14. STUDIES ON LITHIFICATION AND DIAGENESIS

14.1. LITHIFICATION OF PELAGIC-HEMIPELAGIC SEDIMENTS AT DSDP SITE 372: OXYGEN ISOTOPE ALTERATION WITH DIAGENESIS

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INTRODUCTION

Isotopic studies of pelagic carbonate sequences from several DSDP sites have shown that there is often a depletion or negative shift in the δO^{18} ratio of the sediment with increased age (Douglas and Savin, 1971; Anderson and Schneiderman, 1973; Coplen and Schlanger, 1973; Lawrence, 1973; Matter et al., 1975). Although the existence of this isotopic depletion is well established, the time and environment of the isotopic adjustment has been variously interpreted. Matter et al. (1975) found that the progressive lithification of carbonate sediments with depth was associated with a systematic increase in cementation and a systematic decrease in the δO^{18} ratio. Lawrence (1973) determined the isotopic ratios of both the carbonate phase and the associated pore water. He noted that the more deeply buried carbonates were nearly in isotopic equilibrium with their pore water and attributed this to recrystallization or isotopic exchange. These depletions then appear to be directly associated with an increased degree of recrystallization and cementation. On the other hand, Coplen and Schlanger (1973) postulated a world wide event, such as an increase in ocean temperature or a decrease in the δO^{18} ratio of ocean water, to explain the observed isotopic shift found in Upper Cretaceous sediments. Anderson and Schneiderman (1973) proposed that high temperatures associated with regional volcanic activity during the Late Cretaceous produced the observed depletion in the series of samples they studied. The controversy continues. The observed isotopic depletions may represent either a gradual readjustment after burial and during early stage diagenesis or they may record temperature or isotopic changes in the paleoenvironment.

During Leg 42A, a sequence of progressively lithified sediments from the lower and middle Miocene were recovered at Site 372, East Menorca Rise, Balearic Basin (Figure 1). In light of the above-mentioned studies, one aim of our work was to establish the stable isotope values of the carbonate fraction of a series of samples from this sequence. The results presented here are a preliminary report of a broader study on the lithification of pelagic-hemipelagic sediments from DSDP Sites 372 and 375.

LITHOLOGY

Lithological Units III and IV at Site 372 are composed of open marine sediments, which are progressively indurated with depth (Site 372 Report, this volume). From 207 to 468 meters, the Unit III sediments gradually grade from nannofossil marls into marlstones. The carbonate and detrital content remain fairly constant to a depth of 468 meters. At this point, there is an abrupt change in the sedimentological features. The carbonate content of the sediment drops from 65% to 30%, and there is a corresponding rise in the detrital component from 35% to 60%. This more detritic sediment forms Unit IV and grades from a nannofossil marlstone into a hard to very hard mudstone. See Figure 2.

The gradual increase in the degree of lithification is suggested by several lines of evidence other than the induration. The seismic reflection data indicate a progressive increase in the density of the sediments with depth. Flattened burrows in the mudstone demonstrate the extent of compaction. The downhole decrease in water content represents a corresponding decrease in porosity. SEM micrographs show a general increase in the degree and extent of calcite cementation with age. This aspect of lithification is illustrated in the micrographs of Figure 3. A systematic analysis of the SEM micrographs has not been completed. In Unit III, a general tendency towards syntaxial overgrowths of discoasterids and placoliths with depth was observed.

As reported elsewhere (Matter et al., 1975), cementation begins in discoasterids (Figure 3e) and the central distal areas of placoliths (Figure 3d) with overgrowth on the proximal central areas of placoliths occurring deeper (Figure 3l). Heavy overgrowth on placoliths, as in Figure 3k, may represent reworked speciments. In Unit IV, the increase in the clay content probably contributed to the relatively good preservation of the coccoliths (Figure 3p).

