

THE STABLE ISOTOPE GEOCHEMISTRY OF MARINE COCCOLITHS: A PRELIMINARY COMPARISON WITH PLANKTONIC FORAMINIFERA

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ABSTRACT

The oxygen isotopic compositions of pelagic carbonates in the <44-micron fraction from a Caribbean core of Pleistocene age and from an east Pacific core of the same age vary systematically with the oxygen isotopic compositions of planktonic foraminifera from the same core sample. This covariance suggests that the isotopic compositions of coccoliths, which comprise almost all of the carbonate in the <44-micron fraction, are controlled to some extent by the temperature and the isotopic composition of water in which they grew. The

direction and magnitude of oxygen isotopic fractionation between coccoliths and planktonic foraminifera in the Pacific core are compatible with precipitation of coccoliths near thermodynamic equilibrium with surface ocean water. However, the observed fractionations in the Caribbean core cannot be explained by equilibrium precipitation of coccoliths. We tentatively suggest that biological (nonequilibrium) fractionation related to environmental factors influenced the isotopic composition of Pleistocene coccoliths in the Caribbean.

INTRODUCTION

Variations in the stable isotopic compositions of coccoliths from deep-sea sediment cores could be an important indicator of paleo-oceanographic processes. For example, if coccoliths are deposited in thermodynamic equilibrium with the water in which they live (0–100 meters), then the oxygen isotopic composition of coccoliths in marine carbonate sediments could be used in paleoclimatologic investigations. Also, since coccoliths are the predominant calcareous component of pre-Pleistocene pelagic sediments, isotopic fractionations in coccoliths control in large part the isotopic composition of Tertiary pelagic carbonates.

This study was initiated to obtain some preliminary data on the carbon and the oxygen isotopic composition of coccoliths from deep-sea sediments. In this paper we report the isotopic compositions of carbonates in the <44-micron fraction (hereafter referred to as the coccolith fraction) from the Caribbean core CP-28 (Emiliani, 1964) and the highest core taken at Site 82

of the Deep Sea Drilling Project in the eastern Pacific (Hays and others, 1972). The locations and depths at which the cores were taken are shown on table 2. All the sediments are Pleistocene in age. In order to interpret the isotopic compositions of coccoliths, we also measured the isotopic compositions of a selected group of planktonic foraminifera from most of the core intervals from which the coccoliths were separated.

METHODS

Bulk sediment samples were disaggregated by ultrasonication in distilled water and were size-fractionated by washing through a 44-micron screen. After the solids had settled (1–2 hours for the coarse fraction, 24–48 hours for the fine fraction) the water was decanted off, and the samples were washed in methanol and then dried in an oven at 100°C. Following the procedure of Douglas and Savin (1971), whole tests of planktonic foraminiferal species with globigerine-type morphology were handpicked from the coarse fraction

TABLE 1
Foraminiferal species selected for isotope analyses

	DSDP Site 82	CP-28
<i>Globigerinella aequilateralis</i>	X	X
<i>Globigerinoides sacculifer</i>	X	X
<i>Globoquadrina dutertrei</i>	X	X
<i>Pulleniatina obliquiloculata</i>	X	
<i>Sphaeroidinella dehiscentis</i>	X	

for isotope analysis (see table 1). Depth rankings of planktonic foraminifera based on plankton tow collections suggest that these species occupy waters within and above the upper thermocline for most of their life cycle (Berger, 1969). Scanning electron micrographs of selected foraminiferal samples and of selected coccolith fractions show that the carbonates analyzed in this study were well preserved. The only non-coccolith carbonate material observed in the <44-micron fractions were trace quantities of broken foraminiferal tests.

The coccolith fractions were analyzed isotopically after drying. The foraminiferal samples were cleansed of fine-grain material by ultrasonerating in methanol, light crushing with a glass rod under methanol, and ultrasonerating again. The overall weight loss in this cleaning procedure was 20–40 percent. All carbonate samples were reacted with 100 percent H_3PO_4 at 25°C (McCrea, 1950). The evolved CO_2 was analyzed for

the isotopic composition of carbon and oxygen in a double-collecting mass spectrometer (Nuclide RMS System).

RESULTS

The isotopic compositions are reported in table 2 in the conventional δ -terminology, where

$$\delta \text{ (permil)} = \left[\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right] \times 1000$$

and R is the C^{13}/C^{12} ratio or the O^{18}/O^{16} ratio. The reporting standard is the Chicago PDB standard (Craig, 1957). The precision of an individual isotopic analysis is ± 0.1 permil.

