

26. ISOTOPE STUDIES

26.1. ISOTOPE COMPOSITION OF MESSINIAN SEDIMENTS FROM THE MEDITERRANEAN SEA AS INDICATORS OF PALEOENVIRONMENTS AND DIAGENESIS

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ABSTRACT

Selected samples of Messinian sediments from four Leg 42A sites (Site 372 in the western Mediterranean; Sites 374, 375, and 376 in the eastern Mediterranean) were analyzed for their isotope content. Analyses were performed on carbonates (calcite, dolomite, and magnesite) for ^{18}O and ^{13}C , on sulfates (gypsum and anhydrite) for ^{18}O and ^{34}S , and on the crystallization water of the gypsums for ^{18}O and ^2H .

The large fluctuations of the isotopic contents of carbonates and sulfates correspond to significant changes in the sedimentary environment as follows:

- 1) Change from normal marine salinity to hypersaline condition.
- 2) Occasional influxes of large masses of continental waters and influence of groundwater circulation.
- 3) Variations of the redox potential which reflect changes in the hydraulic regime in the basin.

These are general conditions that pertain to all the sites studied, although specific environmental conditions, as a result of local physiographic features, were noted for each site. The concept that a unique basin existed during the Messinian must be abandoned in favor of a system of minor basins which were partially and intermittently connected allowing sporadic influxes of surficial, underground, and Atlantic waters.

INTRODUCTION

The following scheme for Messinian geographic reconstruction was developed from isotopic and mineralogical study of samples from the Leg 13 (three sites in the eastern Mediterranean and one site in the western Mediterranean): Salinities were normal marine to highly saline; influxes of continental waters were enough to influence the isotopic contents; and redox potentials have fluctuated markedly from highly reducing to oxidizing environments. These observations are now compared with Leg 42A from one site in the western Mediterranean and three sites in the eastern Mediterranean, and these allow us to expand the hypothesis.

GENERAL RESULTS

The samples are subdivided and discussed on the basis of the isotopic and mineralogical data.

Site 372 (Figure 1 and Table 1)

Cores 10, 9

Carbonates

Calcites: The ^{18}O content of the calcites ($-1.0 < \delta^{18}\text{O}/\text{PDB} < +1.5$) is compatible with a marine origin

for these cores with a slight decrease in temperature or increase in salinity during deposition. A large break in $\delta^{13}\text{C}$ values (from -0.4‰ to $-7.8\text{‰}/\text{PDB}$) occurs between Samples 372-9-2, 69-71 cm, and 372-9-2, 20-24 cm. This strong decrease in ^{13}C represents a marked change in redox and hence a change of hydraulic conditions in the basin. The turnover rate of the bottom waters became low compared with the rate of decay of the organic matter. CO_2 came mainly from the decaying organic matter.

Dolomites: A mixture of two kinds of dolomites (stoichiometric and calcium-rich) was found in variable amounts in the sediments analyzed. The stoichiometric dolomite is dominant. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of these dolomites are similar to those reported for the Jurassic dolomites of the Balearic Islands (Fontes and Desforges, 1975). We consider that the stoichiometric dolomites are of detrital origin.

Cores 6, 5, 4

Carbonates

Calcites: The calcites have a large range of isotopic content. This indicates that at the end of the low redox episode there were large variations in the amount of evaporation relative to water supply. The low ^{18}O