STABLE ISOTOPE RESULTS

A series of samples was selected for stable isotope analysis from regularly spaced intervals in Units III and IV. The samples were washed in distilled water to remove soluble salts, heated at 450°C in a helium

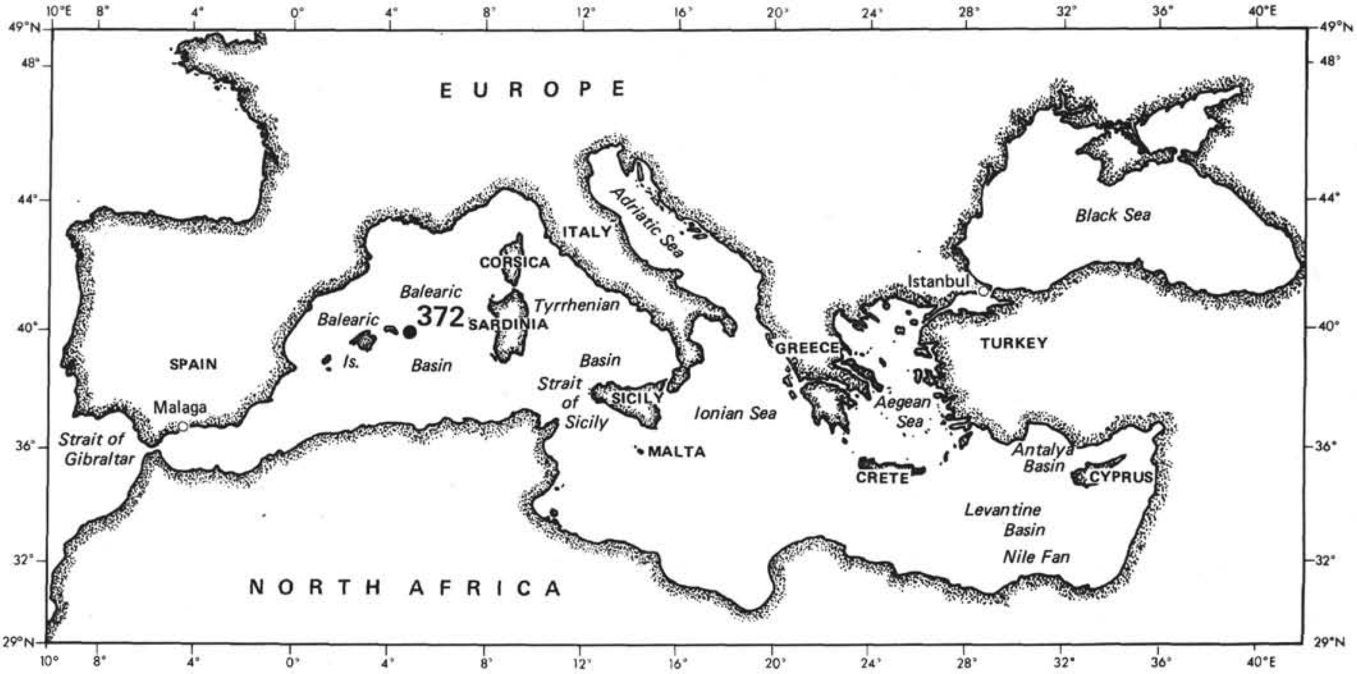

Figure 1. *Location of Site 372.*

stream for 30 minutes to oxidize all organic carbon, and reacted with 100% phosphoric acid to evolve carbon dioxide according to the method described by McCrea (1950). Isotopic measurements of the carbon dioxide were made on a precision, double collector mass spectrometer, the Micromass 603C. The stable isotope data are tabulated in Table 1 and shown graphically in Figure 2. The data represent the isotopic composition of the bulk carbonate and are reported in the δ-terminology ($^{\circ}/_{\circ\circ}$) relative to the Chicago PDB standard. All samples were analyzed in duplicate. The average deviation of the oxygen and carbon isotope analyses are $\pm 0.1^{\circ}/_{\circ\circ}$ and $\pm 0.2^{\circ}/_{\circ\circ}$ respectively.

