

## 30. STABLE ISOTOPE INVESTIGATIONS OF THE MIOCENE EVAPORITES AND PLIOCENE AND PLEISTOCENE SEDIMENTARY ROCKS AND OOZES

### PREFACE

During the thirteenth cruise of the Deep-Sea Drilling Project, carbonate oozes, diagenetically altered sediments, sedimentary rocks, and evaporites have been sampled in the Mediterranean. The purpose of our investigation is to apply

the stable oxygen- and carbon-isotope techniques in order to provide some data useful for the interpretation of the depositional and diagenetic histories of these deposits. The materials were made available to us in connection with the preliminary research necessary to assist in the preparation of the Initial Cruise Report of DSDP Leg 13.

### 30.1. PRELIMINARY ISOTOPIC INVESTIGATIONS OF SAMPLES FROM DEEP-SEA DRILLING IN THE MEDITERRANEAN SEA

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#### ABSTRACT

The oxygen and carbon isotope composition of nine carbonate and three sulphate samples from DSDP Leg 13 were analyzed to provide data for an interpretation of the environments of their deposition and diagenesis. Analyses of dolomite and anhydrite samples yielded data in support of the geological deduction by Ryan, Hsü, and others that the upper Miocene Mediterranean evaporites were formed in desiccated inland basins after the Strait of Gibraltar was closed in the late Miocene.

#### INTRODUCTION

During Leg 13 of the Deep Sea Drilling Project in the Mediterranean, a number of diagenetically altered sediments and sedimentary rocks were sampled. (See Chapter 38, this volume, for location map.) The purpose of this investigation is to apply stable oxygen- and carbon-isotope techniques to provide some data useful for the interpretation of the depositional and diagenetic histories of these deposits. The materials were made available to us in connection with research to assist in the preparation of the Initial Cruise Report of DSDP Leg 13. Our investigations have been jointly supported by the Shell Development Company and the Swiss Federal Institute of Technology.

#### MEDITERRANEAN EVAPORITES

One of the most significant results of the DSDP Mediterranean cruise is the discovery of an upper Miocene

evaporite formation, which underlies most parts of the Mediterranean. The origin of the evaporite is, however, a question of some controversy. The following three alternative hypotheses have been advanced.

1) **Deep-water, deep-basin model.** This hypothesis assumes the deposition of evaporite minerals in a deep-water basin (Schmalz, 1969). At the time of evaporite deposition, the Mediterranean is assumed to have been a deep-water basin, not isolated from the Atlantic, but separated from the latter by a shallow sill. However, the circulation was sufficiently reduced to cause an increased salinity in the Mediterranean. Eventually, carbonates, sulfates, and halite were crystallized out of brine and accumulated on the deep basin floor to form the supposedly deep-water evaporite.

2) **Shallow-water, shallow-basin model.** This hypothesis assumes the deposition of evaporite minerals on the bottom of a shallow restricted shelf sea, which may or may not have an open connection with the Atlantic. The present depth of the Mediterranean was related to post-Miocene subsidence, subsequent to formation of the upper Miocene evaporites.

<sup>1</sup>(EPR Publication No. 608).

3) **Desiccated deep-basin model.** This hypothesis assumes the deposition of evaporite minerals on inland playas, whose flat basin floors were thousands of meters below the Atlantic sea level. The playas owed their origin to the desiccation of the late Miocene Mediterranean, when it was completely isolated from the Atlantic. The return of normal marine conditions in early Pliocene led to the deposition of deep-water pelagic oozes on top of the playa evaporites.

The arguments, pro and con, have been discussed in other sections of this volume. The evidence on the whole may be considered to favor the desiccated deep-basin model. Isotopic analyses were carried out to throw additional light on this problem.

Oxygen and carbon isotope data for Miocene dolomites and dolomitic calcites from the Mediterranean evaporite formation and calcites from overlying Pliocene sediments are given in Table 1. These data are compared in Figures 1 and 2 with analyses reported by Fontes *et al.* (Chapter 30.2 this volume) from the Mediterranean evaporite and with values for Holocene carbonates from lacustrine and marine Miocene environments. Oxygen isotope data on mineral sulfates from the Miocene evaporite formation are given in Table 2. These data are compared with values for marine and lacustrine sulfates in Figure 3.

TABLE 1  
Isotopic Composition of Upper Miocene and Lower Pliocene  
Carbonate Minerals, Mediterranean

Location	Sample No.	Description	Mineral	PDB	
				$\delta O^{18}$	$\delta C^{13}$
Alboran Basin	121-19-1	UM dolomitic limestone	Calcite	-1.6	-3.4
	121-21-1	UM dolomitic limestone UM dense dolomite	Calcite Dolomite (Ca <sub>5</sub> 3)	0.5 1.6	-0.4 -10.2
Levantine Basin	129-2-1	UM Sucrose dolomite	Dolomite (Ca <sub>5</sub> 3)	3.4	-35.8
Tyrrhenian Basin	132-21-2	Pliocene red ooze	Calcite	1.3	0.1
	132-22-1	Pliocene red ooze	Calcite	1.2	0.2

### MIOCENE CARBONATES

Dolomite occurs in the Mediterranean Miocene evaporite deposits in quantities varying from traces to greater than 90 weight per cent. The dolomite is fine-grained and contains excess calcium carbonate, up to 55 mol percent. It is found in both soft marly sediments and in indurated crusts. Layers of relatively pure dolomite are rare and it is usually a minor component of the sediment, on the order of 10 per cent or less (Fontes *et al.*, Chapter 30.2 this volume). The remaining sediment consists of varying admixtures of calcite, quartz, feldspar, gypsum, and a variety of clay minerals.

The most striking feature of the carbonate isotope data is its variability (Figure 1). This variability contrasts sharply

with the rather narrow range of values for Holocene dolomites and dolomitic calcites found in tidal flat deposits associated with shallow-water marine deposition. The variability compares favorably with data reported for dolomites and calcites from lacustrine evaporite deposits, especially the data from a group of Pleistocene lakes from West Texas described by Parry *et al.* (1970).

The West Texas samples are from a group of isolated lake basins which formed in depressions eroded into Pliocene deposits of the Texas high plains. The basins have maximum dimensions on the order of a few miles and are scattered over an area of 5000 square miles. The deposits range in age of from 12,000 to over 37,000 years. Dolomite and calcite are found mixed with quartz, feldspar, clays, and minor amounts of celestite and gypsum. There is almost as much scatter in the isotopic data for individual lake basins as there is among all of the basins. The authors conclude that: "the wide scatter in isotopic compositions of the dolomites indicates that they formed from solutions of widely differing isotopic compositions and temperatures; conditions which could be expected in isolated desiccating fluvial lake systems in which evaporation is extreme" (Parry *et al.*, 1970, p. 830).

According to a recent proponent of the deep-basin, deep-water evaporite formation hypothesis: "There are no active deep evaporite basins today, . . ." (Schmalz, 1969, p. 822). It is not possible, therefore, to make simple isotopic comparisons between this environment and the Mediterranean carbonates as we did above for the shallow-marine and playa lake environments. However, we may speculate on possible isotopic variations on the basis of the proposed model for deep-water evaporite formation.

The essential element of this model is the existence of a shallow sill at the rim of the basin which allows new seawater to enter in a surface layer and dense brine to escape in a lower layer in a continuous refluxing system. Though there are details to the model which are necessary to explain the sequence of salts deposited, the essential isotopic factors are:

- 1) The source of water and salts is seawater from the oceanic reservoir.
- 2) Concentration of salts is by evaporation from a free-water surface.
- 3) Because of density stratification, the floor of the basin can, at times, be stagnant.

Ocean water has a constant oxygen isotopic composition of about 0.0 per mil on the PDB scale. At earth surfaces temperature ( $\sim 25^\circ C$ ), calcites formed in equilibrium with such water would have  $\delta O^{18}$  values of -2 per mil and dolomites  $\delta O^{18}$  values of -1 to +3 per mil.<sup>2</sup> Evaporation from a free-water surface causes isotopic enrichment of seawater to an upper limit of about 6 per mil (Lloyd, 1968a). Such enrichment would effect carbonate values directly. Thus, calcites might range from -1 to +4 and dolomites from 0 to +9 per mil<sup>2</sup> in a deep evaporite basin environment.

<sup>2</sup>The range is given to accommodate the unresolved differences of opinion among isotope workers as to how much, if any, isotopic fractionation exists between dolomite and calcite.

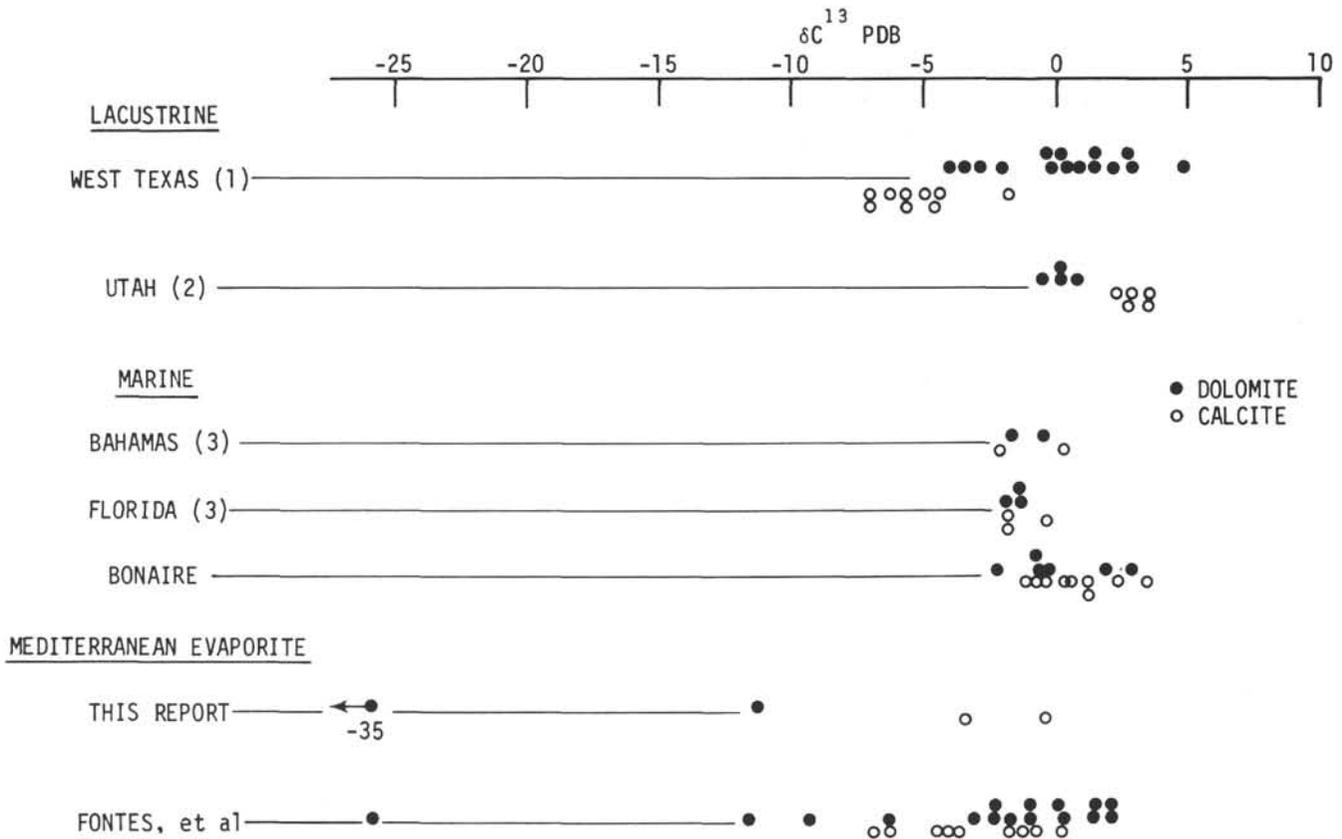


Figure 1. Oxygen isotope data for dolomite and calcite from lacustrine, marine, and Mediterranean evaporite samples. Data from the literature: (1) Parry, et al. (1970); (2) and (3) Degens and Epstein (1964); Fontes, et al. (this volume).