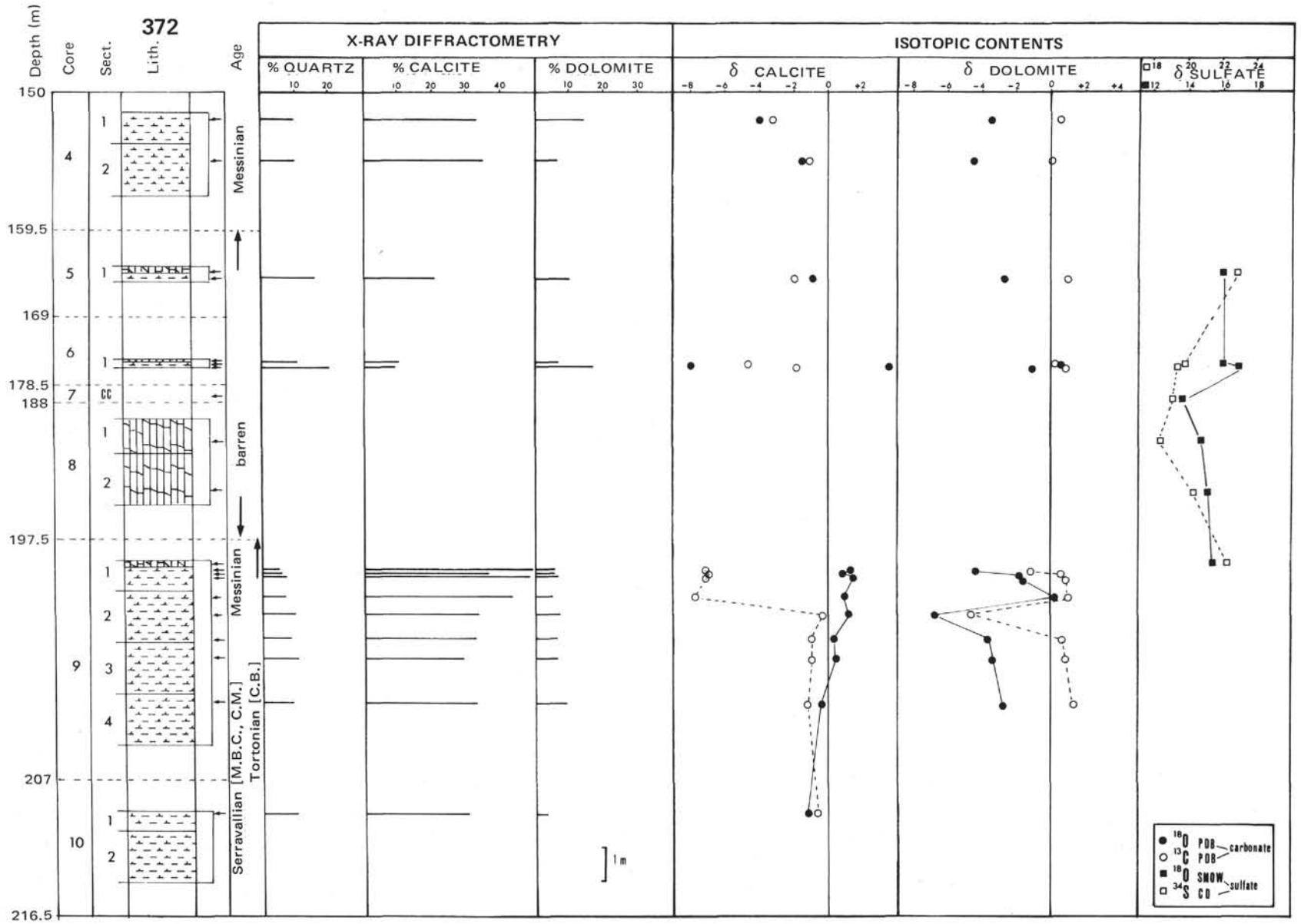


Figure 1.

TABLE 1
 X-Ray Diffractometry and Isotopic Contents, Site 372

Sample (Interval in cm)	X-Ray Diffractometry								Isotopic Contents							
									δ Calcite		δ Dolomite		δ m.w.		δ Sulfate	
	Qz	Ca	Do	Gy	An	Ha	Misc.	% Ca in Dolomite	^{18}O	^{13}C	^{18}O	^{13}C	^{18}O	^2H	^{18}O	^{34}S
4-1, 79-81	10	33	14	0	0	1		Ca ₅₅	-4.0	-3.2	-3.5	+0.6				
4-2, 50-52	10	35	6	1	0	1			-1.5	-1.2	-4.4	+0.1				
5-1, 123-125	0	0	0	100	0	0									+16.1	+22.8
5-1, 137-139	16	21	10	2	0	1			-0.8	-2.0	-2.6	+1.0				
6-1, 125-128	0	0	0	100	0	0									+16.0	+19.7
6-1, 135-137	11	10	6	++	0	1		Ca ₅₂	-8.0	-4.6	+1.4	+0.5			+17.1	+19.5
6-1, 145-147	20	9	17	0	0	1			+3.7	-1.8	-1.1	+0.8				
7, CC	0	0	0	100	0	0							-0.08	+15.0	+13.6	+19.0
8-1, 116-122	0	0	0	100	0	0							+0.60	+20.9	+14.8	+18.4
8-2, 109-112	0	0	0	100	0	0									+15.1	+20.2
9-1, 71-73	0	0	0	100	0	0									+15.4	+22.3
9-1, 84-86	5	51	4	2	0	1		Ca ₅₀	+1.3	-7.2	-4.4	-1.2				
9-1, 99-104	6	36	4	2	0	1			+0.9	-7.0	-1.9	+0.6				
9-1, 112-113	7	49	6	2	0	1		Ca ₅₀ and Ca rich	+1.5	-7.2	-1.7	+0.8				
9-2, 20-24	7	43	5	2	0	1		Ca ₅₀ and Ca rich	+1.1	-7.8	+0.3	+1.0				
9-2, 69-71	10	34	7	0	0	1		Ca ₅₀ and Ca rich	+1.2	-0.4	-6.7	-4.7				
9-2, 143-145	8	33	5	2	0	1		Ca ₅₀ and Ca rich	+0.4	-1.0	-3.8	+0.7				
9-3, 46-48	10	29	5	0	0	1		Ca ₅₀ and Ca rich	+0.5	-1.0	-3.4	+0.8				
9-4, 23-28	9	33	9	0	0	1		Ca ₅₀ and Ca rich	-0.3	-1.3	-2.8	+1.4				
10-1, 100-102	9	30	3	0	0	1			-1.0	-0.6						
11-1, 100-102	10	26	2	0	0	1			-1.8	-0.6						
12-4, 138-147	7	35	0	0	0	1			+0.2	-0.5						

Note: Qz = quartz; Ca = calcite; Do = dolomite; Gy = gypsum; An = anhydrite; Ha = halite; Misc = miscellaneous. δ values of calcites and dolomites are expressed versus P.D.B.; the $\delta^{18}\text{O}$ values for dolomites and magnesites have been corrected for isotopic fractionation effect as given by Sharma and Clayton (1965). $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of the mother waters (m.w.) of the gypsums and of the interstitial water are expressed versus SMOW. $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ of the sulfates are presently expressed versus SMOW and CD.

content of the calcite indicates large influxes of continental waters were poured into the basin.

Dolomites: The dolomites are mainly calcium-rich and therefore are considered to be authigenic. The large isotopic variations ($-4.4 < \delta^{18}\text{O}/\text{PDB} < +1.4$) are probably caused by differences in the isotopic composition of the water as the result of varying amounts of evaporation with respect to the input of continental waters. During episodes of dolomitization, the dissolution of CO_2 was controlled by the atmospheric reservoir ($+0.1 < \delta^{13}\text{C}/\text{PDB} < +1.0$).

Sulfates: (gypsum)

The fluctuations of $\delta^{18}\text{O}$ ($+13.6\text{‰}$ to $+17.1\text{‰}$ /SMOW) and $\delta^{34}\text{S}$ ($+18.4\text{‰}$ to $+22.8\text{‰}$ /CD) are related to variations of the redox potential. Several stages of sulfate reduction are followed by partial reoxidization of the sulfide in waters subjected to evaporation (^{18}O enriched with respect to normal marine sulfate). The observed variations of sulfur and oxygen isotope contents in the sulfates are in good agreement with the concept of rapid changes of the hydraulic conditions in the basin.

Site 374 (Figure 2 and Table 2)

Cores 22 to 16

Carbonates

In this interval, which contains little quartz, the carbonates are authigenic dolomites ($\text{Ca}_{51,5}$ to $\text{Ca}_{54,5}$) and magnesite.

Dolomites: The $\delta^{18}\text{O}$ values ($-0.5 < \delta^{18}\text{O}/\text{PDB} < +4.4$) indicate variations in the amount of water evaporated with respect to the amount of water supply. The ^{13}C content indicates a low redox environment ($-8.7 < \delta^{13}\text{C}/\text{PDB} < -4.3$).