DISCUSSION OF RESULTS

From Figure 2, we can infer that the oxygen-18 composition of the bulk carbonate is gradually depleted with burial depth. This depletion appears to correspond directly to the degree of observed lithification. The isotopic composition remains relatively constant until approximately 400 meters, where there is a change in induration from firm, to firm to hard. At this point, the δO^{18} ratio becomes more negative. This trend continues across the lithologic boundary at 468 meters with the progressive depletion resulting in a δO^{18}_{PDB} value between -2.5 and $-3.5^{\circ}/_{\circ\circ}$ near the base of the drilled section.

The contribution of detrital dolomite to the isotopic content was considered. Below the lithologic boundary at 468 meters, the dolomite proportion of the carbonate minerals increases by 10% to 15% and reflects the greater detrital component of the mudstones. The amount of dolomite in all of the analyzed samples was quantitatively determined from X-ray diffraction scans. Fontes and Desforges (1975) reported the isotopic values of a detrital Mesozoic dolostone transported from the Balearic Islands to deep-sea sediments of the western Mediterranean. The δO^{18}_{PDB} values of this detrital dolomite and its source dolomite range from -4.14 to $-0.69^{\circ}/_{\circ\circ}$. Using the minimum value, adjustment calculations were made on the stable isotope ratios of the Site 372 carbonates to determine the effect of the detrital dolomite. The result of these calculations was a slight positive adjustment of the isotopic values reported in Table 1, but this did not alter the observed trend of progressive depletion with depth.

Corresponding changes in the δC^{13} ratio with depth were not found. The carbon-13 content of the carbonate was not altered by the contribution of carbon from a secondary source. This is further evidence that the oxygen shift is a result of isotopic reequilibration of the fossil carbonate with interstitial waters. At Site 372, the calcite cement appears to originate entirely from the in situ dissolution and reprecipitation of the fossil carbonate.

In deeply buried sediments, the water content is greatly reduced as a result of compaction. The amount of oxygen in the pore water becomes roughly equivalent to the amount in the sediment. A measurable alteration of the isotopic composition of the sediment should be seen in the isotopic content of the water. In fact, recrystallization of fossil carbonate at temperatures greater than 22°C raises the δO^{18} value of the water. The extent of increase should be directly proportional to the temperature, but the natural sedimentary environment is an open system. The enriched water molecules are advected away from the site of exchange by compaction and diffusion. Therefore, a more extensive recrystallization of the carbonate may have occurred than is suggested by a slight enrichment of the δO^{18} ratio of the associated pore fluid (Lawrence et al., 1975).