Table 2 also lists the estimated oxygen isotopic compositions of *Globigerinoides sacculifera* interpolated from the analyses of Emiliani (1964) on core CP-28. Three of the four planktonic foraminiferal samples we analyzed (225 cm, 349 cm, 649 cm) are reasonably in good agreement with the interpolated values inasmuch as (1) our analyses were on a group of foraminiferal species rather than on a single species, and (2) results from different laboratories may differ widely (see Shackleton and others, 1973, p. 179). The fourth sample (539 cm) is 1.5 permil more negative than the interpolated value at this depth interval. We have no explanation for this discrepancy; perhaps our sample

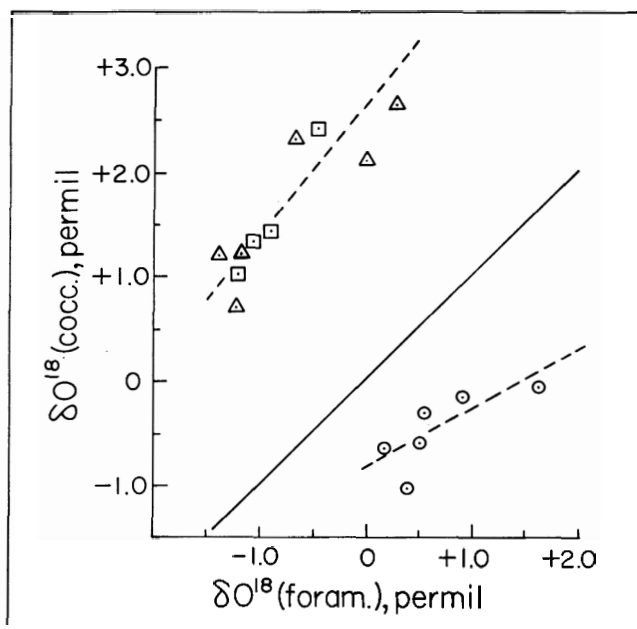
TABLE 2
Results of isotope analyses

	Depth, cm	% carbonate in cocc. fraction*	Coccolith fraction		Globigerine foraminifera		$\Delta O^{18} \dagger$	δO^{18} of <i>G. sacculifera</i> (Emiliani, 1964)
			δC^{13}	δO^{18}	δC^{13}	δO^{18}		
82-1-1	35	89	+0.53	-0.31	+1.80	+0.58	-0.9	
Lat. 02° 35.48' N.	50	87	+0.67	-1.03	+1.67	+0.39	-1.4	
Long. 106° 56.52' W	60	84	+0.20	-0.05	+3.14	+1.62	-1.7	
3689 m depth	85	87	+ .56	-0.63	+1.41	+0.21	-0.8	
	100	86	+0.43	-0.15	+1.65	+0.93	-1.1	
	140	82	+0.23	-0.60	+1.66	+0.52	-1.1	
CP-28	29	52	+0.71	+1.21			+2.6‡	-1.38
Lat. 16° 47.7' N.	59	48	+1.49	+2.11			+2.1‡	0.00
Long. 74° 26.4' W.	225	48	+1.12	+1.43	+2.01	-0.90	+2.3	-0.85
3036 m depth	349	75	+1.58	+1.33	+1.58	-1.04	+2.4	-1.53
	379	49	+1.14	+2.42			+2.9‡	-0.46
	449	51	+0.76	+2.65			+2.4‡	+0.27
	487	55	+1.63	+0.71			+1.9‡	-1.23
	539	58	+1.97	+1.02	+1.45	-1.20	+2.2	+0.26
	589	60	+1.21	+1.22			+2.4‡	-1.18
	649	53	+1.59	+2.32	+1.72	-0.68	+3.0	-0.77

* Calculated from CO_2 yield from H_3PO_4 treatment.

† $\Delta O^{18} = \delta O^{18} \text{ (coccolith)} - \delta O^{18} \text{ (foram.)}$.

‡ Using the δO^{18} values from Emiliani (1964).



TEXT FIGURE 1

Relationship between the oxygen isotopic compositions of the coccolith fraction and of planktonic foraminifera. The solid line represents $\delta^{18}\text{O}(\text{cocc.}) = \delta^{18}\text{O}(\text{foram.})$. $\odot$ DSDP Site 82. $\square$ Core CP-28. $\triangle$ Core CP-28 using the interpolated $\delta^{18}\text{O}$ values of *Globigerinoides sacculifer* from Emiliani (1964).

was mislabelled. In any case, the difference in isotopic composition between coccoliths and foraminifera would be unaffected by such an error.