These ranges accommodate the more positive values for the Mediterranean Miocene carbonates, but fail to account for the very negative oxygen isotope values found in many of the samples from the same unit.

Some of the observed variation in carbon isotope values of the Mediterranean samples might be accommodated by the deep-water, deep-basin hypothesis if we accept the possibility of periods of stagnation of bottom waters. During such periods the normal bicarbonate carbon acquired by the water mass at the surface could be contaminated by more negative carbon from  $\text{CO}_2$  generated by organic decay. It should be pointed out, however, that periods of stagnation were proposed by Schmalz (1969) to account for euxinic sulfide-rich deposits in ancient evaporite basins. We are unaware of similar sediments in the Mediterranean sequence.

The large negative  $\text{C}_{13}$  value of the Levantine (Site 129) dolomite sample is very unusual. The closest match to this is one from a deep-water open marine dolomite, whose genesis was probably related to the bacterial breakdown of hydrocarbons (Russell *et al.*, 1967). Limestones associated with Sicilian sulfur deposits in the Solfifers Formation (an equivalent of the Mediterranean Evaporite) likewise have highly negative  $\text{C}_{13}$  values (-8.8 to -43). These limestones are also believed to have derived their carbonate primarily from oxidized methane enriched in  $\text{C}_{12}$  (Jensen, 1968). In any event, such extreme values speak neither for nor against a deep-water origin.

## PLIOCENE CARBONATES

The Miocene evaporite series is directly overlain by Pliocene carbonate-rich open marine sediments with abundant pelagic organisms and a normal marine benthonic ostracod fauna. Our isotope values (Table 1) and eleven reported by Fontes *et al.* (Chapter 30.2 this volume) all fall within a narrow range of 0.2 to 1.3 per mil for  $\delta\text{O}^{18}$  and -0.1 to +1.2 mil for carbon relative to PDB.

The isotopic composition of the oozes may be construed to indicate formation in cool normal marine waters, on the order of  $10^\circ\text{C}$ . However, partial evaporation of the Mediterranean water may be partly responsible for the positive  $\delta\text{O}^{18}$  values. The present-day waters in the Mediterranean have a  $\delta\text{O}^{18}$  value of about 1.2. If the Pliocene oozes were deposited from waters of similar isotopic composition, our results would suggest that the largely planktonic skeletons were crystallized from a water column with an average temperature of about  $15^\circ\text{C}$ . Benson (Chapter X, this volume) studied the ostracod fauna and found the ostracod assemblage "most likely to occur living in open ocean between 1000 and 1500 meters (bottom temperatures between  $4^\circ$  and  $6^\circ\text{C}$ )." This is consistent with the postulate that the Pliocene bottom waters were much cooler than those of the present-day Mediterranean and that the first Pliocene waters flooded deep, but desiccated Mediterranean basins.

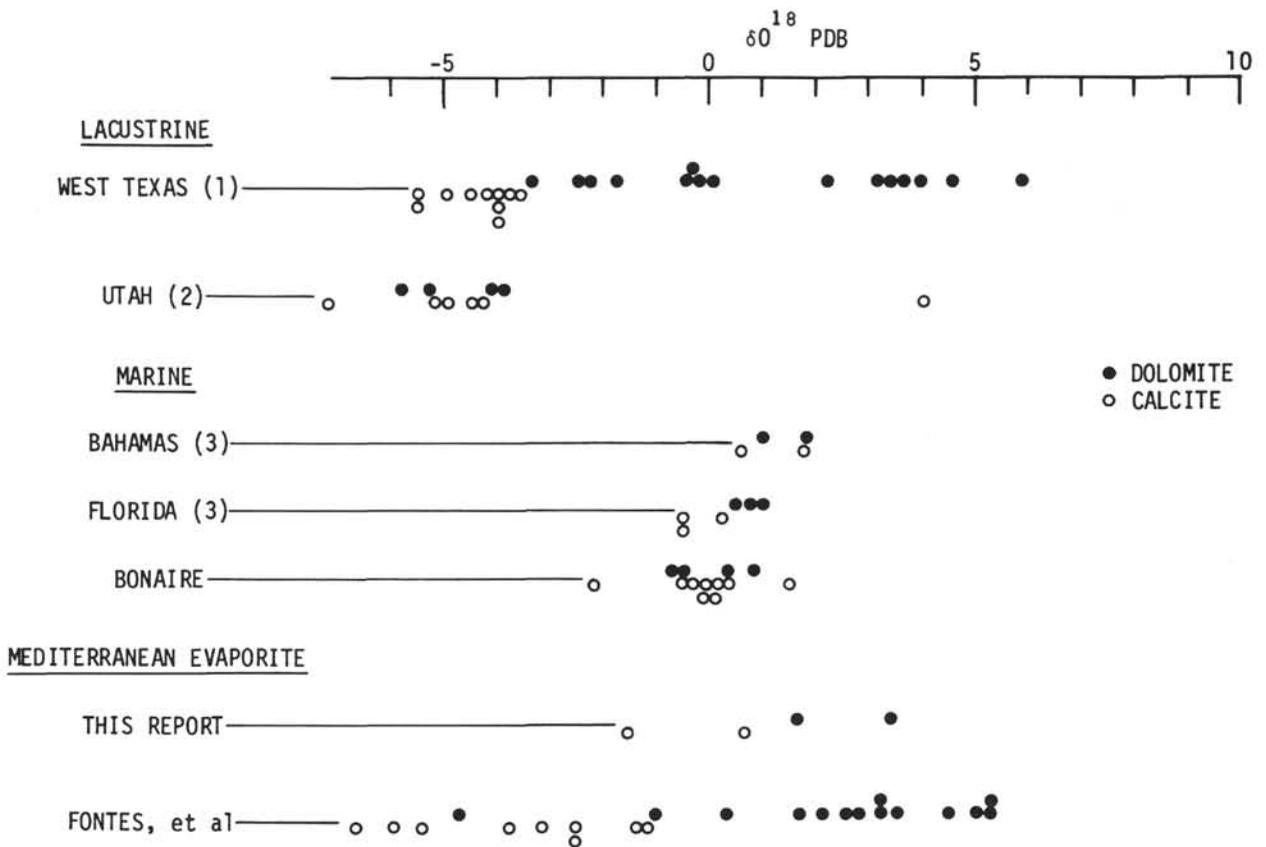


Figure 2. Carbon isotope data for dolomite and calcite from lacustrine, marine, and Mediterranean evaporite samples. Data from the literature: (1) Parry et al. (1970); (2) and (3) Degens and Epstein (1964); Fontes et al. (this volume).

TABLE 2  
Isotopic Composition of Sulphate from Mediterranean Evaporite

Location	Sample No.	Description	Mineral	$\delta O^{18}$ SMOW
Balearic Basin	124-8-1	UM laminated anhydrite	Anhydrite	16.7
	124-10-1	UM nodular anhydrite	Anhydrite	15.8
Tyrrhenian Basin	132-23-1	UM laminated anhydrite	Gypsum	3.8

MIOCENE SULFATES

The most interesting feature of the sulfate isotope values from the Miocene evaporite is again their variability (Figure 3). The fact that the values appear to avoid the range of present-day marine sulfates is only an accident of sampling. Fontes *et al.* (Chapter 30.2, this volume) report a value of 14.3 for a Miocene sulfate from Site 122.

Our knowledge of oxygen isotope variation in sulfates is very limited. Marine oceanic sulfate has a very constant  $\delta O^{18}$  value of about 10 per mil relative to the SMOW standard (Longinelli and Craig, 1967; Lloyd, 1967). Lloyd (1968b) has proposed that this represents a steady-state value in the oxidation-reduction sulfur cycle of the ocean

rather than the true equilibrium exchange value with ocean water. Exchange rates between water and sulfate are extremely slow at earth surface conditions. Therefore, mineral sulfates precipitated from evaporated marine waters would tend to reflect the constant value of marine sulfate (plus a fractionation of crystallization) rather than the conditions of temperature and water isotopic composition at the time of precipitation, which could vary substantially from place to place (Lloyd, 1968b). This accounts, then, for the fact that gypsum derived from marine water occupies a narrow range from 13 to 15 per mil relative to SMOW (Figure 3).

Gypsum samples from lacustrine environments have a wider spread of values and are, in general, more positive. This may represent inherited values from older sulfates dissolved from outcrop (Longinelli, 1968), or perhaps, a different isotopic balance determined by local varieties in the sulfur cycle oxidation-reduction systems.

The fact that the Miocene sulfate samples show no tendency to group near the values for marine-derived sulfates argues against both the shallow-basin, shallow-water and the deep-basin, deep-water models. For mineral sulfates to match the one very negative Miocene sample (9 per mil), there is a report of a thermal spring water containing dissolved sulfate with a  $\delta O^{18}$  of 4.8 per mil (Lloyd, 1967). Gypsum precipitated from this solution would have a value near 9 per mil.

