

## 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
		UM dolomitic limestone	Calcite	0.5	-0.4
	121-21-1	UM dense dolomite	Dolomite (Ca <sub>53</sub> )	1.6	-10.2
Levantine Basin	129-2-1	UM Sucrose dolomite	Dolomite (Ca <sub>53</sub> )	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 ( $\sim 25^\circ \text{C}$ ), 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.

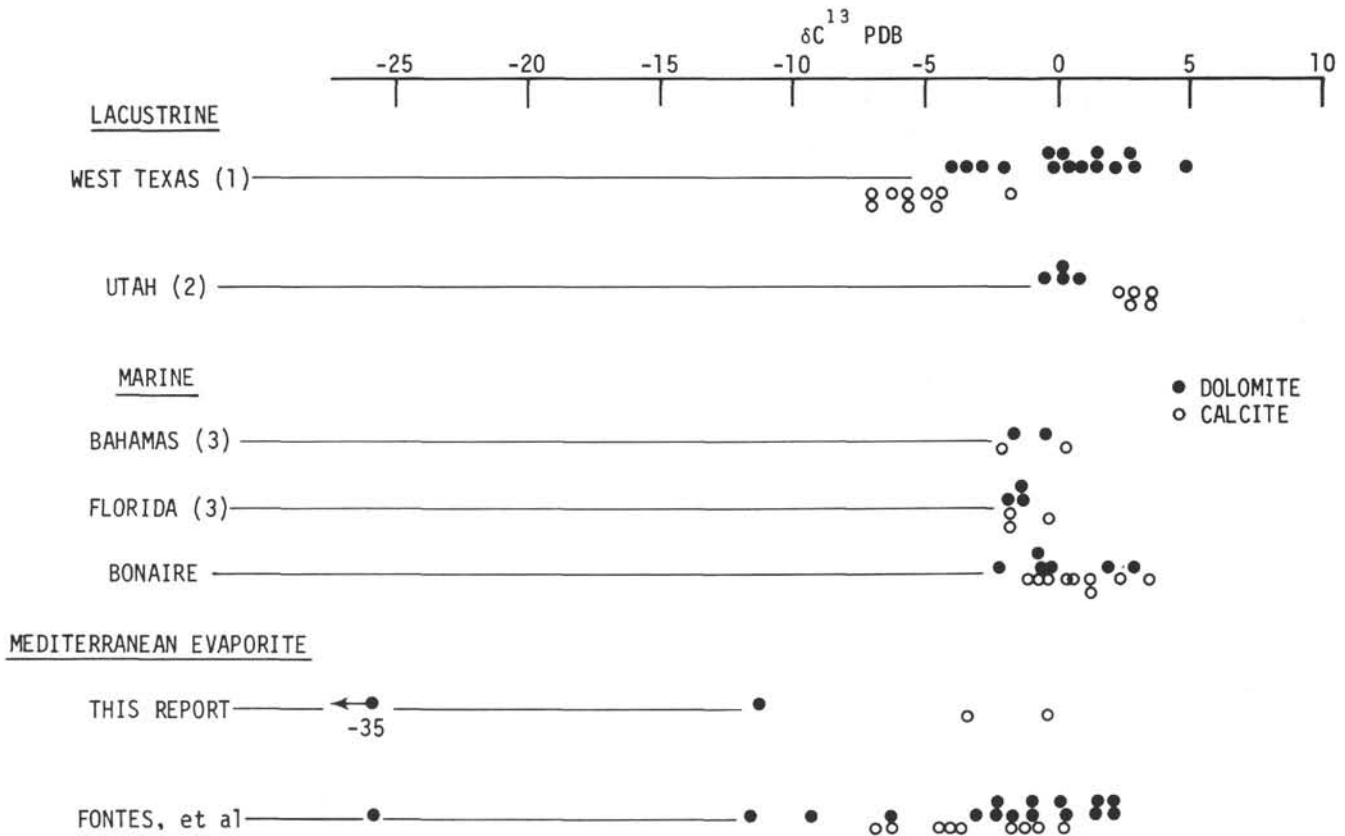


Figure 1. Oxygen isotope data for dolomite and calcite from lacustrine, marine, and Mediterranean evaporite samples. Data from the literature: (1) Parry, et al. (1970); (2) and (3) Degens and Epstein (1964); Fontes, et al. (this volume).