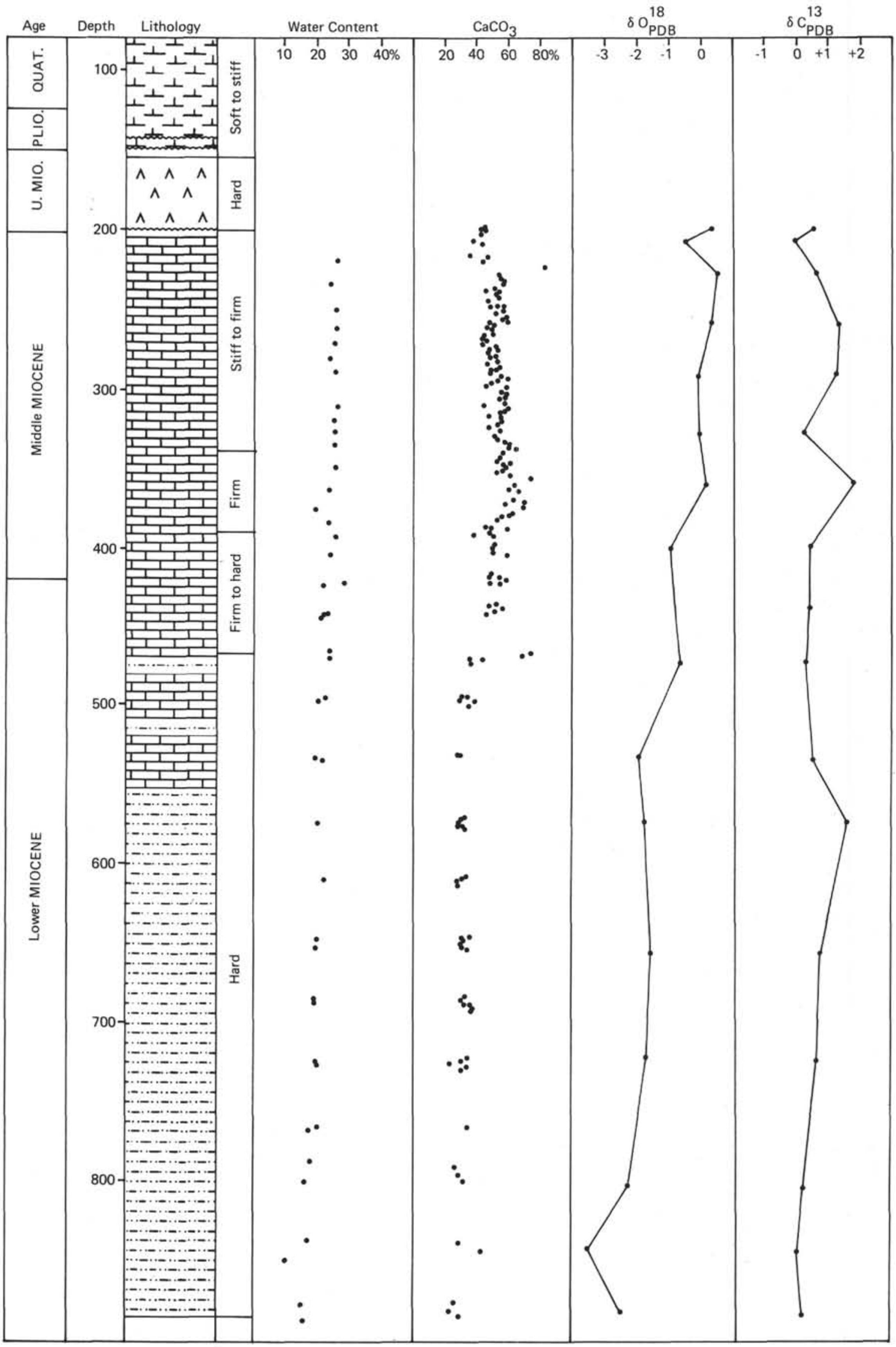

Figure 2. *Stratigraphic section of Site 372 indicating induration, water content, percent calcium carbonate, and stable isotope data for the sediments as a function of depth.*