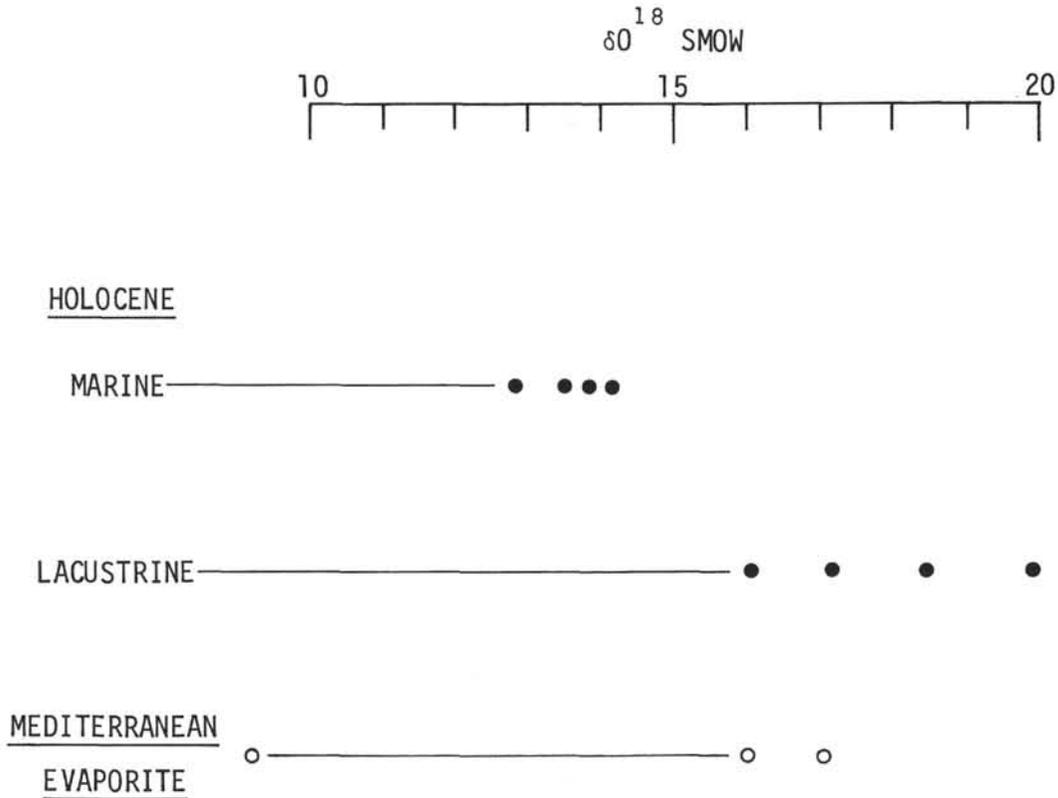


Figure 3. Oxygen isotope data for oxygen in sulfates. Marine data from Lloyd (1967). Lacustrine data from Playa deposits West Texas and New Mexico.

### DISCUSSION

Because of the variability of data, we cannot define, in any exact sense, the environment of formation of any portion of the Mediterranean Miocene evaporite deposits. However, it is this great variability which supports the hypothesis that deposition occurred in a desiccated basin consisting of playas, residual salt ponds, and isolated ephemeral lakes covering a broad flat area of many thousands of square miles. That fresh water from rain and run-off was an important contributor to the basin is demonstrated by the negative carbon and oxygen isotope values for many of the carbonate samples.

The desiccated playa environment might have existed as part of a shallow basin. However, the rapid onset over the entire basin of uniform open marine conditions, indicated by the Pliocene carbonate isotope values, supports the conclusion that the basin was deep.

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## 30.2. OXYGEN, CARBON, SULFUR, AND HYDROGEN STABLE ISOTOPES IN CARBONATE AND SULFATE MINERAL PHASES OF NEOGENE EVAPORITES, SEDIMENTS, AND IN INTERSTITIAL WATERS

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### INTRODUCTION

The relative abundance of certain elements and their stable isotopes sometimes indicates the environmental conditions under which discrete mineral phases originate. In the case of the sediments and sedimentary rocks recovered during Leg 13, we were particularly anxious to examine the environment of formation of the late Miocene (Messinian) evaporites.

The evaporite minerals calcite, dolomite, anhydrite, and gypsum were available from Sites 122, 124, and 134 in the western Mediterranean; Site 132 in the central Tyrrhenian Basin; and Sites 125 and 129 in the eastern Mediterranean (see Figure 1). The materials consist of unaltered authigenic components (fine-grained anhedral dolomite in the gray marls of Cores 6, 7, 10, 11, and 13 of Hole 124) and minerals formed through secondary replacement and hydration (crystals of selenite in the Core Bit sample of Holes 122 and 125A). The scope of this preliminary research included determination of the source of water which supplied the brine basin during precipitation of at least part of the evaporite series, and elucidation of the conditions leading to replacement of anhydrite by gypsum or to the recrystallization of gypsum.

A second objective was an evaluation of the isotopic composition of carbon and oxygen in the bulk carbonate of the Serravallian open-marine sediments below the evaporites, and the Pliocene and Pleistocene pelagic oozes above. The purpose of this effort was to determine the environmental setting of the Mediterranean Basin before and after the late Miocene "crisis of salinity" (Ruggieri, 1967).

### Sample Coverage

In the time allowed for this study we were able to make  $\delta\text{O}^{18}$  and  $\delta\text{C}^{13}$  analyses on 7 samples of Serravallian sediments from Holes 126 and 129, 12 samples of the Pliocene and Pleistocene pelagic oozes from Holes 125A, 132 and 134, and 32 samples of Messinian calcites and dolomites. The results of these analyses, grouped by drillhole, are listed in Table 1. Also included is the mineralogy of these samples and an approximation as to the amount of calcite and dolomite present in each sample.

Two complete  $\delta\text{O}^{18}$  and  $\delta\text{S}^{34}$  analyses of sulfate ions in gypsum from drill bit samples of Holes 122 and 125A were made, as well as  $\delta\text{O}^{18}$  and  $\delta\text{D}$  analyses of water of hydration (Table 2).  $\delta\text{O}^{18}$  and  $\delta\text{D}$  analyses of interstitial waters from dolomitic marls of the evaporite sequence in Hole 132 were also made (Table 3).

### ISOTOPIC COMPOSITION OF THE EVAPORITES

The evaporites illustrated in Figure 1 include layers of carbonate marls, anhydrite, gypsum, and halite. The most complete sections are from Site 124, on the Balearic Rise, and Site 132, in the Tyrrhenian Basin. With the exception of some minor amounts of gypsum in Core 7, the calcium sulfate phase at Site 124, is almost entirely anhydrite (see chapters 6, 21 and 22.1). At Site 132, however, similar anhydrite has been completely replaced by gypsum (see Chapter 22.1). Present at both of these sites, and also at Sites 125A, 129, and 134, are interbeds of steel blue to gray marls, which are occasionally finely laminated, and possess a variable amount of fine-grained anhedral dolomite. Similar dolomitic and calcitic marls were recovered from Holes 125A, 129A, 134 and 134D.

### Oxygen and Carbon Isotopes in the Carbonates

At times calcite and dolomite occur together in the evaporite marls. When fossil tests are present they are always calcitic. Siderite was identified in Sample 132-26-1-20 cm. The total carbonate content is usually less than 30 per cent; the other components consist of terrigenous clastic minerals (fine-grained quartz, clay minerals), pyrite, and disseminated organic matter. Smectites are the most important clay minerals. The relative proportions of other minerals do not seem to change significantly with changes in the abundance of gypsum and anhydrite, as if they represent some kind of background sedimentation.

The isotopic compositions of the carbonates are dispersed between two extremes: pure calcite and pure dolomite.

*Calcites:* The pure calcites, depicted by the solid dots in Figure 2, exhibit: (1) low values of  $\delta\text{O}^{18}$  and  $\delta\text{C}^{13}$  in comparison to normal marine pelagic oozes (open circles), (2) distinctly lower  $\delta\text{O}^{18}$  than the Messinian dolomites, and (3) a large scatter of  $\delta\text{O}^{18}$  and  $\delta\text{C}^{13}$  values, with all the values grouped in the quadrant of negative oxygen and negative carbon ranges.

Because the Pliocene and Quaternary pelagic oozes all cluster in the quadrant of positive oxygen and carbon ranges, it is isotopically easy to delineate the Miocene/Pliocene boundary (see also Figure 2 of Chapter 30.3). In Hole 132 where the Messinian marls in Core 21-2 are calcitic, the evaporite marl/pelagic ooze contact is accompanied by a pronounced decrease in both  $\delta\text{O}^{18}$  and  $\delta\text{C}^{13}$ . In Hole 134 there is a similar change. However, in Hole 125A, from the Mediterranean Ridge in the Ionian Basin, the underlying marls are dolomitic, with no calcite, and thus we observe a decrease only in  $\delta\text{C}^{13}$  (i.e. a trend toward more negative values).

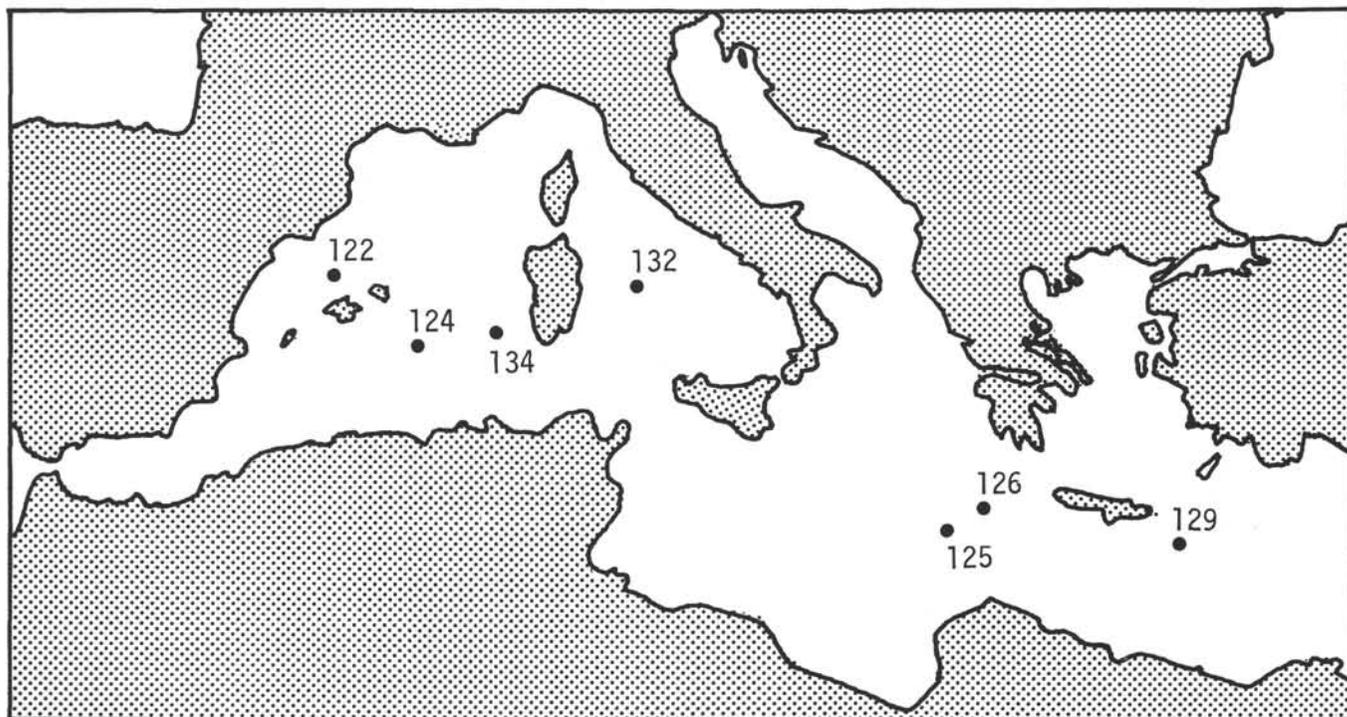


Figure 1. Location of the drill sites from which samples have been taken for the measurements of stable isotopes.