DISCUSSION

Based on the numerous paleotemperature studies of Emiliani (for example, see Emiliani, 1955, and 1966), it is commonly assumed that planktonic foraminifera deposit calcium carbonate in oxygen isotopic equilibrium with the surrounding water. Recently, however, Shackleton and others (1973) report that four species of living planktonic foraminifera collected at the same depth interval, and therefore at the same temperature, may have oxygen isotopic compositions differing by as much as 0.8 permil. For the purpose of discussing our results, we shall assume that planktonic foraminiferal tests are secreted near thermodynamic equilibrium with ocean water. Since coccoliths are secreted at a shallower mean depth than the foraminiferal assemblage we selected for analyses, the coccolith fraction would be somewhat depleted in O^{18} with respect to the foraminifera. Our results indicate that there are systematic iso-

topic fractionations between the coccolith fraction and planktonic foraminifera in both cores but that these fractionations differ between cores. Oxygen isotopic fractionations [expressed as $\Delta \text{O}^{18} = \delta(\text{cocc.}) - \delta(\text{foram.})$] in DSDP Site 82 (equatorial Pacific) are negative, ranging from -0.8 to -1.7 permil (average -1.2); in core CP-28 (Caribbean) the fractionations are positive, ranging from +1.9 to +3.0 permil (average +2.4).

Text figure 1 illustrates the oxygen isotopic fractionations between coccoliths and foraminifera and also show that the δO^{18} values of these components are correlated ($r = 1.01$ for CP-28 and 0.79 for DSDP Site 82). This correlation suggests that the oxygen isotopic composition of coccoliths, as well as of planktonic foraminifera, reflect the temperature and the isotope composition of the water in which they live. This interpretation is generally compatible with the results from DSDP Site 82. In the eastern equatorial Pacific, Recent planktonic foraminiferal assemblages show clear evidence for differential dissolution; the depth to the lysocline surface in the vicinity of DSDP Site 82 is about 3,000 meters (Parker and Berger, 1971). If, as pointed out by Berger (1971), differential dissolution concentrates heavy, thick-walled forms within each species population and these forms build most of their shell in deeper and colder water, then differential dissolution should concentrate shells with a colder water aspect. This possibility has been verified by Savin and Douglas (1973), who report the *Globigerinoides* species from topmost sections of South Pacific cores have δO^{18} values that are approximately 1 permil higher than predicted equilibrium values. If the magnitude of this difference remained constant in low latitudes in the Pacific back through the Pleistocene, then the average ΔO^{18} value of -1.2 permil observed in DSDP Site 82 could be attributed to the precipitation of coccoliths in oxygen isotopic equilibrium with surface ocean water. Differential dissolution of coccoliths is not expected to produce much isotopic bias, since they all grow in the uppermost water.

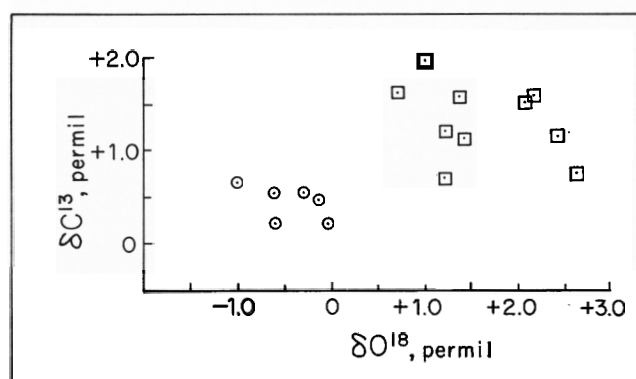
Obviously, however, such an explanation cannot account for the ΔO^{18} values of +2 to +3 permil observed in core DP-28. In order for both the coccoliths and the planktonic foraminifera to reflect equilibrium isotopic fractionation with sea water, then the coccoliths must have been precipitated in water that was either 2 to 3 permil heavier than the water in which foraminifera were precipitated, 8 to 12°C colder, or some combination of the two. There are several possible explanations for the oxygen isotopic fractionations

observed in core CP-28: (1) The coccolith fractions suffered extensive recrystallization in cold bottom water and thus acquired anomalously high δO^{18} values. (2) The coccolith fractions were contaminated by isotopically heavy carbonate such as shell fragments of benthic organisms. (3) Biological isotope effects controlled the isotopic composition of coccoliths in the Caribbean.

The first possibility is not supported by the good state of preservation of coccoliths that we observed in our limited SEM studies and that Stanker (1973) noted in his more detailed investigation of the nannofossils in core CP-28. Stanker does report that the least resistant coccoliths are missing from intervals near 350 cm, 490 cm, and 590 cm. However, the oxygen isotope compositions of the coccolith fractions in these intervals do not appear to reflect this change in species composition.

