

32. ISOTOPIC COMPOSITION OF CRETACEOUS SHALLOW-WATER CARBONATES FROM SITE 384

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INTRODUCTION

At Site 384, about 125 meters of carbonates of shallow water origin were drilled. Although recovery was poor, in most cases zero, some material, totaling about 2.5 meters, was available. This material includes both unlithified carbonate sand and gravel and weakly to strongly cemented carbonate rock, mostly biomicrudites.

From a previous study of lithofacies, it was evident by the presence of moldic porosity that at least part of this material had been exposed to meteoric water (Rothe, this volume). Pre-existing aragonite of skeletal particles had been leached and the resulting vugs were in some cases partly filled with sparry low-magnesian calcite cement.

Since the isotopic composition of marine- and fresh-water carbonates is considerably different (Keith and Weber, 1964), a difference might also be expected between the fresh-water diagenetic carbonates and the unaltered overlying pelagic nannofossil chalk. Stable isotope analysis could provide a further tool for substantiating the suggested diagenetic history of these carbonates.

EXPERIMENTAL TECHNIQUES

Finely powdered samples of 40 mg each were reacted with 100 per cent phosphoric acid after the classical techniques of McCrea (1950), with an excess of P_2O_5 to avoid free water. The CO_2 was determined with an Atlas CH_4 mass spectrometer. All δ values are given relative to PDB; reproducibility is about ± 0.1 per mil. Twenty-nine samples of almost pure carbonate were selected from Site 384; seven additional samples from Site 98, Leg 11, were analyzed for comparison purposes. Because of the limited amount of material, small powdered bulk samples were analyzed.

The carbonate mineralogy according to X-ray diffraction of the same powder samples is almost entirely low-magnesian calcite with the exception of some scarce dolomite. The original skeletal shell material is assumed to have been aragonite and/or high-magnesian calcite. Such metastable carbonates might possibly be preserved in very small amounts, but were not detected in any of the X-ray diffractograms.

The samples, though representing about 125 meters of drilled section, are restricted to a few meters of re-

covered sediment. Nothing can be said with certainty concerning their position within these 125 meters except for the relative succession of the cores.

RESULTS

Two significant results of this study are:

1) Rather uniform and heavy $\delta^{13}C$, with values around +3 (see Table 1).

2) Uniformly negative $\delta^{18}O$ values. The lightest values were found in the lowermost core, whereas $\delta^{18}O$ is a little heavier in the upper core. Core 15, which consists of nannofossil chalk, has an average $\delta^{18}O$ of less than -0.8, Core 16 about -1.0, 19, CC has -1.8, 20 has -2.5, and 21 has -2.7. This indicates a rather continuous development of $\delta^{18}O$ values within the sediment column.

Selected samples of shallow-water carbonates from Site 98 (Leg 11, Hollister and Ewing et al., 1972) revealed an isotopic composition comparable to the material from Site 384: $\delta^{13}C$ values are slightly lighter, but $\delta^{18}O$ values are negative throughout (see Table 2).

DISCUSSION

Formation of the biogenic carbonate sediments at Site 384 must have occurred in a shallow marine environment, and according to actualistic models most probably in warm water that was possibly slightly more saline than the open ocean. Elevated salinity would favor a heavier $\delta^{18}O$ within the carbonates formed.

On the basis of their mineralogical composition, the samples investigated might represent almost 100 per cent diagenetically altered carbonate. Thus, the $\delta^{18}O$ values obtained should reflect the isotopic composition of the water which caused the diagenetic alteration of the carbonates; their original isotopic composition, however, remains an open question. Data from comparable recent environments suggest that $\delta^{18}O$ values ranging from -1 to +3 might be assumed reasonable.

Assuming Cretaceous temperatures to have been similar to those of today, the average rain water isotopic composition might be evaluated according to the relations established by Dansgaard (1964); temperatures may be calculated after the formula given by Craig (1965):