In the apparently continuous section at Site 132 in the Tyrrhenian Basin, the isotopic shift at the Miocene/Pliocene boundary, in Core 21-2, from negative to positive values is obviously related to the abrupt termination of evaporite conditions and the filling of the basin with normal marine water. The shift can be explained as being the result of an influx of cold North Atlantic deep water, replacing a warm water body of meteoric origin, already greatly depleted in the heavy isotope of oxygen. The concept that the terminal phase of the evaporite epoch was accompanied by the widespread occurrence of alkaline lakes is corroborated by the finding of the "Melanopsis-Cyprideis" fauna in the upper Messinian "lago mare" facies of northern Sicily (Ruggieri and Greco, 1965). We doubt that the isotopic shift can be entirely due to temperature because there is also a marked change in the carbon isotope ratio from negative to positive values. Yet the  $C^{13}$  fractionation with temperature is known to be much lower than  $O^{18}$  fractionation (Mook, 1971).

**Dolomites:** The marls characterized by the presences of dolomite without calcite (solid triangles in Figure 2) are, in the vast majority of cases, isotopically distinct from the calcites. Except for three samples from Core 25 of Hole 132, all of the dolomite samples have quite highly positive  $\delta O^{18}$  values, with a mean of about  $+4\text{‰}$  PDB. With one exception, the Site 124 (Balearic Rise) dolomites all group rather tightly (i.e.  $3.34 > \delta O^{18} > 2.14$  and  $2.16 > \delta C^{13} > 0.27$ ) in the positive quadrant of Figure 2 within the range of dolomites related to evaporite environments (Clayton *et al.*, 1968).

The one negative measurement is from Core 7 of this drill hole; the sample has a  $\delta O^{18}$  of  $-4.73\text{‰}$  and is associated with secondary gypsum replacement in the form

of selenite (see Figure 18A of Chapter 22.1). In this case the carbonate is a mixture of calcite and dolomite and the low  $O^{18}$  content can be explained by the predominance of an isotopically light calcite (calcisparite). In each of these samples the  $\delta C^{13}$  is also negative, reaching  $-6.34\text{‰}$  in Sample 132-25-2-70 cm. This suggests that meteoritic water has probably played an important role in the formation of the dolomite—perhaps as secondary dolosparite.

Some very low  $\delta C^{13}$  values have been obtained in samples from the eastern Mediterranean Basin. Both samples, 129-2-1 (Strabo Trench) and 125A-DB (Mediterranean Ridge — Ionian Basin), contain faunas indicative of a brackish water environment (see documentation in Chapters 7 and 10). Thus it is easy to accept that these ratios reflect the input of fresh water into the eastern basins and the development there of Alkaline lakes in late Messinian time (see Chapter 36.2).

However, the low  $\delta C^{13}$  values may also be attributed to the contribution of carbon dioxide of biogenic origin in the bicarbonate ion system. In fact, sample 134-10-1 ( $\delta C^{13} = -9.57\text{‰}$ ) is from an interval rich in gasoline range hydrocarbons (see Chapter 32). The suggestion of biological influence has been presented by Dessau *et al.* (1960) and Cheney and Jensen (1965) for carbonates connected with the Sicilian evaporite beds and by others (Russell *et al.*, 1967; Hathaway and Degens, 1970; Deuser, 1970) for various sedimentological systems at other locations.

Whereas the primary isotopic composition of calcites may change during diagenesis, dolomites generally do not undergo very much exchange (Fritz, 1971). The negative  $\delta C^{13}$  values for the dolomitic marls of Sites 125A and 129 are lower than those given by Fritz (1970) for secondary dolomite and suggest that some of the very fine anhedral

TABLE 1  
Oxygen and Carbon Isotopic Composition of Selected Samples  
of the Evaporitic Marls and Pelagic Sediments

## WESTERN MEDITERRANEAN DRILLSITES

Site 122 – Valencia Trough					Balearic Basin	
Age	Sample	Per Cent		Mineralogical Content and Other Components	$\delta O^{18}$ vs PDB	$\delta C^{13}$
		Calcite	Dolomite			
-162 my	Core Bit	++	T	n.d.	-3.24	+0.02
Mio- cene						
Site 124 – Balearic Rise					Balearic Basin	
-350m.y.	6	0	60	I, Ch, Q, M, G	+2,14 <sup>x</sup>	+1,27
	7	+	+	G, Q + n.d.	-4,73	-2,43
	10-1 (113)	0	+	n.d.	+3,34 <sup>x</sup>	-2,16
	10 CC	0	+	n.d.	+2,42 <sup>x</sup>	+2,15
	10 CC	0	+	n.d.	+2,56 <sup>x</sup>	+2,22
	11-1 (124)	0	85	Q, I, M, K	+3,08 <sup>x</sup>	+1,74
	13-2 (35)	0	++	n.d.	+3,29 <sup>x</sup>	+0,27
Miocene						
Site 132 – Tyrrhenian Rise					Tyrrhenian Basin	
	19-3 (100)	60	0	I, K, Q	+0,24	+0,77
	20-4 (40)	80	0	I, Q	+1,33	+1,25
	20-4 (90)	60	0	I, Q	+1,05	+1,09
	21-2 (60)	30	0	I, Q	+1,12	+0,59
Pliocene						
-88	21-2 (76)	6	0	M, I, Chl, G	-1,59	-1,37
25 my	21-2 (100)	12	2	I, M, Chl, G, K	-1,09	-1,66
	22-1 (78)	4	0	n.d.	-2,67	-1,29
	22-1 (140)	+	0	G + n.d.	-3,72	-4,23
	23-1 (120)	2	0	G, Q, I, Chl	-6,37	-6,53
	25-1 (50)	0	8	G, I, Q, Chl, K, M		
	25-1 (90)	+	+	n.d.	-2,44	-2,60
	25-2 (70)	0	2	G, Q, I, Chl, M	-4,87	-6,34
	25-2 (110)	n.d.	n.d.	n.d.	-5,85	-4,0
	25-2 (135)	0	10	n.d.	-1,17 <sup>x</sup>	-2,66
	25-2 (140)	0	0	M, I, Q, K, Chl, F		
	26-1 (20)	0	15	I, M, Q, K, Chl, S	+0,19 <sup>x</sup>	0,00
	26-1 (24)	n.d.	n.d.	n.d.	-2,70	-6,66
	26-1 (110)	n.d.	n.d.	n.d.	-1,11	-4,49
Miocene						
Site 134 – Balearic Abyssal Plain					Balearic Basin	
	3-1 (126)	+	0	n.d.		
	3-2 (130)	+	0	n.d.	+0,68	+0,25
	3 CC	+	0	n.d.	+0,91	+0,55
	5 CC	+	0	n.d.	+0,99	+0,82
Pliocene						
-326m.y.	7-5 (140)	+	+	n.d.	+0,10	+0,08
Mio- cene	7 CC (24)	15	15	Q, I, M, Chl.	-1,76	-1,32
	10-1 (115)	0	++	A, H, Q	+4,60 <sup>x</sup>	-9,57
Site 134 – Western Sardinia Slope					Balearic Basin	
-183 my	1-1 (90)	14	2	G, M, I, Ch, Q	+2,41	+1,93
Mio- cene	1-1 (144)	T	T	G, Q, I, Chl, M	+2,96	+1,92

dolomite in the evaporite marls might indeed be an early diagenetic product.

A more detailed petrographic analysis is needed to fully evaluate the problems of diagenesis. However, if, as we believe, some of the dolomites and calcites have preserved their original primary isotopic composition it must be

accepted that the Mediterranean Sea at certain times was fed predominantly from rivers and rainfall and that the evaporite basins were isolated from the open sea. The great variations in the isotopic composition of the calcite indicate that the influence of fresh water was intermittent. In the case of the dolomites of Site 124, the mineral phase was

TABLE 1—Continued

## EASTERN MEDITERRANEAN DRILLSITES

Site 125A – Mediterranean Ridge					Ionian Basin	
Age	Sample	Per Cent		Mineralogical Content and Other Components	$\delta O^{18}$ vs PDB	$\delta C^{13}$
		Calcite	Dolomite			
Plio- cene	2-2 (66)	60	0	G, Q, I	+0,37	-0,04
	5-3 (48)	64	4	I, Q, K	+1,10	+0,91
	6-1 (25)	65	10	I, Q, K	+1,48	+1,23
-81 my Mio- cene	6-1 (150)	0	++	n.d.	+5,20 <sup>x</sup>	-1,08
	7 CC (140)	0	25	I, Q, K, F	+4,38 <sup>x</sup>	-0,92
	9-1 (113)	0	++	n.d.	+5,23 <sup>x</sup>	-3,28
	Drillbit	0	++	A + n.d.	+5,09 <sup>x</sup>	-11,66
Site 126 – Cleft in Mediterranean Ridge					Ionian Basin	
Quater- nary	1-4 (90)	60	4	I, Q, K, Chl	+1,35	+0,49
	-106m.y.					
Serra- villian	5-1 (130)	12	0	M, K, Q, I	+0,48	+0,27
	5 CC	6	0	M, K, Q	+0,72	+0,33
	6-1 (130)	3	0	M, K, I, Q	+2,71	+0,65
	6 CC	4	0	Q, + n.d.	+0,19	-2,83
Site 129 – Strabo Trench					Levantine Basin	
Miocene	2-Centerbit	++	0	n.d.	-6,81	-1,92
	2-1 (136)	0	25	Q, M, Chl, I, G	+1,60 <sup>x</sup>	-26,90
	3-1 (49)	n.d.	n.d.	n.d.	-0,83	-8,22
	3 CC	15	13	M, Q, I, Chl, K	+0,17	-7,51
Site 129A – Strabo Mountains					Levantine Basin	
Mio- cene	2 CC	15	10	M, Q, I, Chl	-2.21	-1.97

LEGEND: T = trace, n.d., not measured. G = gypsum, I = illite, M = montmorillonite, Q = quartz, K = kaolinite, F = feldspars  
Chl = chlorite, A = clays, H = halite, S = siderite.

The mineralogical components are given in the order of their relative importance. The isotopic values for pure dolomites (x) have been corrected for isotopic fractionation effect as given by Sharma and Clayton (1965).

