core was collected on R/V ATLANTIS II cruise 20 during an extensive study in the Romanche Fracture Valley that involved bathymetry, coring, and dredging. [A preliminary report on the results of this cruise is in preparation.] The core was obtained with a "Dart Corer"—essentially a high-mass high-velocity gravity corer—at a depth of 3530 m on the south wall of the Romanche Fracture Valley (Heezen et al. 1964) at 00°07' S, 17°34' W. The main core tube contained 203 cm of coccolith ooze; the ooze was stiffly plastic but not lithified and showed no obvious stratification. In contrast, the pilot corer contained about 8 cm of lithified

1. Accepted for publication and submitted to press 13 september 1968.

coccolith ooze that was much less pure and showed several laminae arranged almost parallel to the axis of the core. The core has been identified as ATLANTIS II-20 core 6.

Preliminary examination of the ooze from the main core revealed discoasters that have been tentatively described as late Tertiary (T. C. Moore, personal communication). Samples were submitted subsequently to M. N. Bramlette, who assigned the following stratigraphic ages: early Pliocene, to the top of the main core; Mio-Pliocene or early Pliocene, to a sample 106 cm down; Mio-Pliocene, to a sample 196 cm down. Pelagic Foraminifera were recovered from samples at several levels of this core; they never exceeded 1% of any sample and were wholly lacking at most levels. Richard Cifelli (USNM) examined Foraminifera from several levels and assigned ages identical to those assigned by M. N. Bramlette. We are most grateful to Drs. Bramlette and Cifelli for permission to quote this information.

*Analytical Technique and Results.* One portion of each selected sample was dissolved in hot (80°C) 25% acetic acid and filtered; the insoluble fraction was dried and weighed. The acetic solutions were analyzed by direct-reading emission spectrometry, using the vacuum-cup technique (Zink 1959). Excitation was by means of an air-interrupted high-voltage AC spark with 40 mH inductance, 0.0025  $\mu$ F capacitance, and 4.5 amp RF current. The duration of excitation was 20 seconds following a 5-sec preburn. Mg 2795.5 and Sr 4077.7 were the measured wavelengths; Be 3130.4 was used as the internal standard line.

The trace element concentrations were determined on an untreated portion of the sample. D. C. arc excitation was employed, following the technique of Thompson and Bankston (to be described).

The results of the analyses are presented in Table I.

#### *Discussion.*

**MINERALOGY.** X-ray diffractometry (Table I) showed that our samples are primarily calcite and low in magnesium; analysis confirmed that, in fact, the magnesium content is very low—0.10 to 0.12%. There is some uncertainty in the literature about the mineralogy of coccoliths. They are generally referred to as being calcite (Arrhenius 1963), but specific reports differ: Tan-Sin-Hok (1928, quoted in Vinogradov 1953), believed them to be aragonite, and Hart et al. (1965) reported X-ray evidence for aragonite in a South African coccolith from Cretaceous deposits. On the other hand, Bramlette (personal communication) found, using X-ray diffraction, that one of Tan-Sin-Hok's specimens was in fact calcite; this and other analyses convinced Bramlette (quoted in Revelle and Fairbridge 1967) that coccoliths are typically calcite. Black (1963, 1965) also found only calcitic coccoliths as did Lewin and Chow (1961) in the case of cast plates of *Syracosphaera carterae*,

Table I. Analyses of coccolith ooze in a core (A-11-20 core 6) from the deep tropical Atlantic.\*

Sample no.	Depth of sample in core (cm)	X-ray diffract.	% insoluble in 25% acetic acid	Mg: % in acid soluble	Sr: % in acid soluble	Elements, ppm whole dry samples †												
						B	Ba	Co	Cr	Cu	Li	Mn	Ni	Sr	Ti	Y	Zn	Zr
6-23	7.5	low-mg calcite	2.09	0.10	0.16	30	135	3	5	10	4	265	4	1440	95	11	4	18
6-13	97.5	low-mg calcite	2.15	0.12	0.15	40	195	4	6	13	7	280	4	1540	140	15	6	21
6-5	169.5	low-mg calcite	2.39	0.11	0.14	35	195	5	5	15	7	245	4	1425	105	15	5	19

\* The fractions analyzed were especially low in skeletons of Foraminifera.