Magnesites: The magnesium carbonate generally occurs in the hypermagnesian solutions associated with evaporites at the margins of continental and marine environments (Kinsman, 1966). The variations in the ^{18}O content of the magnesites indicate a highly evaporitic ($+2.9 < \delta^{18}\text{O}/\text{PDB} < +5.4$) to continental environment ($+0.3 < \delta^{18}\text{O}/\text{PDB} < +0.8$). The low values of $\delta^{13}\text{C}$ ($-9.8 < \delta^{13}\text{C}/\text{PDB} < -6.8$) are related to a secondary contribution of biogenic CO_2 which probably came from a partial reduction of the sulfate. At least a part of the magnesite could have been produced

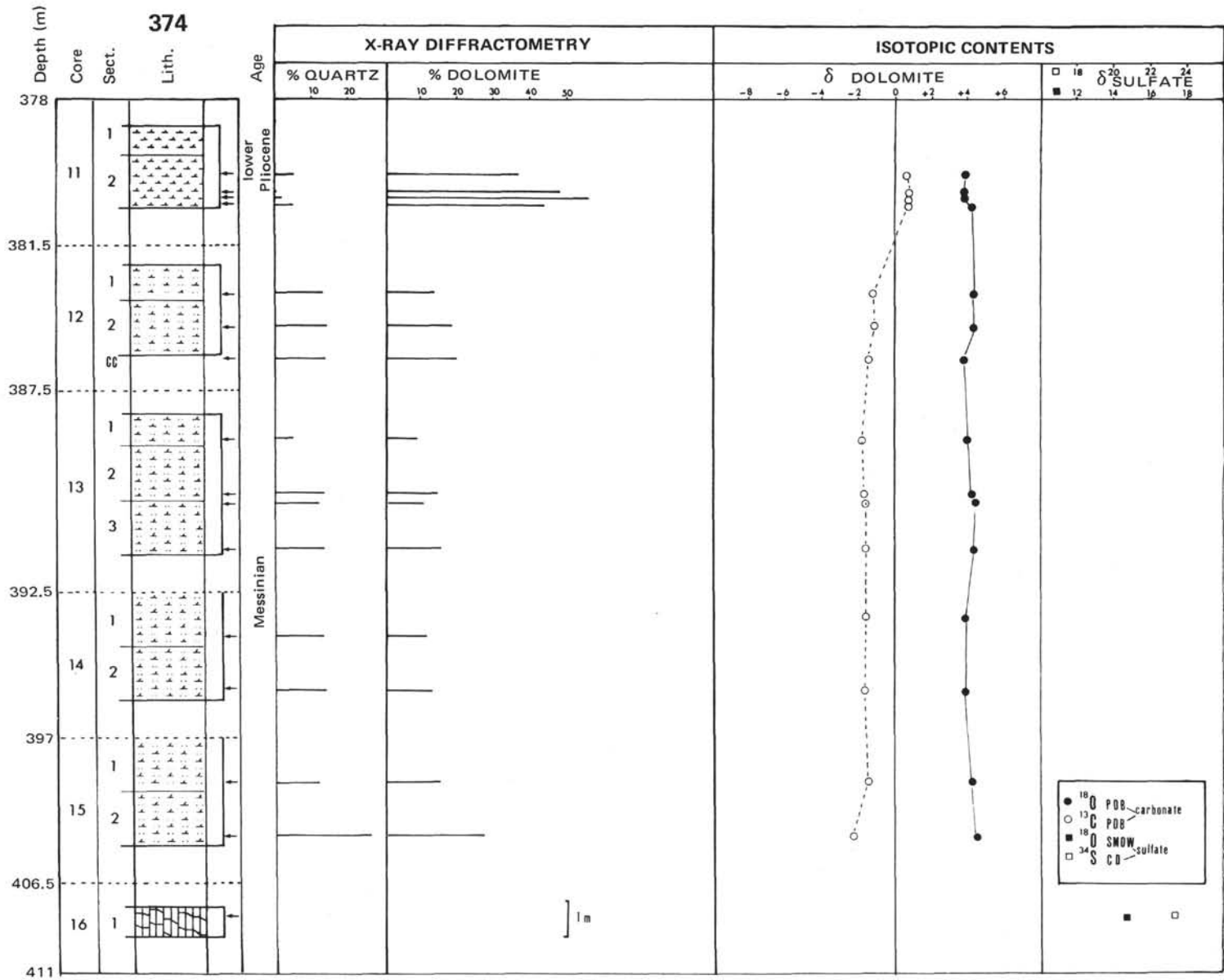


Figure 2.