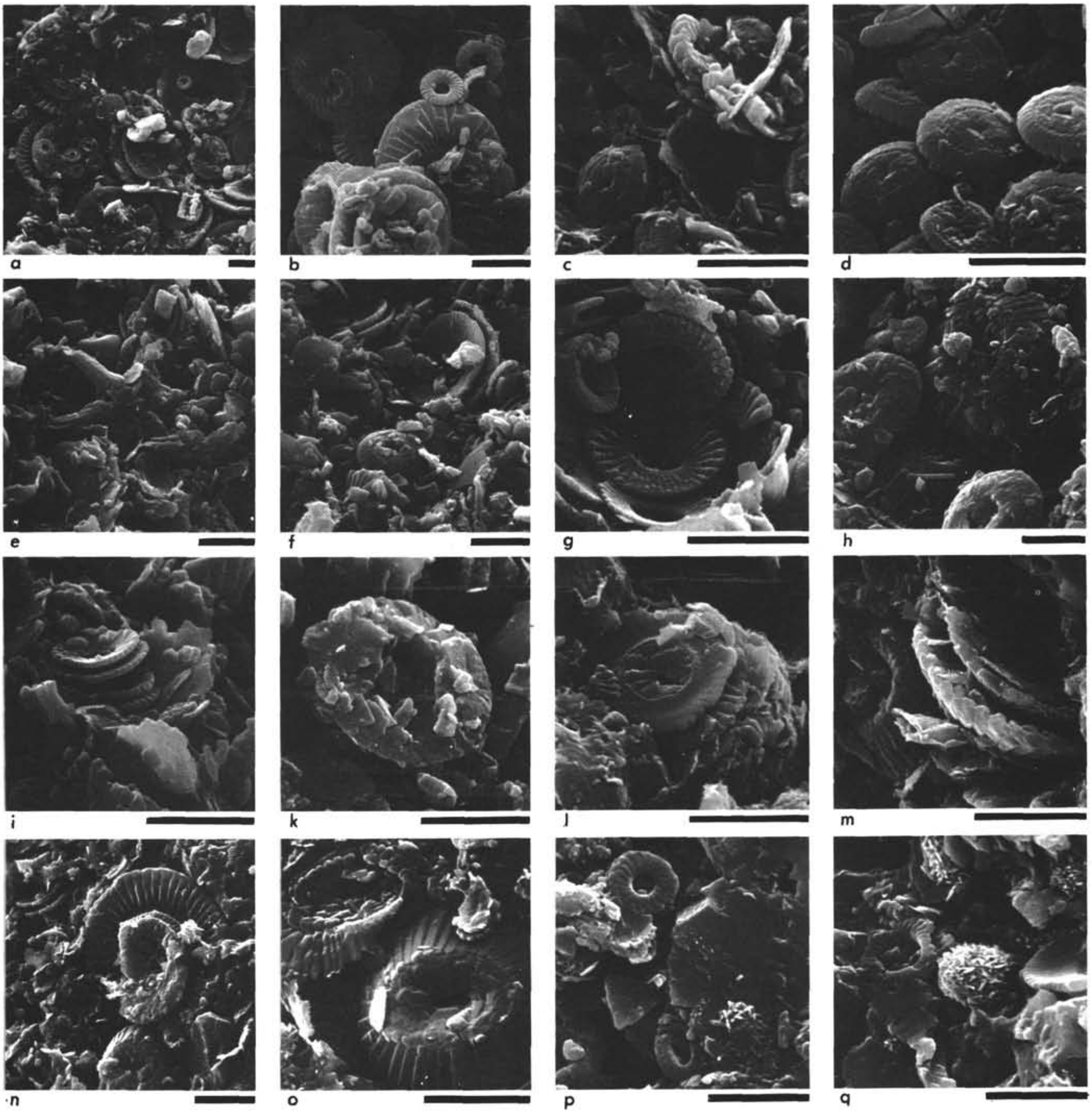

Figure 3. *SEM micrographs of pelagic-hemipelagic sediments, lower to middle Miocene, Site 372. All scale bars are equivalent to 3 μm (a,b) 10-2, 65-67 cm; (c,d) 12-4, 125 cm; (e,f) 15-2, 10-12 cm; (g,h) 18-2, 80 cm; (i,k) 26-5, 22-23 cm; (l,m) 30-2, 130-137 cm; (n,o) 33-3, 33 cm; (p,q) 40-4, 92 cm.*

With the temperature and isotopic composition of the pore water, a hypothetical isotopic equilibrium value for the carbonate sediment at a given depth can be calculated (O'Neil et al., 1969). At Site 372, the isotopic composition of the pore waters has been determined (McDuff et al., this volume), and temperatures at varying depths can be calculated from the in situ heat-flow measurements. The oxygen-18 content of the pore waters was slightly enriched over present-day Mediterranean bottom waters by approximately 1.5‰. The hypothetical δO^{18} values are plotted in Figure 4 alongside the observed isotopic values. A high heat flow in the Balearic Basin of 1.5 times the mean global average accounts for the high temperature gradient (Site 372 Report, this volume).