TABLE 2  
Isotope Composition of Gypsum

Site	Location	Sample	Facies	Crystallization Water		Sulfate Ion	
				$\delta O^{18a}$	$\delta D^a$	$\delta S^{34b}$	$\delta O^{18a}$
122	Valencia trough	Core Bit	Selenite gravel	+4.07	-16.0	+22.0	+14.3
125A	Ionian Basin	Core Bit	Selenite chips +++ traces Fe	+3.89	-8.5	+22.6	

<sup>a</sup> vs SMOW

TABLE 3  
Isotope Composition of Interstitial Waters

Site	Location	Sample	Dry Residue	Pore Water	
				$\delta O^{18a}$	$\delta D^a$
132	Tyrrhenian Basin	25-2125 cm	53.8 0/00	-0.78	+6.4
132	Tyrrhenian Basin	25-1,15 cm	55.0 0/00	-0.88	+4.3

<sup>a</sup> vs SMOW

<sup>b</sup> vs C.D

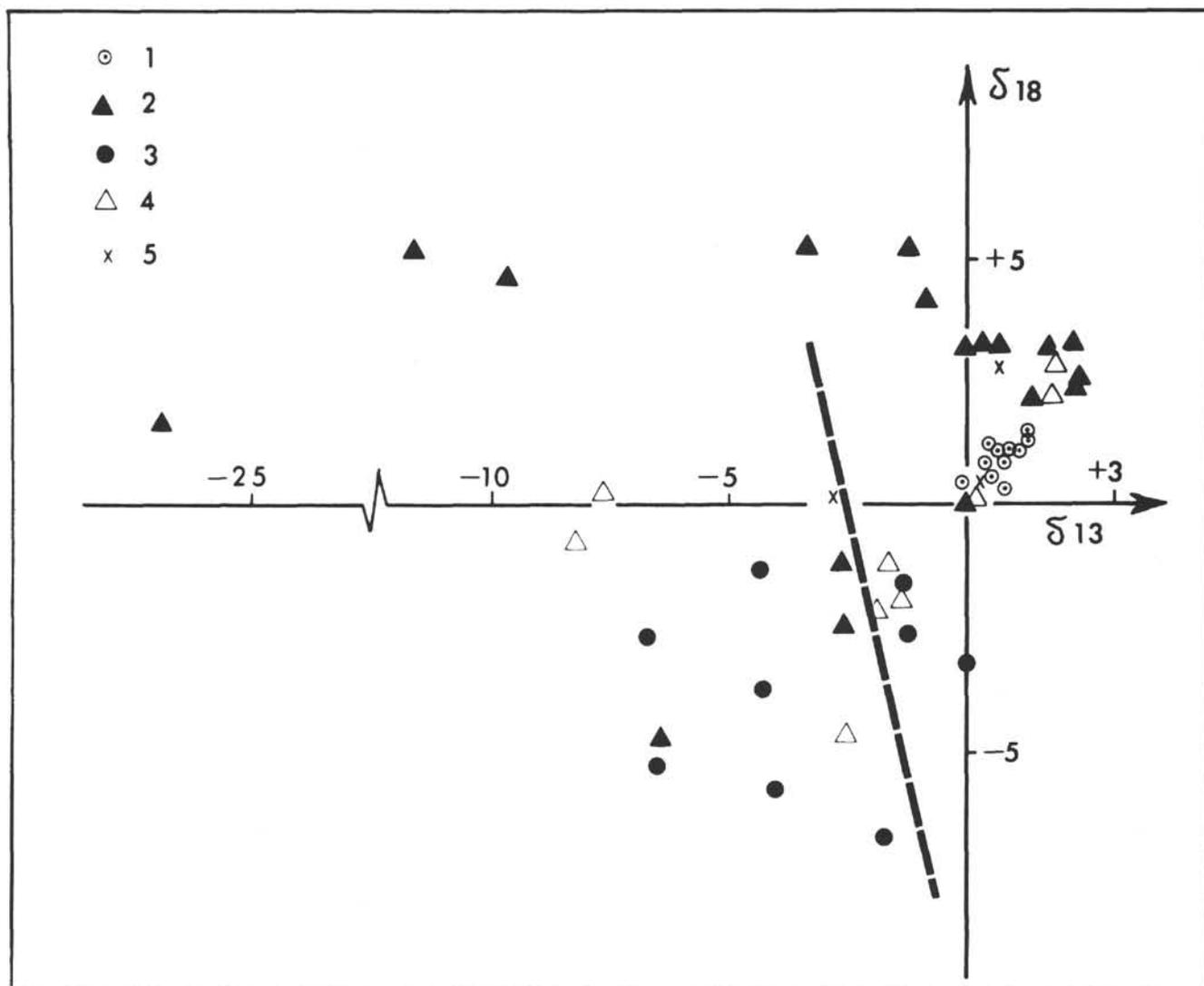


Figure 2. A plot of  $\delta O^{18}$  against  $\delta C^{13}$  for samples investigated. 1 = Pliocene and Quaternary pelagic oozes, 2 = Upper Miocene (Messinian) dolomites, 3 = Upper Miocene (Messinian) calcites, 4 = A mixture of the calcites and dolomites, and 5 = Calcites of Middle Miocene (Serravallian) age. The dashed line represents the function  $2(\delta C^{13} + 50) = 0.5(\delta O^{18} + 50)$  given by Keith and Weber (1964) to separate carbonates of marine origin (right of the line) from carbonates of fresh-water origin (left).

apparently crystallized from concentrated water with a modified ionic content.

#### Oxygen, Sulfur, and Hydrogen Isotopes in the Sulfates

For natural samples, the effects of isotopic fractionation between the sulfate ion ( $SO_4^{2-}$ ) and the water of crystallization are difficult to relate to experimental data (Longinelli and Craig, 1967; Lloyd, 1967; and 1969; and Misutani and Rafter, 1969).

*Oxygen 18 in the Sulfate Ion:* Studies of the data  $\delta O^{18}$  values of brines and of gypsum in saline ponds bordering the Mediterranean has shown that the data  $\delta O^{18}$  content of the sulfate ion has been enriched; also precipitated gypsum has an enriched data  $\delta O^{18}$  of +14 to 15 ‰ (Fontes and Schwartz, unpublished data). We have obtained values of 14.3 and 15.1 ‰ in the sulfate of core bit samples of Site 122 and 125A. We interpret those values as an indication of

$\delta O^{18}$  enrichment due in the processes of brine concentration.

It is generally admitted (Longinelli and Craig, 1967) that in the range of biological temperatures and pH, isotopic exchange between the oxygen in sea water and that in the sulfate ion is very slow, with a half reaction time in the range of 100 to 1000 years. It appears that under peculiar conditions of confinement (i.e., inhibited circulation, strong evaporation, high temperatures and high brine concentration) sulfates should more rapidly initiate an isotopic equilibration with the water.

Consequently, and as a present working hypothesis, one can reasonably assume that the measured values of +14.3 and 15.1 ‰ correspond to precipitation of calcium sulfate in situations well isolated from the open sea for which, however, the original supply of sulfate ions was from the open sea.

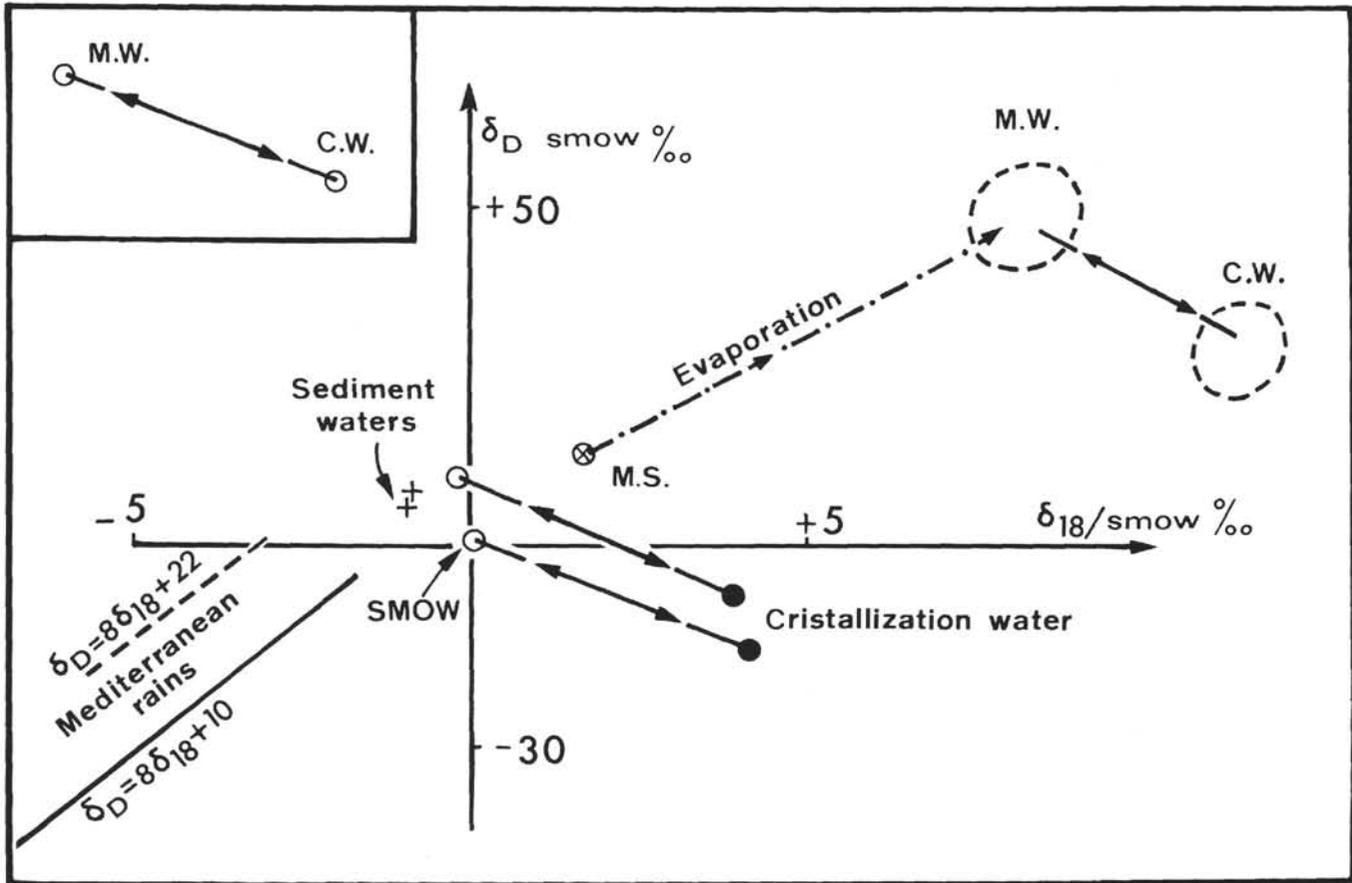


Figure 3. A plot of  $\delta D$  against  $\delta O^{18}$  for the interstitial waters of Cores 132-25 and 132-26 (+ signs) and the crystallization waters of the Core Bit samples from Sites 122 and 125 A (solid dots). The insert in the upper left hand corner shows the correction (because of fractionation) to be applied to convert the isotopic value of crystallization water (C.W.) to its mother water (M.W.) value. As an example, if present Mediterranean sea water (M.S.) is concentrated by evaporation to precipitate gypsum, the M.W. circle shows the isotopic range of the saturated mother water and the C.W. circle the range of the crystallization water in the newly formed gypsum. At the lower left are the localization lines for worldwide precipitation (solid line) and eastern Mediterranean precipitation (dashed line).