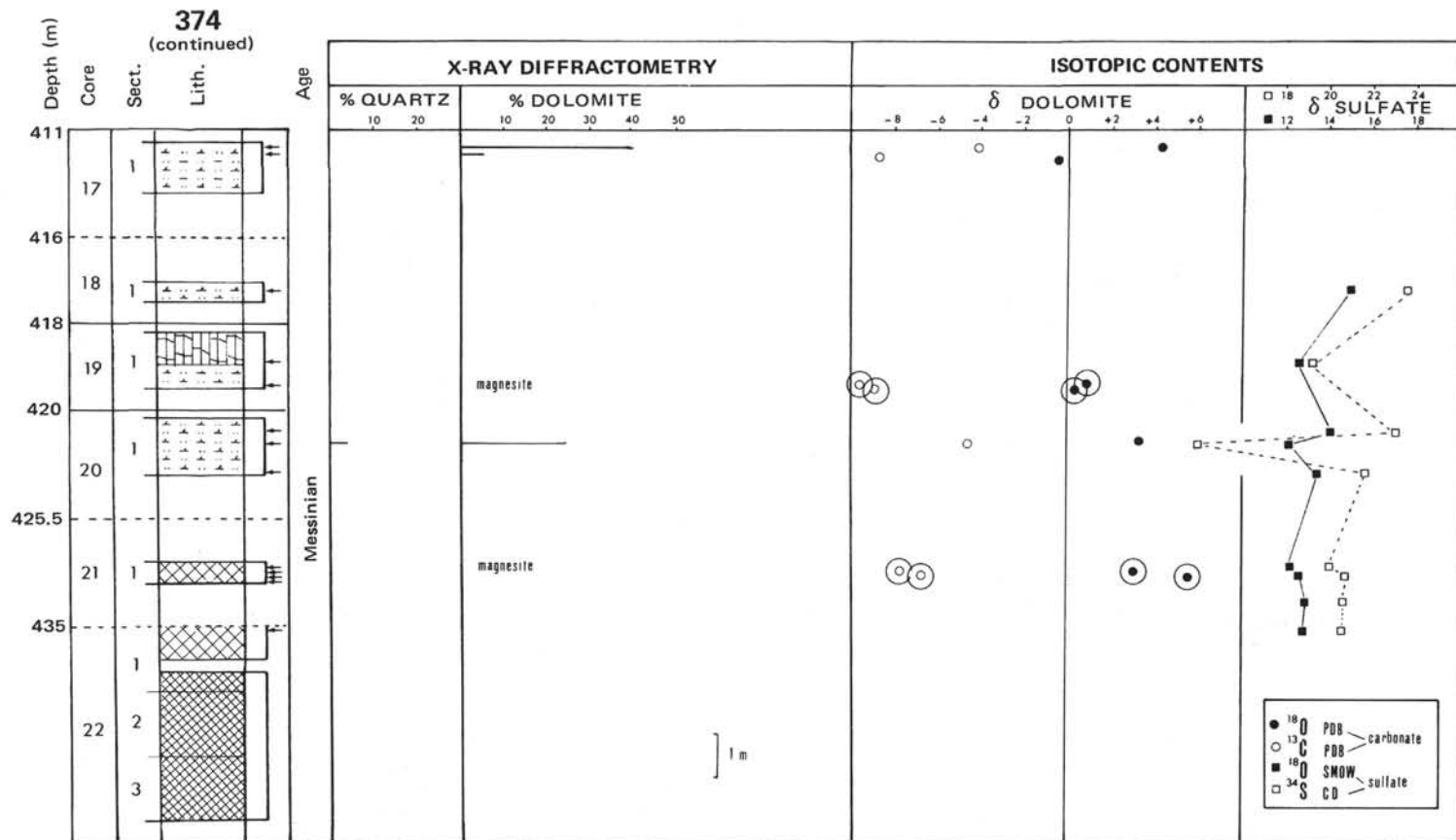


Figure 2. (Continued).

TABLE 2
X-Ray Diffractometry and Isotopic Contents, Site 374

Sample (Interval in cm)	X-Ray Diffractometry								Isotopic Contents							
	Qz	Ca	Do	Gy	An	Ha	Misc.	% Ca in Dolo- mite	δ Calcite		δ Dolomite		δ m.w.		δ Sulfate	
									¹⁸ O	¹³ C	¹⁸ O	¹³ C	¹⁸ O	² H	¹⁸ O	³⁴ S
11-2, 52-54	5	0	37	0	0	2.5		Ca _{54.5}		+3.9	+0.6					
11-2, 104-106	1	0	48	0	0	4.4		Ca ₅₅		+3.9	+0.7					
11-2, 116-119	2	0	56	0	0	5		Ca ₅₅		+3.9	+0.7					
11-2, 138-141	5	0	45	0	0	4		Ca ₅₅		+4.3	+0.7					
12-1, 132-134	13	0	14	0	0	4.4		Ca _{54.5}		+4.4	-1.1					
12-2, 70-73	14	0	18	0	0	5.6		Ca ₅₅		+4.3	-1.1					
12, CC	14	0	20	T	0	4.7		Ca _{54.5}		+3.8	-1.4					
13-1, 135-137	5	0	9	0	0	1.8	pyrite	Ca _{54.5}		+4.1	-1.8		(pyrite)			-44
13-2, 130-132	13	0	14	0	0	4.3		Ca ₅₄		+4.2	-1.7					
13-3, 0-10	13	0	11	0	0	2.5		Ca _{53.5}		+4.4	-1.6					
13-3, 130-132	13	0	15	0	0	4.9		Ca _{53.5}		+4.4	-1.6					
14-1, 122-124	13	0	11	0	0	4.6		Ca _{52.5}		+3.8	-1.6					
14-2, 113-115	14	0	13	0	0	4.6		Ca ₅₂		+3.9	-1.7					
15-1, 121-123	12	0	15	0	0	4.8		Ca _{51.5}		+4.3	-1.5					
15-2, 119-121	26	0	27	0	0	4.8		Ca ₅₃		+4.5	-2.3					
16-1, 87-91	0	0	0	100	0	0						-0.41	+13.8	+14.7	+23.3	
17-1, 37-47	1	0	40	2	0	1		Ca _{54.5}		+4.4	-4.3					
17-1, 60-62	1	0	5	+++	0	12		Ca _{52.5}		-0.5	-8.7					
18-1, 122-124	0	0	0	100	0	0									+15.1	+23.5
19-1, 92-96	0	0	0	100	0	0						+0.06	+16.8	+12.7	+19.3	
19-1, 144-145																
black laminae	3	0	0	++	0	10	magnesite			+0.8	-9.8					
white laminae	0	0	0	++	+	3.6	magnesite			+0.3	-8.9					
20-1, 42-48	0	0	0	100	0	0						+0.34	+14.9	+14	+23.1	
20-1, 73-75	4	0	25	++	0	1.7		Ca _{51.5}		+3.1	-4.6				+12.2	+14.1
20-1, 143-146	0	0	0	0	100	0									+13.2	+21.6
21-1, 118-120	0	0	0	0	100	0									+12.2	+20.1
21-1, 122-124	0	0	0	0	+++	2	magnesite			+2.9	-7.9					
21-1, 126-131	0	0	0	0	+++	7	magnesite			+5.4	-6.8				+12.5	+20.7
21-1, 146-147	0	0	0	0	100	0									+12.8	+20.6
22-1, 2-7	0	0	0	0	100	0									+12.7	+20.5

Note: See Table 1 for explanation.

from the reaction of CO₂ released by the reduction of the sulfates in a magnesian solution.