The carbonate near the top of the sequence appears to be in isotopic equilibrium with the interstitial water. Isotopic equilibrium has not been reached below 210 meters. The system is still in the process of approaching equilibrium through the dissolution and reprecipi-

TABLE 1
Stable Isotope Analyses of Bulk Carbonate From Site 372, Balearic Basin

Sample (Interval in cm)	Depth (m)	Lithology	Induration	δO^{18}_{PDB}	δC^{13}_{PDB}
9-2, 135-136	200	Nannofossil marl	Soft to stiff	+0.28	+0.52
10-2, 65-67	209	Nannofossil marl	Soft to stiff	−0.38	−0.12
12-4, 125-127	232	Nannofossil marl	Stiff to firm	+0.46	+0.62
15-2, 10-12	256	Nannofossil marl	Stiff to firm	+0.35	+1.34
18-2, 80-83	285	Nannofossil marl	Stiff to firm	−0.09	+1.20
22-1, 60-62	322	Nannofossil marl	Stiff to firm	−0.10	+0.16
26-5, 20-23	365	Nannofossil marl	Firm	+0.09	+1.76
30-2, 130-137	400	Nannofossil marl	Firm to hard	−0.94	+0.36
32-1, 56-64	440	Nannofossil marl	Firm to hard	−0.92	+0.35
33-3, 33-39	467	Nannofossil marl	Firm to hard	−0.68	+0.18
35-1, 95-101	530	Clayey mudstone	Hard	−1.97	+0.37
36-5, 48-54	574	Clayey mudstone	Hard	−1.74	+1.50
38-4, 50-60	650	Clayey mudstone	Hard	−1.64	+0.67
40-4, 92-100	725	Clayey mudstone	Hard	−1.76	+0.64
43-4, 104-110	800	Clayey mudstone	Hard	−2.33	+0.23
45-2, 112-117	840	Clayey mudstone	Hard	−3.45	−0.03
46-3, 110-115	886	Clayey mudstone	Hard	−2.50	+0.22

tation of fossil carbonate. The increased clay content below the lithological boundary may, in fact, aid in the preservation of the fossils and hinder the reprecipitation process. This effect would decrease the amount of isotopic equilibration occurring in the clay-rich sediments. Continued diagenesis at these temperatures will further deplete the oxygen-18 content of the carbonate while enriching the water. The full extent of the isotopic alteration cannot be measured in the pore solutions, as seen by the slight increase in the δO^{18} ratios obtained by McDuff et al. (this volume). The system is open, and the enriched water is moved away from the exchange site by advection. The diagenesis is best recorded in the isotopic depletion of the carbonate phase.

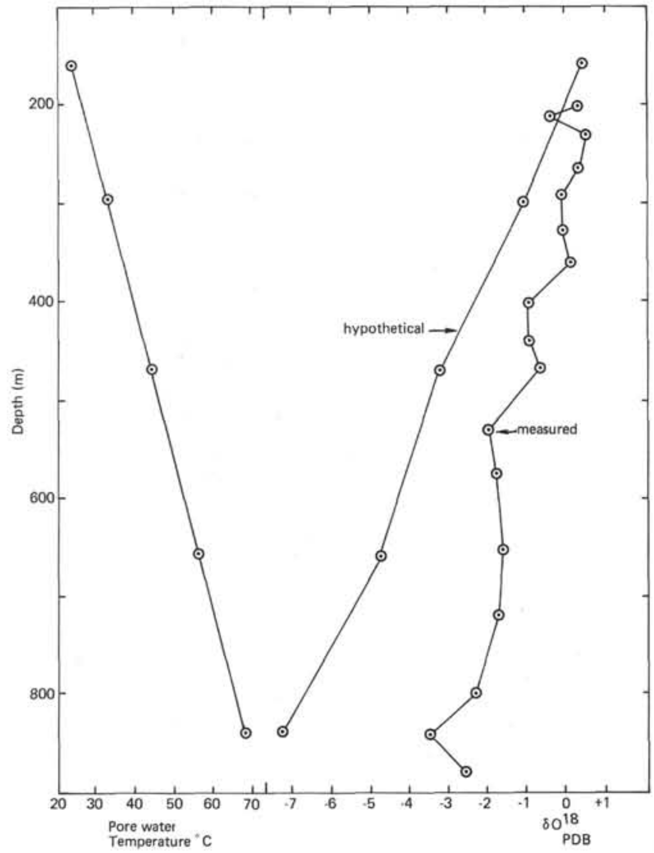

Figure 4. *The hypothetical* $\delta\ O^{18}_{PDB}$ *value for calcite in equilibrium with the pore water at the correspondent temperature and the actual measured* $\delta\ O^{18}_{PDB}$ *value of the bulk carbonate from Site 372 plotted as a function of depth.*