$$t^{\circ}C = 16.9 - 4.2\Delta + 0.13\Delta^2$$

TABLE 1
Site 384 Stable Isotope Composition of Shallow-Water Carbonates

Sample (Interval in cm)	Material	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
15-5, 10-11	Nanno chalk	3.2	-1.1
15-5, 90-91	Nanno chalk	3.2	-0.8
15-6, 5-6	Nanno chalk	2.7	-0.9
15-6, 99-100	Nanno chalk	2.8	-0.5
15-6, 147-148	Nanno chalk	2.9	-0.5
16-1, 30-35	Carbonate sand (well-rounded and moderately sorted)	3.4	-1.1
16-1, 45	Carbonate sand (well-rounded and moderately sorted)	3.5	-0.9
16-1, 48-52	Carbonate sand (well-rounded and moderately sorted)	3.5	-1.0
16-1, 66-70	Carbonate sand and gravel-size shell fragments	3.5	-1.1
16-1, 87-89	Limestone	3.5	-1.2
16-1, 103-108	Carbonate sand and gravel-size shell fragments	3.8	-0.9
16-1, 105	Coarse skeletal sand	3.3	-1.1
16-1, 110	Limestone	3.5	-1.1
16-1, 116-121	Gravel of limestone and skeletal debris	3.3	-1.0
16-1, 120	Shell fragments (probably pelecypods)	3.9	-0.8
16-1, 130-150	Limestone	3.7	-0.7
16-1, ~140	Limestone	3.5	-0.8
16, CC, 5-10	Limestone debris down to coarse sand	3.6	-1.0
19, CC	Limestone debris and sand	3.0	-1.8
20-1, ~100	Limestone	3.1	-2.0
20-1, ~100	Limestone	3.2	-2.3
20-1, ~100	Limestone	3.3	-1.9
20-1, 120-127	Limestone, yellow	2.9	-2.7
20, CC, 20	Limestone, gray	2.6	-3.0
21-1, av. section	Skeletal	2.9	-1.8
21-1, 115-120	Limestone gravel, white and gray	3.4	-2.2
21-1, 130	Limestone, gray	3.7	-2.8
21-1, 140-150	Limestone, gray	4.2	-2.8
21, CC, 5	Limestone, gray	3.6	-3.1

TABLE 2
Site 98 Stable Isotope Composition of Shallow-Water Carbonates

Sample (Interval in cm)	Material	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
13-1, 135	Foram-nanno ooze	3.8	-1.3
13-1, 145	Limestone	2.0	-1.5
14-1, 65	Limestone	-0.7 ^a	-2.3 ^a
14-1, 75	Micritic chalk	2.7	-1.4
14-1, 120	Micritic chalk	2.4	-1.3
14-1, 138	Micritic chalk	2.0	-1.3
15-1, 105-107	Limestone	2.2	-1.3

^aVery small amount of sample

Dansgaard (1964) has demonstrated that for marine climates at medium to high latitudes the oxygen isotopic composition of rain averaged over a whole year varies linearly with the mean annual temperature difference between the place of evaporation (the tropical ocean) and the place of precipitation (figure 29a in Hoefs, 1974, p. 73). This suggests that at 45°N the average oxygen isotopic composition should have been around -5, assuming Cretaceous temperature distribution to have been similar to those of today. If Cretaceous temperatures were higher, which is not unreasonable, then the isotopic composition might even be around -3, so that the data of -3 PDB obtained from the carbonates at Site 384 may reflect 100 per cent diagenetic alteration, as indicated by their mineralogy.

The $\delta^{13}\text{C}$ values found show little variation. They are heavy (around +3, see Table 1) which is in favor of replaced carbonate. Friedman (1964) gives heavy values of $\delta^{13}\text{C}$, that are typical of carbonate cement.

It should be noted, however, that there is no obvious difference in the isotopic composition between the lithified and unlithified carbonates of Site 384. This may be explained either by a similar diagenetic history for both, meaning that the sediments were not lithified prior to isotopic exchange, or that the unlithified sediments represent former, and diagenetically altered rock that was reworked after alteration.

The diagenetically active meteoric water is assumed to have contained only minor amounts of CO_2 , in agreement with general observations for rain water in mid-ocean areas. Little change in $\delta^{13}\text{C}$ might thus be expected, since the carbon isotopic composition of the percolating rain water would remain constant. In fact, rather constant values of about +3 were found (see Table 1). The observed downhole increase of light $\delta^{18}\text{O}$ values might reflect the system of percolating rain water at the time of subaerial exposure. The lowermost carbonates of Cores 20 and 21 represent the immediate sediment cover on the basaltic basement. Rain water might thus have episodically been confined within the carbonates, causing leaching of aragonite, transformation of high-magnesian calcite, and precipitation of low-magnesian calcite of rain water isotopic composition.

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