Sulfates: (anhydrite and gypsum)

The ¹⁸O and ³⁴S contents are slightly enriched from the base to the top of the sulfate sequence which indicates an increasing amount of reduction. Two levels are marked by a large contribution of sulfates which came from the oxidation of sulfide (δ³⁴S = +14.1‰ and +19.3‰/CD). This suggests that the gypsum precipitation continued while the redox condition changed from a reducing to an oxidizing environment.

Cores 15 to 12

Carbonates

These cores are all dolomitic marls and the Ca content of the dolomites increases from Ca_{51.5} at the base to Ca₅₅ at the top. The δ¹⁸O values are rather constant along the profile (+3.8 < δ¹⁸O/PDB < +4.5), whereas the δ¹³C values increase from the base (δ¹³C/PDB = -2.3) to the top (δ¹³C/PDB = -1.1). Such values are consistent with an evaporitic and possibly slightly reducing environment. Pyrite derived from sulfate reduction (δ³⁴S = -44‰/CD) occurs in Sample 374-13-1, 135-137 cm, and indicates that very

low redox episodes have taken place during the diagenesis.

Core 11 (Section 2)

The samples studied are dolostones whose dolomites are calcium rich (Ca₅₅). Mean values of δ¹⁸O and δ¹³C (δ¹⁸O = +4‰/PDB, δ¹³C = +0.7‰/PDB) indicate they were formed in an environment which is in (or close to) equilibrium with the atmosphere. The hydraulic conditions changed from a reducing environment to one with well-mixed waters. The sediment succession here is very similar to that of Site 125A of Leg 13 where the indurated zone (125A-6-1, 130-135 cm) was also very rich in ¹⁸O (Pierre, 1974).

In both these areas we can attempt to calculate the temperature and ¹⁸O content at time of crystallization¹

¹ At sedimentary temperatures, carbon isotopic fractionation during calcite precipitation is accounted for by:

$$t^{\circ}\text{C} = 147.7 - 14.81(\delta - \delta_{\text{CO}_2}) + 0.266(\delta - \delta_{\text{CO}_2})^2$$

in which the temperature is related to the enrichment between gaseous CO₂ and solid carbonate. Assuming a value for δ_{CO₂}, one calculates the isotopic temperature and thus solves the oxygen isotope paleotemperature equation for δ_{H₂O}:

$$t^{\circ}\text{C} = 16.9 - 4.2(\delta - \delta_{\text{H}_2\text{O}}) + 0.13(\delta - \delta_{\text{H}_2\text{O}})^2$$

by assuming isotopic equilibrium with the atmosphere. Calculations according to the equations of Fontes et al. (1973), using the value of $\delta^{13}\text{C} = -8.5\text{‰}$ for the gaseous CO_2 which controls the equilibria of the dissolved carbon (Fontes and Pouchan, 1975) give:

	Site 125A (Leg 13)	Site 374 (Leg 42A)
t °C	31°	34°
$\delta^{18}\text{O}_{(\text{H}_2\text{O})}$	+8.5‰/SMOW	+7.7‰/SMOW

This hypothetical treatment should be checked by analysis of trace elements in the carbonates.

Site 375 (Figure 3 and Table 3)

Core 4 (Tortonian)

Carbonates

Calcites: The calcite is depleted in heavy isotopes ($\delta^{18}\text{O} = -5.5\text{‰}/\text{PDB}$, $\delta^{13}\text{C} = -5.1\text{‰}/\text{PDB}$) and probably was deposited as a detrital intercalation in a normal marine sequence ($\delta^{18}\text{O} = -1.3\text{‰}/\text{PDB}$, $\delta^{13}\text{C} = -1.2\text{‰}/\text{PDB}$).

Dolomites: The detrital dolomite occurs with the detrital calcite. The authigenic dolomite (Ca_{57}), however, was not formed in the same environment as the associated calcite (strongly different $\delta^{13}\text{C}$ values). The authigenic dolomite was probably formed as a result of diagenesis of marine calcite in waters evaporated and isolated from the atmosphere ($\delta^{13}\text{C} = -27.9\text{‰}/\text{PDB}$ indicates that the CO_2 is exclusively of organic origin). Two hypotheses are proposed: (1) large variations of salinity and redox conditions occurred throughout the whole system; (2) brines were concentrated on the margin of the basin which moved inward and downward beneath the normal marine waters. In both cases, the bottom of the basin would be anoxic.

Cores 1 and 2

Carbonates

The δ values of the calcite and dolomite are similar to those of the Tortonian. Between the evaporitic episodes, normal marine waters entered the basin. Detrital components could have formed interbeds in the normal marine sediments.

Sulfates (gypsum)

The $\delta^{18}\text{O}$ values of the gypsums at the base (Core 2, Section 4) are 1.5 to 2‰ lower than those at the top of the unit. The $\delta^{34}\text{S}$ values showed a similar variation. The difference in $\delta^{18}\text{O}$ can be interpreted as a change of the $\delta^{18}\text{O}$ of the water (increasing evaporation from base to top) if we allow for a mechanism of total reoxidation of reduced sulfur in evaporated waters. In addition to this effect, the sulfate reduction continued which accounts for the similar variations of the $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ contents.

Site 376 (Figure 4 and Table 4)

Cores 20 to 16 (16-1, 101-104 cm)

Sulfates (gypsum)

The sulfates at the base of the selenitic layers have normal marine ^{18}O and ^{34}S contents. Moving upward, successive changes in the ^{18}O and ^{34}S contents are related to complex processes which include successive partial reduction and reoxidation of the sulfide in the waters subjected to evaporation (high $\delta^{18}\text{O}$ values).

Samples 16-1, 68-70 cm to 7-1, 48-49 cm

Carbonates

Calcites: The ^{18}O and ^{13}C contents show that significant changes occurred in the depositional environments which ranged from a normal marine (δ close to zero) to one diluted by influx of continental water (δ negative). Thin sections show the occurrence of calcite of dedolomitization in the levels corresponding to the lowest δ values (376-15-1, 108-110 cm; 376-7-2, 85-87 cm; 376-7-1, 95-97 cm; 376-7-1, 48-49 cm). The presence of this calcisparite indicates that the recrystallization of the carbonate took place in the vadose zone.