Contamination of the <44-micron fractions with non-coccolith carbonate would be a more serious problem in core CP-28 than in DSDP core 82 since this size fraction in the former contains a lower proportion of carbonate (table 2). A relatively few large grains of carbonate that were deposited in cold bottom water could make the oxygen isotopic composition of bulk carbonates in the <44-micron fraction heavier than the composition of coccoliths. If we assume, for the sake of this argument, that coccoliths should have approximately the same oxygen isotopic composition as planktonic foraminifera in core CP-28, then the proportion of benthic detritus in the <44-micron fraction would have to be in excess of 50 percent of the total carbonate in order to yield the anomalously heavy oxygen isotopic compositions we observed. Our examination of the <44-micron fraction from core CP-28 revealed only trace quantities of non-coccolith carbonate. Moreover, in order to account for the systematic fractionations between the coccolith fractions and planktonic foraminifera, contamination of the <44-micron fraction would have to be constant throughout the core. This possibility seems unlikely.

Biological isotope effects have been observed in several important groups of marine organisms and are apparently the result of the utilization of metabolic carbon and oxygen in the secretion of calcium carbonate. Duplessy and others (1970) and Vinot-Bertouille and Duplessy (1973) show that biological isotope effects in benthic foraminifera yield carbon and oxygen isotopic compositions that are displaced systematically from the predicted equilibrium compositions. Text



Carbon and oxygen isotopic compositions of the coccolith fractions. $\circ$ DSDP Site 82. $\square$ Core CP-28.

figure 2 shows that, while there is little correlation of δC^{13} and δO^{18} values of coccolith fractions within a core, each core shows either high or low δ values for both carbon and oxygen. It is difficult to explain the differences in isotope geochemistries of the coccolith fractions of these two cores by some species-dependent isotope effect since both contain essentially the same species (Bukry, 1972; Gartner, 1972; Stanker, 1973). Moreover, in core CP-28 the proliferation of *Emiliania huxleyi* above 300 cm (where, according to Stanker, it is the dominant coccolith species) is not reflected by any systematic change in the carbon or the oxygen isotopic composition of the coccolith fractions. In addition, biological isotope effects in benthic foraminifera and in other marine organisms that result from the incorporation of metabolic carbon and oxygen yield correlated δC^{13} and δO^{18} values that trend from equilibrium values to more negative values (Weber and Raup, 1966; Weber and Woodhouse, 1970). In text figure 2, the trend is from apparent equilibrium values (DSDP Site 82) to more positive values (CP-28).

Thus, while "vital" isotope effects may be responsible for the anomalously heavy oxygen isotopic compositions of coccoliths in core CP-28, these effects must be controlled as much by environmental factors as by purely physiological factors. The correlation between the oxygen isotopic compositions of coccoliths and planktonic foraminifera also suggests that the isotopic composition of coccoliths is sensitive to environmental influences.

Our results indicate that differences in carbon isotopic compositions between coccoliths and planktonic foraminifera are not the same for DSDP Site 82 and

for core CP-28. Until considerably more data on the carbon isotope composition of deep sea biogenous carbonates is available, it is not worthwhile to speculate whether this difference is due to biological isotope effects, variations in the isotopic composition of particulate carbon in the ocean, or some other cause.

CONCLUSIONS

Variations in the oxygen isotopic composition of coccoliths and planktonic foraminifera are correlated in the two cores we studied. This covariance suggests that the oxygen isotopic composition of coccoliths reflect the temperature and the δO^{18} of water in which they grew. Oxygen isotopic fractionations between coccoliths and planktonic foraminifera from DSDP Site 82 are compatible with the precipitation of coccoliths close to thermodynamic equilibrium with surface ocean water. However, coccoliths from core CP-28 are too enriched in O^{18} to have been precipitated at isotope equilibrium. It is unlikely that either partial recrystallization of coccoliths or contamination by carbonates deposited in bottom water can account for this anomaly. In some manner yet to be determined, Pleistocene coccoliths in the Caribbean were evidently deposited with an oxygen isotopic composition differing significantly from the thermodynamically predicted value. Nonetheless, the covariance of the oxygen isotopic composition of coccoliths and of planktonic foraminifera imply that the composition of coccoliths is sensitive to environmental factors.

Isotopic variability in coccoliths may provide new insights into the variations in paleo-oceanographic environments. However, additional isotopic data of the kind presented here is needed in order to more fully understand the isotope geochemistry of coccoliths, particularly the large variations in compositions that may exist between oceans.

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