† Al, Fe, and Si were each present in excess of 0.1%. The following elements were also sought but each was below its detection limit: Ag (1 ppm), Bi, Cd, Ga, Mo, Pb (2 ppm), Rb, Sn, V (5 ppm).

grown in synthetic media. It is possible of course, as Hart et al. (1965) have suggested, that coccoliths may be either aragonite or calcite in response to environmental variables or even that coccolith mineralogy has changed over geologic time. The experiments of Wilbur and Watabe (1963) support the hypothesis that coccolith mineralogy varies in response to ecological variables; in two strains of *Coccolithus huxleyi*, nitrogen deficiency—a common experience of marine planktonic algae (Vaccaro 1965)—induced a change from either lack of calcification or the formation of calcitic plates to the formation of plates of mixed aragonite, calcite, and vaterite, the proportions depending on temperature. As Wilbur and Watabe noted, it is by no means clear that such mineral mixtures would be stable for any prolonged period. Our data do show that, at equatorial water temperatures, calcite coccoliths are deposited in abundance. The depth of recovery, 3530 m (corrected), is shallower than the depths at which rapid carbonate dissolution occurs; we believe that the possibility of selective solution of an original aragonitic component can be neglected.

Our samples contained magnesium in the range 0.10 to 0.12%; Lewin and Chow (1961) found 0.1% to 0.15% Mg in coccoliths from algae grown in a medium containing only 4.2 mmol Mg/L compared with the 53 mmol Mg/L in normal seawater. We believe that coincidence of our values with theirs, over so wide a range of Mg in the medium, indicates that calcitic coccoliths are always low in Mg. Revelle and Fairbridge (1957) noted that Vinogradov's (1953) various statements on magnesium in Coccolithophoridae imply that it is everywhere low and that coccolith calcite is less than 1 mol % Mg. Our data and those of Lewin and Chow would indicate that the statement should read "much less than 1 mol %". As we discuss below, this appears to be equally true for the calcite of planktonic Foraminifera.

COMPOSITION. The ratio 1000 × Sr atoms/Ca atoms in our samples of cocco-

lith ooze ranges from 1.6 to 1.8; this may be compared with data of Thompson and Chow (1955), who have stated that such ratios range from 2.9 to 3.5 for algae of the family Corallinaceae and from 2.8 to 3.3 for various Foraminifera (however, a "Globigerina ooze" from the Pacific gave 1.5). Statistically, ratios of less than 2 are unusual in Thompson and Chow's series, being found only among Mollusca and Brachiopoda Articulata. Odum (1957) and Kulp et al. (1952) reported ratios of 1.5 to 2.7 for pelagic foraminiferal oozes. For *Syracosphaera carterae*, Lewin and Chow reported atom ratios (calculated as above) ranging from 2.9 to 8.6; however, their specimens were coccoliths from cultures in media at high Sr:Ca ratios: respectively 140, 280, and 550, calculated as above! It is not unreasonable, perhaps, that, under such changed conditions (from seawater), Lewin and Chow found mean discrimination factors Sr:Ca in coccoliths/Sr:Ca in medium about 0.02 compared with about 0.2 calculated from our data. Clearly, both *Syracosphaera* in culture and our coccolith-ooze population discriminated against Sr in their tests to a degree that is close to the maximum known for marine carbonate-secreting organisms. Such discrimination has been reported by Lowenstam (1964) for aragonite deposited in the complex skeletons of a variety of bivalve Mollusca; among other invertebrate classes, however, Lowenstam concluded: "The crystal chemistry constitutes a first order effect on the uptake of Sr in their aragonites and calcites." We would expect much more Sr in aragonitic than in calcitic coccoliths.

Nicholls (personal communication) has suggested to us that the words "discriminated against," although commonly used to describe cases where the biogenic element or atom ratio is less than that in the medium, are clearly misleading: even the lowest reported Sr contents in biological calcite significantly exceed the content to be expected in calcite that is inorganically precipitated from seawater. Nicholls, after correcting the distribution factors of Oxburgh et al. (1959) for "complexing, temperature and activity effects," has estimated that the thermodynamic Sr:Ca distribution coefficient should be about 0.1 for calcite; recently, Lerman (1965) followed Holland (unpublished) in using a distribution factor (at 25°C) of 0.13 for Sr:Ca in calcite. Certainly, the frequency of distribution coefficients that are much higher than 0.1 to 0.13 in biogenic calcites could be indicative of a general biological discrimination in favor of Sr; this could be mediated either by enriching the Sr:Ca ratio in the solutions from which skeletal calcite is precipitated or by performing such precipitations in the presence of organic complexing agents that depress Ca ion activity more than that of Sr. Lerman's calculations, however, indicate another possibility, at least for calcitic coccoliths: the distribution coefficients calculated above are for calcite containing about 1 mol % Mg, the low-Mg form that Lerman believes to be stable in seawater. Possibly in calcite that is much lower than 1 mol % in Mg (as in the coccoliths), more sites in the crystal lattice would be occupied by Sr ions, even if the Sr:Ca ion-activity ratio were not changed from that of seawater; this could be indicated by the very

high (10 mol %)  $\text{SrCO}_3$  content that Terada (1963) found to be a stable crystal phase in the binary system  $\text{CaCO}_3$ - $\text{SrCO}_3$ . Until more is known in detail about the thermodynamics of the Ca-Mg-Sr-Ba quaternary carbonate system, it may be premature to conclude a specific biological effect except in the case of Mg.