Dolomites: Dolomite occurs as detrital (Ca_{50}), authigenic (Ca_{55}), or mixed species dolomites. The difference is isotopically well marked with negative $\delta^{18}\text{O}$ values for detrital dolomites, highly positive $\delta^{18}\text{O}$ values for authigenic dolomites, and intermediate $\delta^{18}\text{O}$ values for a mixing of the two dolomites.

Samples 7-1, 42-43 cm and 6-4, 20-23 cm:

Carbonates

Calcites: The ^{18}O and ^{13}C contents of these calcites mark the end of continental influences and the return to a normal marine environment.

Dolomite: The Ca-rich dolomites (Ca_{55}) may be associated with calcites in mineralogical pairs with an ^{18}O enrichment in the range +2.5 to +4.4‰ for the dolomite. These values are in good agreement with data previously published (Clayton and Epstein, 1958; Engel et al., 1958; Weber, 1964, 1965; Northrop and Clayton, 1966; O'Neil and Epstein, 1966; Clayton et al., 1968; Fontes et al., 1967, 1969, 1970; Fritz and Smith, 1970).

PALEOENVIRONMENTAL INTERPRETATION

Oxygen 18 and Carbon 13 in Carbonates

Figure 5 summarized the conclusions reached from the study of each site.

The evidence for mixing of continental and marine waters is seen in both the ^{13}C and ^{18}O content in the calcites. Evidence for the same kind of mixing can also be seen in the dolomites, but generally, the relatively low ^{13}C content indicates an equilibrium with atmospheric CO_2 (except at Sites 374 and 376 where it corresponds to more reduced conditions). Some low ^{13}C contents associated with low ^{18}O values indicate reworked detrital dolomites. The high ^{18}O content of

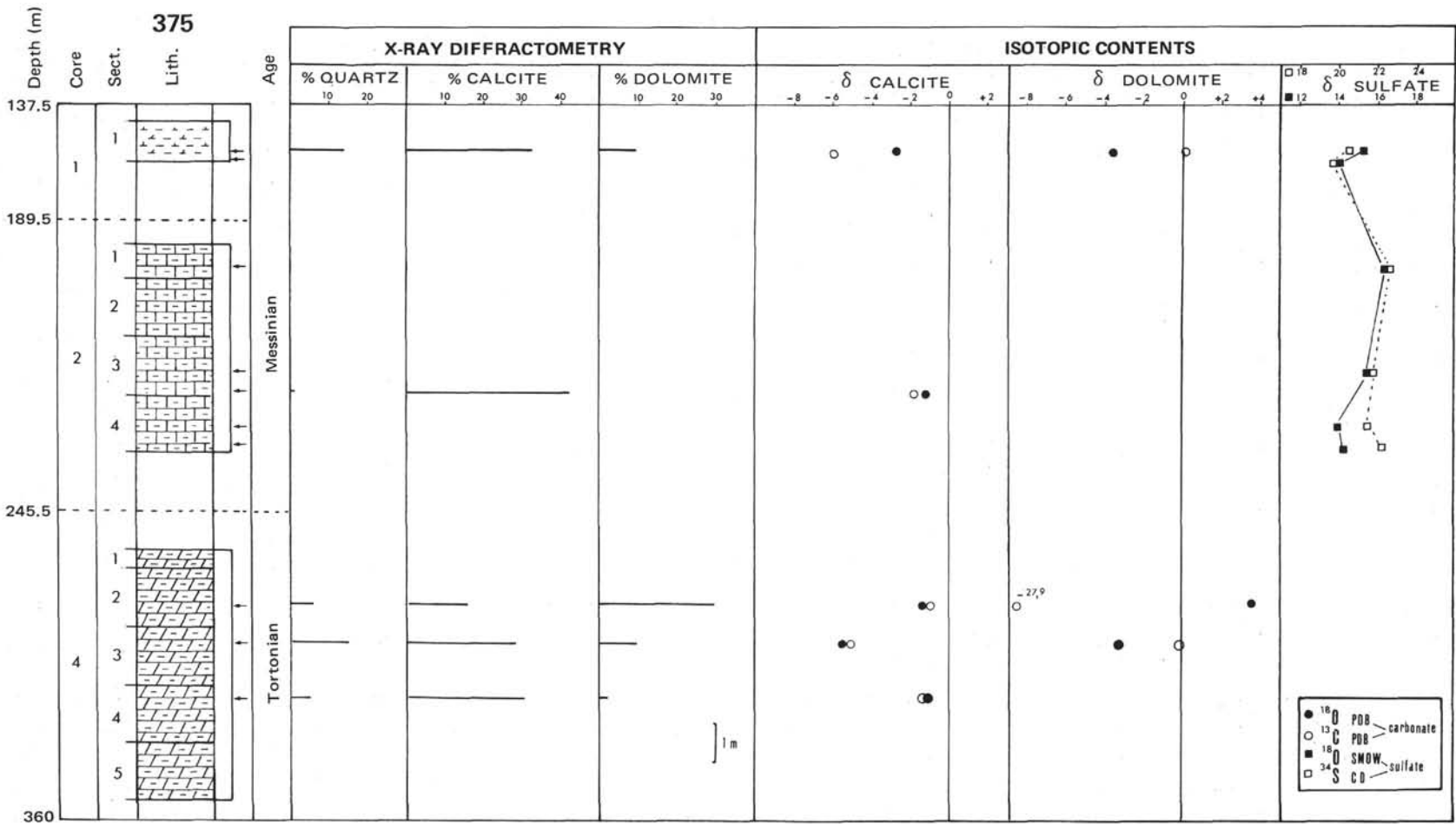


Figure 3.