**Sulphur 34 in the Sulfate Ion:** Two samples of gypsum, one from Site 122 and one from Site 125A, have provided  $\delta S^{34}$  values of +22.0 and +22.6 ‰ vs. Cañon Diablo; these are similar to measured values from recent marine sulfates. Because  $\delta S^{34}$  values have remained quite constant since the beginning of the Tertiary (Nielson, 1965 and Nielsen and Rambow, 1969), and since the older Mesozoic and Paleozoic salt deposits of Europe and North Africa are characterized by much lower  $\delta S^{34}$  values, it is unlikely that erosion of older sedimentary rocks has supplied the sulfate to the Messinian basin. It is more probable, in light of what has already been concluded about the oxygen isotopes, that the sulfate ions were derived directly from the open ocean.

**Oxygen 18 and Deuterium in the Water of Crystallization:** Isotope fractionation during the hydration of anhydrite to gypsum is known to be an equilibrium or near-equilibrium process (Gonfiantini and Fontes, 1963; Fontes and Gonfiantini, 1967). In the interval of +15°C to +60°C, which covers the ordinary range of temperatures for the precipitation of evaporites, the fractionation is also known to be independent of temperature.

The following enrichment factors of the isotopes between the mother water (Vine) and crystallization water can be defined:  $\epsilon O^{18} = +4.0$  ‰,  $\epsilon D = -16$  ‰ with  $\epsilon \approx \delta$  (mother water) -  $\delta$  (crystallization water).

Present-day values close to +8 ‰ for  $\delta O^{18}$  and +50 ‰ for  $\delta D$  vs. SMOW are obtained for mother water of directly precipitated gypsum from the concentration of Mediterranean sea water, when the original liquid has been concentrated to one-fifth its original volume (Fontes, 1966).

As shown in Table 2, crystallization waters of the selenite (gypsum) crystals from Sites 122 and 125A, though similar in isotopic composition, cannot correspond to evaporatively concentrated, calcium-sulfate-saturated sea water. These evaporite specimens have quite obviously undergone recrystallization. The macro- and microscopic fabric of the sample from Site 125A (see Figures 14 and 15 of Chapter 7), which indicates complete alabastrization, supports this conclusion.

The question now arises as to the origin of the water leading to the crystallization. If, as shown in Figure 3, we take the isotopic values of the measured crystallization water (solid dots) and correct these data for fractionation

(open circles) we arrive at a composition for the ancient mother water far different from what would be obtained by taking present day Mediterranean water (circle with a cross) and evaporating it. A clue to the origin of the ancient mother water comes from an examination of interstitial water in the evaporitic marls.

*Oxygen 18 and Deuterium in Interstitial Waters:* It turns out that the isotopic composition of connate waters of Messinian age, extracted by squeezing sediments from Cores 25 and 26 at Site 132 (see Table 3 and plus sign in Figure 3), lies close to the values of the crystallization water corrected for fractionation during the formation of gypsum (open circles of Figure 3). The isotopic composition of the interstitial waters can be attributed to that of seawater without any sign of enrichment by evaporation (Craig and Gordon, 1965). It is believed to antedate the general enrichment of marine water masses in heavy isotopes due to the balancing effect of the glaciations and the relative isolation of the Mediterranean basins. We consider that the mother water, now locked within the sediment both as pore water and crystallization water, is most likely Atlantic Ocean water brought in during brief marine invasions during the Messinian and, in the case of the Site 122 sample at the upper contact of the evaporite layer, by the marine waters of the Pliocene (see Chapter 47). It is unlikely that the ancient mother water was solely meteoric because its corrected values lie well off the trend (dashed line of Figure 3) of rain water from arid or semi-arid areas (Craig, 1961 and IAEA, 1969 and 1970).

If we consider that the mother water was supplied during marine invasions from the Atlantic Ocean, it will be of further interest to compare its inferred isotopic composition (open circles of Figure 3) with that of the Pliocene carbonate sediments deposited at a time when we know there was open communication between the Mediterranean and the Atlantic (Benson, 1971).

#### ISOTOPIC COMPOSITION OF THE PELAGIC OozES

Oxygen and carbon isotope determinations were made on the carbonate fraction of pelagic open-marine sediments of Sites 125A, 126, 129, 132 and 134. The samples from Sites 126 and 129 include sediment of pre-evaporite age (middle Miocene), and the remainder are samples of earliest Pliocene to Quaternary age.

#### Oxygen and Carbon Isotopes in the Pliocene and Quaternary Sediments

The Pliocene-Quaternary pelagic oozes are generally rich in calcium carbonate ( $30\% < \text{CaCO}_3 < 70\%$ ), as shown in Figure 1 of Chapter 30.3.

The clustering of the isotopic compositions ( $+0.24 \leq \delta\text{O}^{18} \leq +1.35$  and  $-0.04 \leq \delta\text{C}^{13} \leq +1.25$ ), which appears as the group of open circles with dots in Figure 2, is related to the crystallization of carbonate skeletal material in a large mass of water, which acts as an isotopic buffer. Sample 126-1-4-90, assigned to the "pre-glacial" Pleistocene, is slightly heavier than the Pliocene carbonates and does not show the important variation correlated with the "temperature and/or water-isotopic-composition effect" known for the cold climate epochs of later glacial times. A

similar observation has been made by Emiliani *et al.* (1961) on pericontinental Pliocene/Calabrian deposits.

The most positive values of  $\delta\text{O}^{18}$  in the pelagic oozes occurs in Sample 125 A-6-1-25 cm, just above the Miocene/Pliocene contact where a significant amount of the carbonate (1/6th) is in the form of detrital dolomite reworked from the subjacent evaporitic marls with a  $\delta\text{O}^{18}$  of  $+5.20$  ‰. Detrital dolomite has been observed to have a similar effect on the bulk isotopic composition of carbonate sediment from the Persian Gulf (Sugden, 1963).

The values of  $-0.78$  and  $-0.88$  ‰ vs. SMOW for the oxygen isotopic composition of the interstitial waters of late Miocene age suggest that the ancient sea water was perhaps 1.5 to 2.3 ‰ lighter in  $\text{O}^{18}$  than today. This assumed value of  $-0.8$  ‰ for Mediterranean Sea water implies that the budget of the Mediterranean Sea was quite different from that of the present. Therefore the values of  $+0.24 \leq \delta\text{O}^{18} \leq +1.33$  ‰ U.S.P.D.B. for the earliest Pliocene oozes of Cores 19 to 21 of Site 132 suggest that the temperature was near  $8^\circ\text{C}$  to  $13^\circ\text{C}$  at maximum — rather close to that of the recent Mediterranean bottom water, and perhaps lower. This problem will be discussed in greater detail in Part V of Chapter 47. However, we can state that the situation revealed in the present study is quite distinct from the compositional balance of the oceanic masses as discussed by earlier authors (i.e. Emiliani, 1966; Shackleton, 1967; Dansgaard and Tauber, 1969; Letolle *et al.*, 1971).

#### Oxygen and Carbon Isotopes in the Middle Miocene Sediments

The carbonate content of the middle Miocene (Serravalian) sediments of Site 126 is only 3 to 12 per cent by weight but it is entirely calcitic—mostly nannofossils. The isotopic data show a much broader scatter (+ signs in Figure 2) than for the Pliocene and Quaternary sediments with a  $\delta\text{C}^{13}$  value of  $-2.83$  ‰ for the core catcher sample of Core 6. Perhaps the light values are related to density stratification during Serravalian time, leading to oxygen depletion in the bottom water mass of the Ionian Basin (no benthic fauna was present). It is also possible that some part of the Serravalian calcite was recrystallized during Messinian immersions.

Similar light values have been recorded in Quaternary sediments from layers of sapropel mud rich in organic matter and influenced by exchanges of water with the Black Sea.

Markedly negative values of the  $\delta\text{C}^{13}$  were observed in the samples from Core 3 of Hole 129. These samples contain the euryhaline ostracod *Cyprideis* (see Chapter 36.2), which is suggestive of an alkaline lake deposit.

#### CONCLUSIONS

The carbonates of the evaporite layer exhibit a large scatter in their  $\delta\text{O}^{18}$  and  $\delta\text{C}^{13}$  values. The calcites are all negative, whereas the dolomites have generally positive  $\delta\text{O}^{18}$  values with  $\delta\text{C}^{13}$  values that reach  $-26.9$  ‰ PDB. Some of the fine-grained dolomite is interpreted as a primary precipitate or a very early diagenetic product. As a whole, the  $\delta\text{O}^{18}$  range for the carbonates is  $-6.81 \leq \delta\text{O}^{18} \leq +7.13$ . We believe these measurements indicate that at

times during the Messinian "crisis of salinity" the Mediterranean basins became isolated from the open ocean and were supplied to a great extent by river and rain water.

The markedly negative values of  $\delta C^{13}$  in the dolomites might be related to diagenesis associated with carbon dioxide derived from organic matter depleted in the heavier isotope. The positive values might correlate with the intervention of atmospheric carbon dioxide at a time when the basins were very shallow and abiotic.

The sulfates examined appear to be of marine origin, indicating periodic influxes of appreciable amounts of water from the open ocean. This conclusion is corroborated by the presence of marine fossils (foraminifera and coccoliths) in interbeds within the evaporite sequence.

The hydration of anhydrite to gypsum and the formation of selenite at Sites 122 and 125A in both the western and eastern Mediterranean basins was caused by integration of marine sea water in the crystal lattice.

The late Miocene/early Pliocene water was perhaps significantly lighter (perhaps 1.5 to 2.3 ‰) in  $O^{18}$  than present day Mediterranean water. The earliest Pliocene surface water at Site 132 in the Tyrrhenian Basin was probably as cold or colder than present day Mediterranean bottom water.

Negative  $\delta C^{13}$  values from the middle Miocene (Serravallian) pre-evaporite calcite sediments are correlated with evidence that the Mediterranean basins were stagnant or nearly stagnant at that time, leading to an enrichment of organic matter in the stratified surface water mass.

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### 30.3. STABLE OXYGEN AND CARBON ISOTOPE VARIATIONS IN BULK CARBONATES FROM LATE MIOCENE TO PRESENT, IN TYRRHENIAN BASIN – SITE 132

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#### INTRODUCTION

This investigation was undertaken to determine to what degree the  $O^{18}/O^{16}$  and  $C^{13}/C^{12}$  ratios of full carbonate sediments represent depositional conditions versus diagenetic conditions. If appreciable diagenesis can be discounted, then the measured isotopic values should reflect the surface water temperature at the time of growth of the carbonate organisms and the  $O^{18}/O^{16}$  and  $C^{13}/C^{12}$  content of the surface waters. If, on the other hand, significant isotopic exchange has occurred during diagenesis, the isotopic values should yield information about the temperatures and mechanisms of diagenesis.