Goldberg and Arrhenius (1958) have reported barium analyses of two largely coccolithic pelagic oozes: in a modern subequatorial Pacific ooze they found that BaO was 0.90% in the  $3.2\ \mu$  to  $62\ \mu$  fraction, but in a Pacific Miocene ooze, BaO was only 0.020%. This latter sample was of exceptional purity (99.5% soluble in weak acetic acid), and the Ba was found almost wholly in the insoluble fraction, associated with mineral aggregates, which they believed to be fossil fecal pellets. The range of Ba concentrations in our samples is close to the range in their Pacific Miocene core, and much lower than that in their modern core; we have so far no data to show whether our samples, also, contain most of the Ba in insoluble mineral aggregates. Since our coccolith Ba concentrations differ insignificantly from the range (160 to 185 ppm) shown by a series of noncoccolith calcareous oozes from about  $22^\circ\text{N}$  in the Atlantic (data to be published), we agree with the conclusion of Goldberg and Arrhenius that coccoliths are not of any special importance in Ba sedimentation.

In fact, our data in Table I, compared with analyses of other pelagic carbonate sediments, show that coccolith carbonates are unusually pure: only the Ba and Sr contents of the coccolith carbonates fall within what we consider to be the normal range of Atlantic Ocean sediments or of the sediments described by Goldberg and Arrhenius; other constituents are well below average. Emiliani (1955) and Krinsley (1960) presented analytical data showing that several planktonic Foraminifera also deposit calcite that has a magnesium content that is well below 1 mol % and is very pure with respect to a variety of other elements. Of the elements reported by Emiliani, only Sr, Mg, Ti, and Mn are represented on our list. We agree with Emiliani that Sr "probably substitutes for Ca in the calcite lattice"; our data appear to show that coccolith calcite is somewhat richer in Sr than is foraminiferan calcite. Our data, plotted against either Ti or "insoluble residue," do not agree with Emiliani's surprising finding that, in foraminiferan calcite, Mg "goes to zero for zero" aluminosilicate; we believe that coccolith calcite contains a small but uniform component of  $\text{MgCO}_3$  in solid solution. Neither Mn or Ti, in coccoliths, varies consistently with the "insoluble residue," so they cannot be concluded to be constituents extraneous to the calcite skeleton. Krinsley's data show that his foraminiferan calcite was closer, in contents of Mg, Mn, and Ti, to our coccolith samples than to Emiliani's Foraminifera. It is possible that Krinsley's samples were even lower in Mn than were ours. Krinsley also reported values for Cu and Ni; our Cu values for coccoliths are essentially the same as Krinsley's for Foraminifera, but our nickel values are significantly lower. Arrhenius (1963)

quoted an unpublished analysis of a mixed foraminiferan sample, but several of the values are so unexpected (notably B, Ba, Sr, Ti, and Ag) and the technique so cryptically described that we are inclined to reserve judgment.

If, as suggested by Bramlette (1958), coccoliths were, during a period in the ocean's history, much more important vectors of calcium carbonate removal than they have been since the Foraminifera reached full development, then the available data on trace-element composition of coccoliths seem to show that such a situation might have had significant implications geochemically. Important trace elements such as cobalt, nickel, and zinc may well have built up, during such a period, to levels sufficiently high so that their concentrations were controlled by processes not now operative.

Clearly, more mineralogical and more analytical data are needed on this important class of calcareous skeletons, from both the modern ocean and earlier geological time periods.

*Acknowledgments.* We are grateful to G. D. Nicholls, University of Manchester, England, and H. A. Lowenstam, California Institute of Technology, U.S.A., for reading and commenting on our manuscript. Our work has been supported by the U.S. Atomic Energy Commission under Contract AT(30-1)-2174; this is report number NYO-2174-76.

This is Contribution Number 2161 from the Woods Hole Oceanographic Institution.

#### REFERENCES

ARRHENIUS, G. O. S.

1963. Pelagic sediments. *In* The Sea, Ideas and Observations, vol. 3, pp. 655-727. Ed., M. N. Hill. Interscience, N.Y. 963 pp.