TABLE 3
X-Ray Diffractometry and Isotopic Contents, Site 375

Sample (Interval in cm)	X-Ray Diffractometry								Isotopic Contents										
									δ Calcite		δ Dolomite		δ m.w.		δ Sulfate				
	^{18}O	^{13}C	^{18}O	^{13}C	^{18}O	^2H	^{18}O	^{34}S											
1-1, 124-126(A)	17	22	8	0	0	0													
1-1, 124-126(B)	0	0	0	100	0	0													+15.3 +20.6
1-1, 124-126(C)	14	33	9	+	0	T													
1-1, 144-148	0	0	0	100	0	0													
2-1, 119-122	0	0	0	100	0	0								+5.05	+34.3				+13.8 +20.0
2-3, 88-91	0	0	0	100	0	0								+0.2	+4.2				+16.5 +22.6
2-3, 136-139	1	42	0	0	0	0													+15.6 +21.8
2-4, 78-81	0	0	0	100	0	0													
2-4, 120-140	0	0	0	100	0	0													+14.1 +21.6
4-2, 89-92	6	16	30	0	0	0													+14.2 +22.3
4-3, 41-43	15	28	10	T	0	T													
4-4, 37-38	5	30	2	0	0	0.6													

Note: See Table 1 for explanation

TABLE 4
X-Ray Diffractometry and Isotopic Contents, Site 376

Sample (Interval in cm)	X-Ray Diffractometry								Isotopic Contents											
									δ Calcite		δ Dolomite		δ m.w.		δ Sulfate					
	^{18}O	^{13}C	^{18}O	^{13}C	^{18}O	^2H	^{18}O	^{34}S												
6-4, 20-23	1	47	7	0	0	1.4														+0.7 +0.5 +3.2 -0.5
7-1, 42-43	1	46	6	0	0	0.5														-0.2 -0.7 +4.2 -0.1
7-1, 48-49	7	30	17	0	0	0.6														-4.6 -1.9 +4.6 -0.2
7-1, 95-97	11	18	25	0	0	0.7														-4.2 -4.1 +1.8 -1.5
7-2, 85-87	9	18	28	0	0	0.4														-2.7 -7.5 -1.9 -0.7
8-3, 74-76	7	20	14	0	0	0.4														-5.2 -3.1 -0.8 -2.6
9-3, 140-150	7	23	15	0	0	0														-4.7 -4.5 +0.6 -2.7 +0.52 +12.1 (I.W.)
11-2, 114-116	1	54	0	0	0	0.5														+0.1 +0.3
12-1, 115-117	4	31	2	T	0	0														-1.6 -3.3
12-2, 128-130	7	19	2	0	0	0														-2.9 -3.3
12-3, 77-79	4	38	2	0	0	0														-0.5 -2.2
13-2, 73-76	7	35	2	0	0	0.4														-0.9 -0.9
13-4, 99-101	7	20	0	0	0	0.4														-1.8 -1
14, CC	5	23	0	0	0	0.2														-1.3 -0.3
15-1, 108-110	10	20	6	15	0	0.2														-7.1 -7.3 -3.5 -0.5
15-2, 78-80	6	20	3	0	0	0.2														-4.3 -3.8
16-1, 68-70	5	32	2	5	0	0.2														-2.8 -2.9
16-1, 101-104	0	0	0	100	0	0														+1.42 +26 +14.7 +19.7
17-1, 135-137	0	0	0	100	0	0														+15.7 +21.5
18-1, 63-65	0	0	0	100	0	0														+16 +21.9
18-1, 98-100	0	0	0	100	0	0														+14.7 +20.2
18-1, 129-133	0	0	0	100	0	0														+16 +20.4
10-1, 146-150	0	0	0	100	0	0														+1.23 +23.8 +14.6 +24
20-1, 133-136	0	0	0	100	0	0														+11.6 +21.7

Note: See Table 1 for explanation.

the dolomites is related to waters highly concentrated by evaporation.

Oxygen 18 and Sulfur 34 in Sulfates

The ^{34}S content of present-day oceanic sulfate is constant and has undergone little change since the Tertiary ($\delta^{34}\text{S} = +20\text{‰}/\text{CD}$. Ault and Kulp, 1959; Thode et al., 1961; Sasaki, 1972). The $\delta^{18}\text{O}$ value of oceanic sulfate is also constant ($\delta^{18}\text{O} = +9.7\text{‰}/\text{SMOW}$ Lloyd, 1967; Longinelli and Craig, 1967;

Rafter and Mizutani, 1967). This value, however, is not in agreement with the extrapolations at 25°C of the experimental data concerning the fractionation of ^{18}O between SO_4^{2-} and H_2O (Lloyd, 1967). Thus oceanic sulfate does not appear to be in isotopic equilibrium with ocean water.

The isotopic fractionation between dissolved sulfate and solid sulfate is $+1.65\text{‰}$ for ^{34}S (Thode and Monster, 1965) and $+2$ to $+3\text{‰}$ for ^{18}O (Fontes and Schwarcz, unpublished data). Hence, the occurrence of