The sediments from Site 132 consist of evaporites of Miocene age overlain unconformably by a continuous section of pelagic oozes of Pliocene to Recent age (see Chapter 13). The Miocene evaporites consist mostly of gypsum, dolomite, calcite and silicate detritus and contain, in several horizons, brackish water fossils. These sediments have undergone lithification and recrystallization to a moderate degree since deposition. The Plio-Pleistocene oozes consist of coccoliths (70-95%) and foraminiferal (5-30%) shells formed in surface and near surface waters, plus a variable amount of silicate detritus (see Figure 1). Very little lithification and recrystallization has taken place in these younger sediments (see Chapter 13).

Bulk samples, representing one centimeter horizons at 19 intervals throughout the entire core, were analyzed for  $O^{18}/O^{16}$  and  $C^{13}/C^{12}$  content of the carbonate fraction by the method described by McCrea (1950). All  $C^{13}/C^{12}$  and  $O^{18}/O^{16}$  analyses are reported in the  $\delta$ -notation with  $\delta$ -values being reported with respect to PDB and SMOW, respectively.

#### RESULTS AND DISCUSSION

Variations in the  $CaCO_3$  content of sediments from Site 132 are shown in Figure 1. There is an abrupt increase in

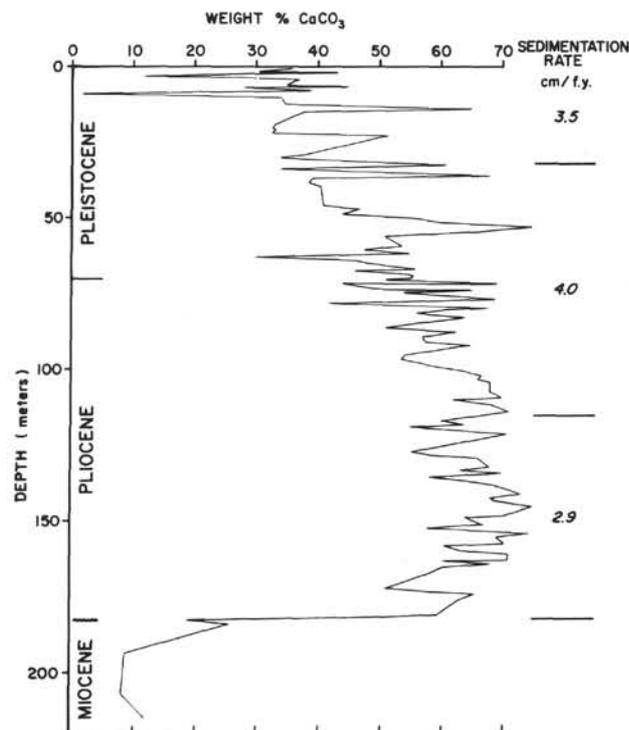


Figure 1. Weight per cent of  $CaCO_3$  in the sediments from Site 132, Leg 13 plotted as a function of depth. The average sedimentation rates in centimeters per thousand years are also shown.

$CaCO_3$  content of the sediments across the Miocene-Pliocene unconformity. This is not unreasonable considering the drastic change from an evaporite sequence to normal marine pelagic oozes.

The  $CaCO_3$  content of the Pliocene sediments is relatively uniform, with a decrease in the upper Pliocene which continues into the Pleistocene. Comparison of the changes

in  $\text{CaCO}_3$  content with the changes in total sedimentation rate suggests, on an average basis, a twofold increase in the amount of silicate detritus going from the late Pliocene to the Pleistocene. Also, the magnitude of shorter term fluctuations of  $\text{CaCO}_3$  content are much greater in the Pleistocene than in the Pliocene. These variations in  $\text{CaCO}_3$  content probably reflect the effects of continental glacial cycles in Europe and Asia during the Pleistocene.

The isotopic data and  $\text{CaCO}_3$  contents of the analyzed samples are illustrated in Figures 2 and 3. In the discussion which follows, it is assumed that there are no large changes in  $\text{O}^{18}/\text{O}^{16}$  or  $\text{C}^{13}/\text{C}^{12}$  due to changes in the biologic makeup of the carbonate.

The largest changes in  $\text{O}^{18}/\text{O}^{16}$  and  $\text{C}^{13}/\text{C}^{12}$  are observed across the Miocene-Pliocene unconformity. The  $\text{O}^{18}/\text{O}^{16}$  and  $\text{C}^{13}/\text{C}^{12}$  of most of the samples above the boundary are in the range expected for  $\text{CaCO}_3$  in equilibrium with surface waters similar in temperature and isotopic composition to those of the Mediterranean Sea today (see Figures 2 and 3). The samples below the boundary are, in contrast, distinctly depleted in  $\text{O}^{18}$  and  $\text{C}^{13}$ , which strongly suggests that the water in which the carbonates were formed, or recrystallized, was meteoric in origin. Also, the fact that the isotopic values display a sharp break over a

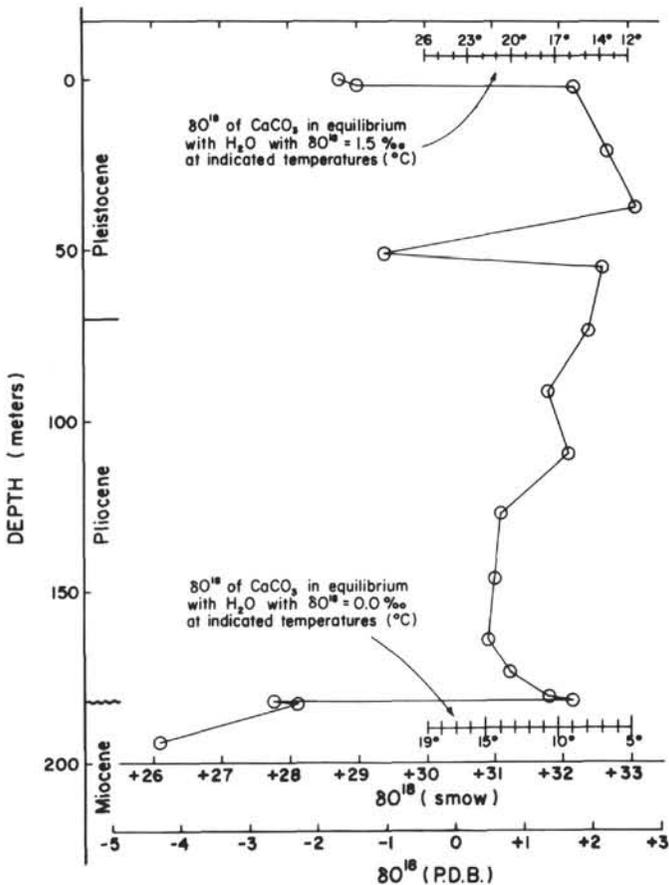


Figure 2.  $\delta\text{O}^{18}$  of the bulk carbonate from Site 132, Leg 13 sediments. The temperature- $\delta\text{O}^{18}$  scales shown were calculated using the carbonate temperature scale of Epstein et al. (1953). One is based on  $\delta\text{O}^{18}\text{H}_2\text{O} = +1.5$  percent representing  $\text{CaCO}_3$  in equilibrium with present-day surface waters in the Mediterranean; the other on  $\delta\text{O}^{18}\text{H}_2\text{O} = 0.0$  per mille representing  $\text{CaCO}_3$  in equilibrium with Atlantic Ocean Deep Water.

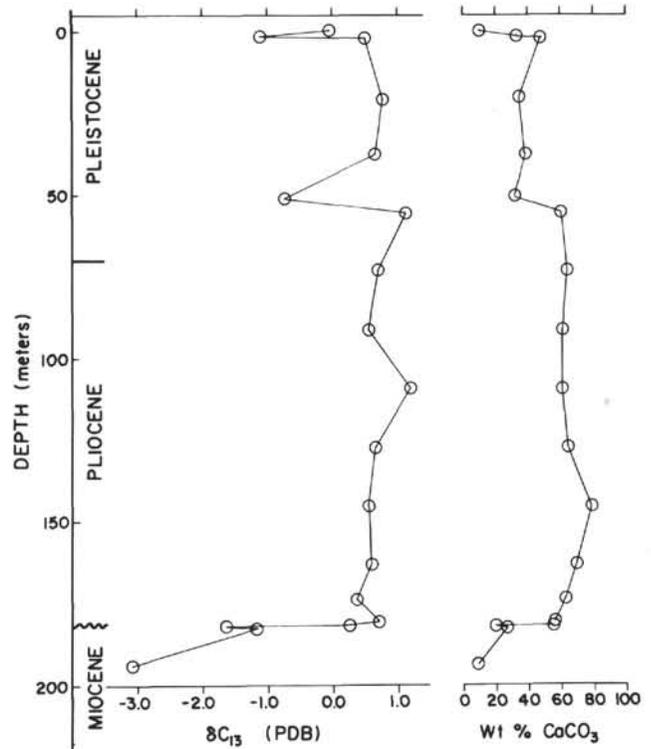


Figure 3.  $\delta\text{C}^{13}$  of the bulk carbonate from Site 111, Leg 13 sediment. The weight per cent of  $\text{CaCO}_3$  in the isotopically analyzed samples is also shown.

4 cm interval (the two samples at the Mio-Pliocene boundary are only 4 cm apart) suggests that no large degree of isotopic change as a result of diagenesis has occurred since the deposition of the Pliocene sediments.

Three samples in the Pleistocene, two sapropel horizons<sup>1</sup> (at 2 and 53 m) and a layer containing a high percentage of silicate detritus (at 1 m, the peak of the Wisconsin glacial stage), are depleted in  $\text{O}^{18}$  and  $\text{C}^{13}$  compared to the bulk of the Plio-Pleistocene samples. These large decreases are probably due mostly to influxes of  $\text{O}^{18}$  and  $\text{C}^{13}$  depleted glacial melt waters into the surface waters of the Mediterranean. Part of the decrease in  $\text{O}^{18}/\text{O}^{16}$  may be due to a warming of surface waters, since the sapropel horizons can be correlated with warming trends following glacial maximums (see Chapter 46).

The remainder of the Plio-Pleistocene samples exhibit no obvious trends in  $\text{C}^{13}/\text{C}^{12}$  but do show significant changes in  $\text{O}^{18}/\text{O}^{16}$ . There is a decrease in  $\delta\text{O}^{18}$  of  $1^\circ/\text{‰}$  over a period of 300,000 years, starting with the sudden appearance of pelagic oozes in the late Pliocene. This could be attributed to a warming of the surface waters of the Mediterranean of from  $4^\circ$  to  $5^\circ\text{C}$ , to a decrease in the  $\delta\text{O}^{18}$  of the surface waters of  $1^\circ/\text{‰}$ , or to a combination of the two factors.

Paleontological evidence suggests the sudden appearance of pelagic oozes was the result of a sudden influx of cold

<sup>1</sup>Sapropels are organic-rich sediments which may have been formed during eutrophication of Mediterranean surface waters, perhaps associated with an influx of water from the Black Sea.

Atlantic Deep Water. The initial  $O^{18}/O^{16}$  of the Mediterranean surface waters would be expected to be free of influence from the Atlantic source. Subsequent excess evaporation in the Mediterranean would increase the  $\delta O^{18}$  of the surface waters. The observed progressive decrease in the  $\delta O^{18}$  of the carbonate from  $+32\text{‰}$  to  $+31\text{‰}$  could only be brought about if temperature effects overrode those of the isolation. Consequently the  $4^{\circ}$  to  $5^{\circ}\text{C}$  inferred warming is a minimum value.