BLACK, MAURICE

1963. The fine structure of the mineral parts of Coccolithophoridae. *Proc. linn. Soc. London.* 174th session, 1961-1962, part 1: 41-46.

1965. Coccoliths. *Endeavour*, 24: 131-137.

BRAMLETTE, M. N.

1958. Significance of coccolithophorids in calcium carbonate deposition. *Bull. geol. Soc. Amer.*, 69: 121-126.

EMILIANI, CESARE

1955. Mineralogical and chemical composition of the tests of certain pelagic Foraminifera. *Micropaleontology*, 1 (4): 377-380.

GOLDBERG, E. D., and G. O. S. ARRHENIUS

1958. Chemistry of Pacific pelagic sediments. *Geochim. Cosmochim. Acta*, 13: 153-212.

HART, F. F., R. N. PIENAAR, and R. CAVENEY

1965. An aragonite coccolith from South Africa. *S. Afr. J. Sci.*, 61: 425-427.

HEEZEN, B. C., E. T. BUNCE, J. B. HERSEY, and MARIE THARP

1964. Chain and Romanche Fracture Zones. *Dee-sea Res.*, 11: 11-33.

KRINSLEY, DAVID

1960. Trace elements in the tests of planktonic foraminifera. *Micropaleontology*, 6 (3): 297-300.

KULP, J. L., K. K. TUREKIAN, and D. W. BOYD

1952. Strontium content of limestones and fossils. *Bull. geol. Soc. Amer.*, 63: 701-716.

LERMAN, ABRAHAM

1965. Paleocological problems of Mg and Sr in biogenic calcites in light of recent thermodynamic data. *Geochim. Cosmochim. Acta*, 29: 977-1002.

LEWIN, R. A., and T. J. CHOW

1961. La enpreno de strontio en Kokolitoforoj. *Plant Cell Physiol. (Japan)*, 2: 203-208.

LOWENSTAM, H. A.

1964. Coexisting calcites and aragonites from skeletal carbonates of marine organisms and their strontium and magnesium contents. In, *Recent Researches in the Fields of Hydrosphere, Atmosphere and Nuclear Geochemistry*, pp. 373-404. Ed., Yasuo Miyake and Tadashiro Koyama. Maruzen Co., Ltd., Tokyo, Japan. vi + 404 pp.

MCINTYRE, ANDREW, and A. W. H. BÉ

1967. Modern Coccolithophoridae of the Atlantic Ocean. I. Placoliths and Cyrtoliths. *Deep-sea Res.*, 14: 561-597.

ODUM, H. T.

1957. Biogeochemical deposition of strontium. *Publ. Inst. mar. Sci. Univ. Texas*, 4: 38-114.

OXBURGH, U. M., R. E. SEGNET, and H. D. HOLLAND

1959. Coprecipitation of strontium with calcium carbonate from aqueous solutions. *Bull. geol. Soc. Amer.*, 70: 1653-1654.

PARKE, MARY, and P. S. DIXON

1964. A revised check-list of British marine algae. *J. Mar. biol. Ass. U. K.*, 44: 499-542.

REVELLE, R. R., and R. W. FAIRBRIDGE

1957. Carbonates and carbon dioxide. *Mem. geol. Soc. Amer.*, 67: 1, 239-296.

TAN-SIN-HOK

1928. Over de samenstelling en het ontstaan van krijt-en mergelgesteenten van de Molukken. *N. jb. Min. Geol. Palaont.*, 1928: 340.

TERADA, J.

1953. Crystal structure of Ba-Sr-Ca triple carbonate. *Nature, London*, 171: 517-518.

THOMPSON, T. G., and T. J. CHOW

1955. The Sr-Ca atom ratio in carbonate-secreting marine organisms. *Pap. Mar. Biol. Oceanogr.*, *Deep-sea Res.*, 3 (Supplement): 20-39.

VACCARO, R. F.

1965. Inorganic nitrogen in sea water. In *Chemical Oceanography*, vol. I, pp. 365-408. Ed., J. P. Riley and Geoffrey Skirrow. Academic Press, London. xix + 712 pp.

VINOGRADOV, A. P.

1953. The Elementary Chemical Composition of Marine Organisms. *Mem. Sears Found. Mar. Res.*, 2; xiv + 647 pp.

WILBUR, K. M., and NORIMITSU WATABE

1963. Experimental studies on calcification in molluscs and the alga *Coccolithus huxleyi*. *Ann. N. Y. Acad. Sci.*, 109: 82-112.

ZINK, T. H.

1959. A "vacuum-cup" electrode for the spectrochemical analysis of solutions. *Appl. Spectroscopy*, 13: 94-97.