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  $CO_2$  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  $C_{13}$  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  $C_{13}$  values (-8.8 to -43). These limestones are also believed to have derived their carbonate primarily from oxidized methane enriched in  $C_{12}$  (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  $\delta O^{18}$  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  $10^\circ C$ . However, partial evaporation of the Mediterranean water may be partly responsible for the positive  $\delta O^{18}$  values. The present-day waters in the Mediterranean have a  $\delta O^{18}$  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  $15^\circ C$ . 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  $6^\circ C$ ). 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 dessicated Mediterranean basins.

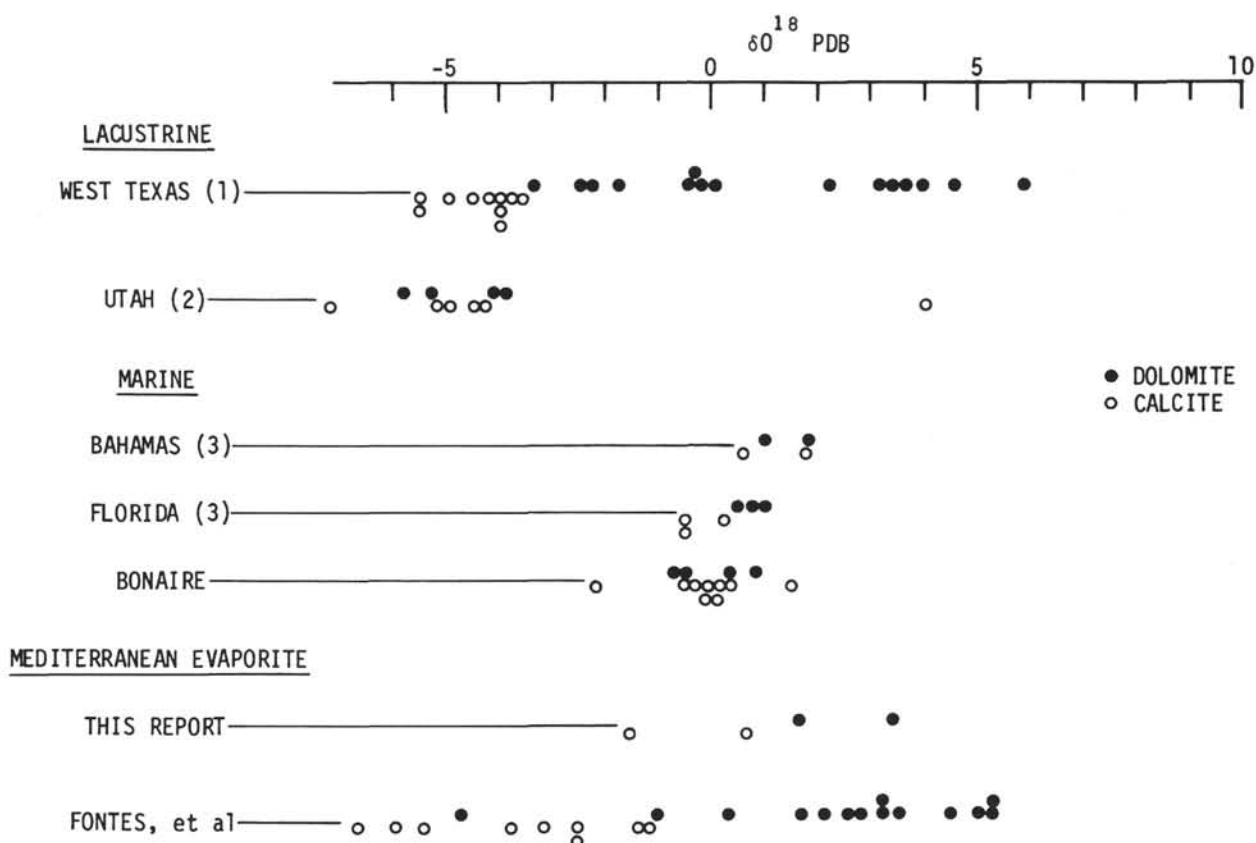


Figure 2. Carbon isotope data for dolomite and calcite from lacustrine, marine, and Mediterranean evaporite samples. Data from the literature: (1) Parry et al. (1970); (2) and (3) Degens and Epstein (1964); Fontes et al. (this volume).

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.

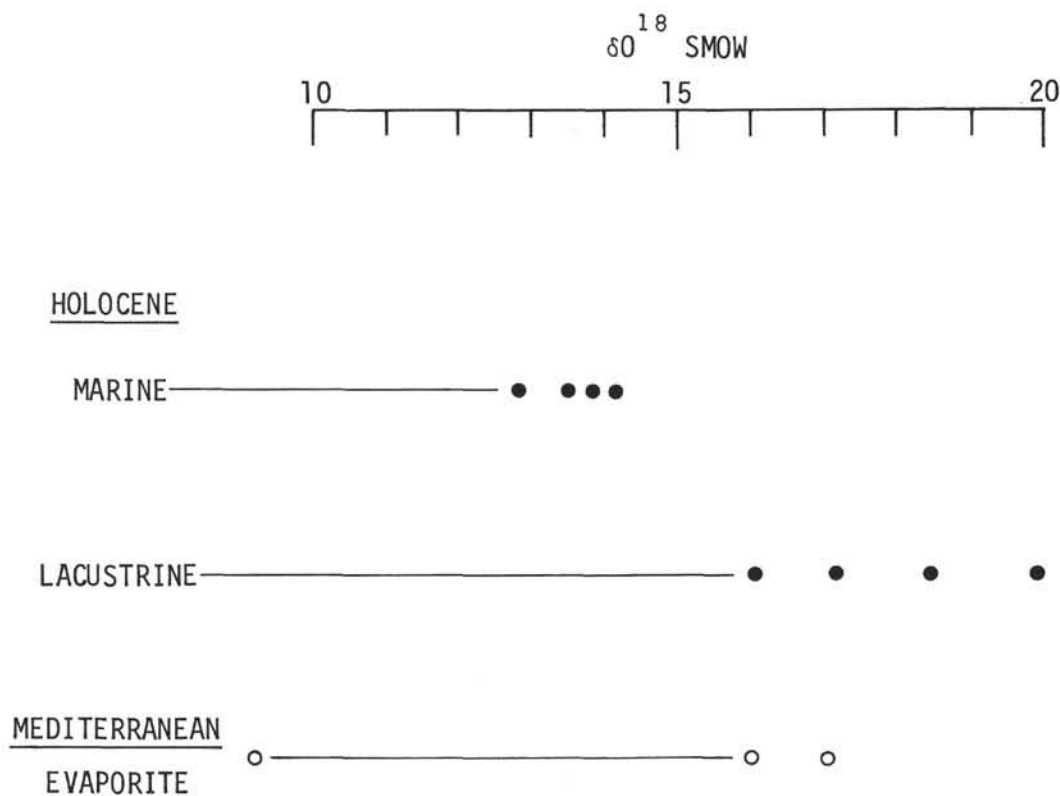


Figure 3. Oxygen isotope data for oxygen in sulfates. Marine data from Lloyd (1967). Lacustrine data from Playa deposits West Texas and New Mexico.

### 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 support 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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