From the Late Pliocene to the Pleistocene, there is a 1.5 to  $2\text{‰}$  increase in the  $\delta O^{18}$  of  $\text{CaCO}_3$ . If no large isotopic changes had taken place as a result of diagenesis, this could be attributed to: (a) an increase in the  $\delta O^{18}$  of the surface waters of 1.5 to  $2\text{‰}$  as a result of progressive isolation of the Mediterranean from the Atlantic (see Chapter 47.4), (b) to a cooling of the surface waters by  $6^{\circ}$  to  $9^{\circ}\text{C}$ , or (c) to a combination of both factors. It is probable that both cooling and an increase in the  $\delta O^{18}$  of the surface waters occurred with an increase in glaciation. An increase in glaciation is consistent with dropping temperatures. But also, increased glacial uptake of water would drop sea level and decrease circulation between the Atlantic and the Mediterranean. Increased isolation of the Mediterranean would have a greater effect on increasing the  $O^{18}/O^{16}$  of the Mediterranean surface waters.

The variations in  $O^{18}/O^{16}$  and  $C^{13}/C^{12}$  of the bulk carbonate at Site 132 are consistent with changes in surface water temperatures or with  $O^{18}/O^{16}$  and  $C^{13}/C^{12}$  variations in the surface waters as inferred from physical or paleontological changes in the sediment. In addition, sharp changes in  $O^{18}/O^{16}$  and  $C^{13}/C^{12}$  occur over short time intervals in the sediments. Isotopic exchange or recrystallization of the bulk carbonate would tend to smooth such sharp isotopic gradients. These facts suggest that the isotopic values of most of the carbonate, with the exception of the Miocene sediments, is largely unaffected by diagenesis. Isotopic studies on individual carbonate fossils should verify this and determine to what degree changes in biologic makeup of the carbonate portion of the sediments (ignored in this discussion) have determined the  $O^{18}/O^{16}$  and  $C^{13}/C^{12}$  of the bulk carbonate.

Lamont-Doherty Geological Observatory Contribution No. 1860.

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### 30.4. OXYGEN ISOTOPIC COMPOSITION OF BENTHONIC AND PLANKTONIC FORAMINIFERA OF EARLIEST PLIOCENE AGE AT SITE 132 – TYRRHENIAN BASIN

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#### INTRODUCTION

Although it has been shown that some foraminifera do not deposit calcium carbonate in isotopic equilibrium with the surrounding water, the deviations noted are relatively small (up to  $-1.0\text{‰}$ ). For this reason it was considered worthwhile to analyse specimens of both benthonic and planktonic foraminifera from a single sample of pelagic ooze of earliest Pliocene age from Site 132 ( $40^{\circ} 15.7'\text{N}$ ;  $11^{\circ} 26.5'\text{E}$ , depth 2835 m). It was hoped to obtain information about the structure of the Mediterranean water mass following re-introduction of marine conditions at the end of the late Miocene "crisis of salinity".

A quarter core section from 52 to 75 cm in Section 4 of Core 20 was sampled and washed. The sample interval is from a level only a few meters above the Miocene/Pliocene boundary (see Chapter 47).

#### RESULTS

##### Benthonic Foraminifera

The sample of benthonic foraminifera had a weight of about micrograms. It was roasted in vacuo before analysis at the University of Cambridge. Carbon dioxide was released by the action of 100 per cent orthophosphoric acid in vacuo at  $50^{\circ}\text{C}$ , and it was analysed in a double-collecting mass spectrometer. Results were calibrated by the analysis of standard carbonates in identical conditions. The result (relative to the PDB standard) was:

$$\delta O^{18} = (+0.3 \pm 0.1)\text{‰}$$

$$\delta C^{13} = (+0.7 \pm 0.1)\text{‰}$$

The analytical method is routine in this laboratory; the quoted uncertainty represents the standard deviation

among replicate analyses of small samples of calcium carbonate under the same conditions ( $1-\sigma$ ).

### Planktonic Foraminifera

Two species of foraminifera, *Globigerina bulloides* and *Sphaeroidinellopsis seminulina* were isolated from the washed residues and analysed separately. The specimens were crushed and then shell fragments were washed ultrasonically to remove any chamber fillings present. They were then vacuum dried at room temperature. The carbonate material was reacted with 100 per cent orthophosphoric acid in vacuo at 25°C without having been roasted. The analysis was carried out in the Geochemistry Laboratory of the Lamont-Doherty Geological Observatory in a double-collecting mass spectrometer, and, as in the case of the benthonic foraminifera, the results are reported with respect to the PDB standard.

<i>G. bulloides</i>	$\delta O^{18} = (+1.0 \pm 0.15)^\circ/\text{‰}$
	$\delta C^{13} = (+0.3 \pm 0.15)^\circ/\text{‰}$
<i>S. seminulina</i>	$\delta O^{18} = (+0.4 \pm 0.03)^\circ/\text{‰}$
	$\delta C^{13} = (+1.39 \pm 0.09)^\circ/\text{‰}$

Measurements on the specimens of *Sphaeroidinellopsis seminulina* are considered to be the most reliable. Results shown above are an average of three separate analyses. The sample comes from the *Sphaeroidinellopsis* Acme-zone (see Chapter 47.1) where this taxon sometimes comprises up to 70 per cent of the foraminifera population. The substantial number of tests of *Globigerina bulloides* seems to suggest cold temperatures of the surface waters since, according to Bé and Tolderlund (1971), this is a dominant species in subarctic and subantarctic waters with a peak abundance in water masses having a temperature range of from 3° to 19°C.

### DISCUSSION

The most obvious, and probably the most significant, observation is that the oxygen isotopic composition of the benthonic foraminifera is extremely close to that of the planktonic foraminifera. The higher value of  $+1.0^\circ/\text{‰}$  from *Globigerina bulloides* perhaps indicates that this taxon lived at shallower depths in the surface water layer than *Sphaeroidinellopsis seminulina* (personal communication, M. B. Cita). At these depths the  $O^{18}$  content is slightly enriched as the result of evaporation and higher salinity.<sup>1</sup>

It is somewhat hazardous to translate the  $\delta O^{13}$  values directly to paleotemperatures without knowledge of the isotopic composition of the Mediterranean water mass of early Pliocene age. The value of  $+0.3$  would correspond to a temperature of about 15°C if the fossil tests were in isotopic equilibrium with present day North Atlantic Deep Water.<sup>2</sup> The true value would be lower by a few degrees, at most, if the species analysed did not deposit carbonate in

isotopic equilibrium. It would also be lower if account were taken of a change in the isotopic composition of the oceans such as the one which would result from a reduction in the amount of ice on Antarctica. This last correction may perhaps be ignored for Pliocene material.

At present the surface and deep waters in the Mediterranean have an isotopic composition about  $1.2^\circ/\text{‰}$  heavier than North Atlantic Deep Water in consequence of the excess evaporation (Epstein and Mayeda, 1953; corrected by Craig and Gordon, 1965). Benthonic foraminifera living at 13°C today would be expected to have an isotopic composition of about  $+2.0^\circ/\text{‰}$ . The Pliocene sample analysed would represent a temperature of around 21°C in present-day Mediterranean water, an improbably high value. However, a lower temperature than this would be derived if the salinity excess were much less than today as the consequence of a more open exchange with the Atlantic Ocean.

If we allow ourselves to examine the working hypothesis of a more open exchange in early Pliocene times between the Mediterranean and the Atlantic (see Chapter 47.4), we also have to ask how this exchange was initiated in the first place. After all, during the late Miocene evaporite deposition, the passageway, to all intents and purposes, was blocked.

From stratigraphic considerations (see Chapters 47.1 and 47.2), the Mediterranean sample of pelagic ooze investigated here was deposited within approximately 100,000 years after the first truly effective opening of the Gibraltar portal, this opening established permanent open marine conditions in the Mediterranean. The isotopic value of  $\delta O^{18} = 0.3$  for the benthonic foraminifera could imply that the Mediterranean then communicated with the Atlantic over a sill at a depth corresponding to a temperature of about 15°C or a little less, and that bottom water in the Mediterranean entered over this sill. This implies a wide enough sill to permit free exchange in both directions.

The similarity of the isotopic composition of the planktonic and benthonic foraminifera indicates a thermal homogeneity in the Mediterranean water structure. A speculative model which would account for both the similarity in the oxygen isotopic composition of the planktonic and benthonic foraminifera and its composition at 0.3 to  $0.4^\circ/\text{‰}$ , invokes a catastrophic flooding of the Mediterranean basins following the late Miocene evaporite epoch. In this model, water entering the Mediterranean would be comprised of both cold North Atlantic Deep Water (down to the level of the sill eroded away) and warmer surface water, well mixed as it poured into the partially desiccated basin (see Chapter 43). The oozes in Section 4 of Core 20 at Site 132 could have been deposited either while the basin was still flooding or before it established a steady-state thermocline.

The depth of the sill at Gibraltar necessary to produce a water column in the Mediterranean with a mean temperature of around 15°C is extremely difficult to estimate. There is evidence, though, that bottom water temperatures in the open oceans were warmer in early Pliocene times than they are today.

From similar measurement of benthonic foraminifera in cores from the Pacific Ocean, Emiliani (1954) reported a cooling trend in the Pacific Bottom Waters from 10.4°C in

<sup>1</sup>The oxygen isotope composition of the surface layer of the Caribbean is measurably heavier than that of the bottom water for the same reason (Craig and Gordon, 1965).

<sup>2</sup>According to Craig and Gordon (1965) North Atlantic Deep Water has a present composition of  $+0.1^\circ/\text{‰}$  (SMOW).

the middle Oligocene to 7.0°C in early-middle Miocene to 2.2°C in the late Pliocene. We have been able to substantiate that this cooling trend also was present in the Atlantic Ocean. A study by two of us (T.S. and J.V.D.) of the isotopic composition of benthonic foraminifera of late Miocene and early Pliocene age in DSDP cores from the South Atlantic (Site 15 at 31°S) reveals that the Atlantic waters were as warm as 5°C at the time the pelagic oozes were deposited in Core 20 of Site 132.

The present day mean surface water temperature of the Atlantic west of Gibraltar is 22°C in August. It reaches 24°C in the Mediterranean near Site 132. Since flooding, therefore, would have had to involve a considerable amount of North Atlantic deep water to bring the average temperature down to 15°C, we can roughly infer that the incision of Gibraltar might have been as deep as 1000 meters in order to effect the required exchange.

We can conclude that, although the measurement of benthonic foraminifera alone does not exclude the possibility of bottom water formation locally within the Pliocene Mediterranean, the measurements on both the benthonic and planktonic foraminifera can be more easily understood in terms of entry of water into the Mediterranean from the Atlantic over a sill at Gibraltar of appreciable depth and width.

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