CONCLUSIONS

The results of this preliminary isotope study indicate that the down-hole depletion in the oxygen-18 content of the bulk carbonate from Site 372 is directly associated with the progressive lithification of the sediment. The oxygen-18 shift results from the isotopic re-equilibration of the carbonate ions during diagenesis at temperatures greater than 20°C. Depending upon the temperature of re-equilibration the process of cementation and recrystallization can significantly alter the isotopic composition of the carbonate sediments and the pore fluids. The δO^{18} value of the bulk carbonate becomes progressively more negative with increased burial depth, while the pore waters take up the released oxygen-18. This phenomenon is effectively seen at Site 372 because of the relatively uncomplicated nature of the lithology and the elevated temperatures produced by the high heat flow in the Balearic Basin.

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14.2. PHILLIPSITE CEMENTATION IN A FORAMINIFERAL SANDSTONE AT HOLE 373A AND "THE CASE OF THE VIOLATED FORAM"

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ABSTRACT

Pliocene foraminiferal sandstone at Site 373A contains about 35% phillipsite as pore-filling cement. The sediment originated as a well-sorted foram-rich sand which was redeposited from an adjacent area and which had very high initial porosity. Following compaction, precipitation of phillipsite in intergranular pore space cemented the sand. Phillipsite crystals also precipitated within foraminiferal chambers where, in places, they replaced micrite. Some zeolite crystals also breach shell walls by penetrating their pores. This precipitation of phillipsite appears to be the consequence of unusual pore water chemistry, the proximity to altered basalt, and the high porosity of the sand layer.

INTRODUCTION

Foraminiferal sandstone cemented by zeolites forms a thin interval between 81 and 87 centimeters in Section 1, Core 2 at Site 373A on the flanks of a seamount in the Tyrrhenian Basin of the Mediterranean Sea (Figure 1). This rock has unusual compositional and textural properties which shed light on sedimentological and diagenetic processes in zeolitic carbonate sediments.

The sandstone is of Pliocene age and occurs interbedded with soft foraminiferal nannofossil marls and thin, calcareous volcanic ash layers at a sub-bottom depth of about 269 meters. It appears to lie 60 to 100 centimeters above the contact between Pliocene soft sediment and basaltic breccias at the top of the underlying seamount (see Site Report, Chapter 4).

PETROLOGY AND MINERALOGY

The sandstone is somewhat friable and porous, very well laminated and, possibly, cross laminated. Color is light gray (5Y 7/1). Some laminae are very well sorted, but others appear to have discontinuous lenses of micritic matrix. Upon close examination, these lenses turn out to be compactionally squeezed clasts of micritic limestone. The rock consists mainly of sand to coarse silt-size grains cemented in finely crystalline, clear zeolites. Grains in this sandstone comprise three major kinds of components: planktonic foraminiferal tests; coarse silt to fine sand size, very angular clasts of quartz and plagioclase; and irregular to rounded lithoclasts of micritic limestone. Many of the micritic lithoclasts are compactionally flattened, and some of them contain clasts of planktonic foraminifera. Present in small amounts are biotite, glauconite, muscovite, pyroxene, plant fragments, and both altered and fresh, pale brown, vesicular glass. Trace amounts of benthic foraminiferal shells, broken echinoid spines, and unidentified skeletal fragments also are present.

X-ray diffraction indicates the rock has an approximate mineralogical composition, by weight, as follows: 35% phillipsite, 30% plagioclase (labradorite to bytownite), 20% quartz, 10% calcite, 3% illite or muscovite, and 2% dolomite.

As noted, compaction has squeezed some micritic limestone clasts between more resistant grains. It has