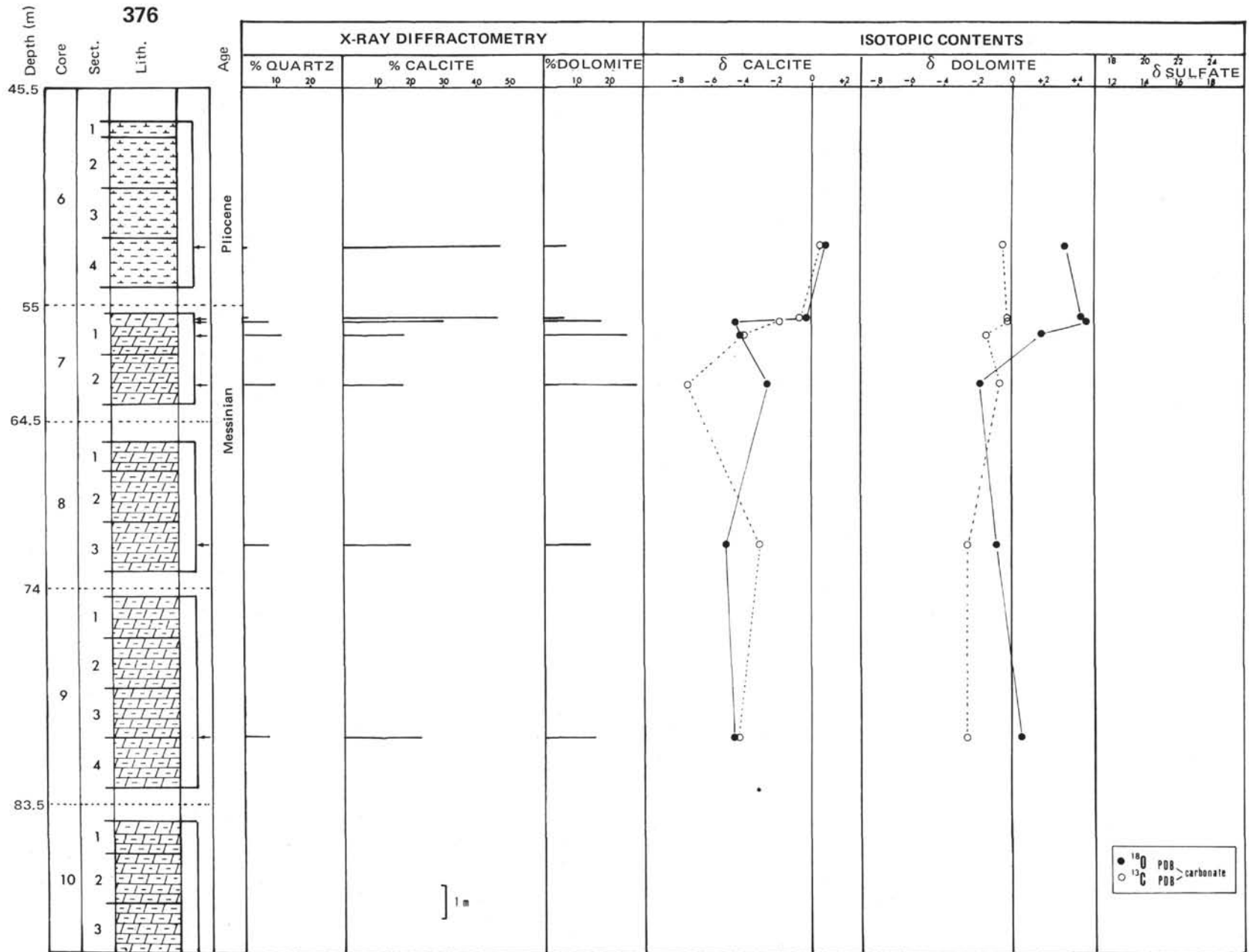


Figure 4.

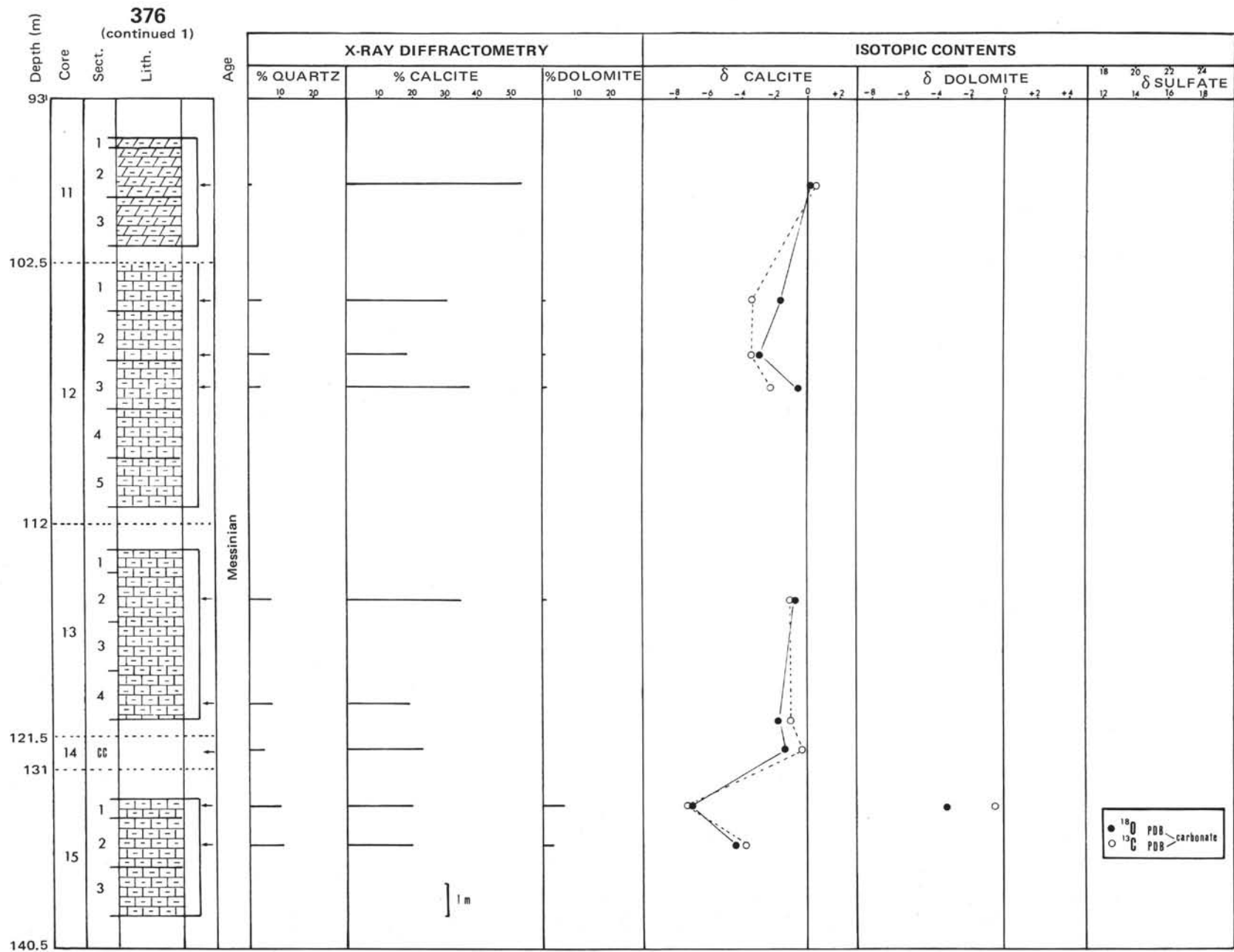


Figure 4. (Continued).

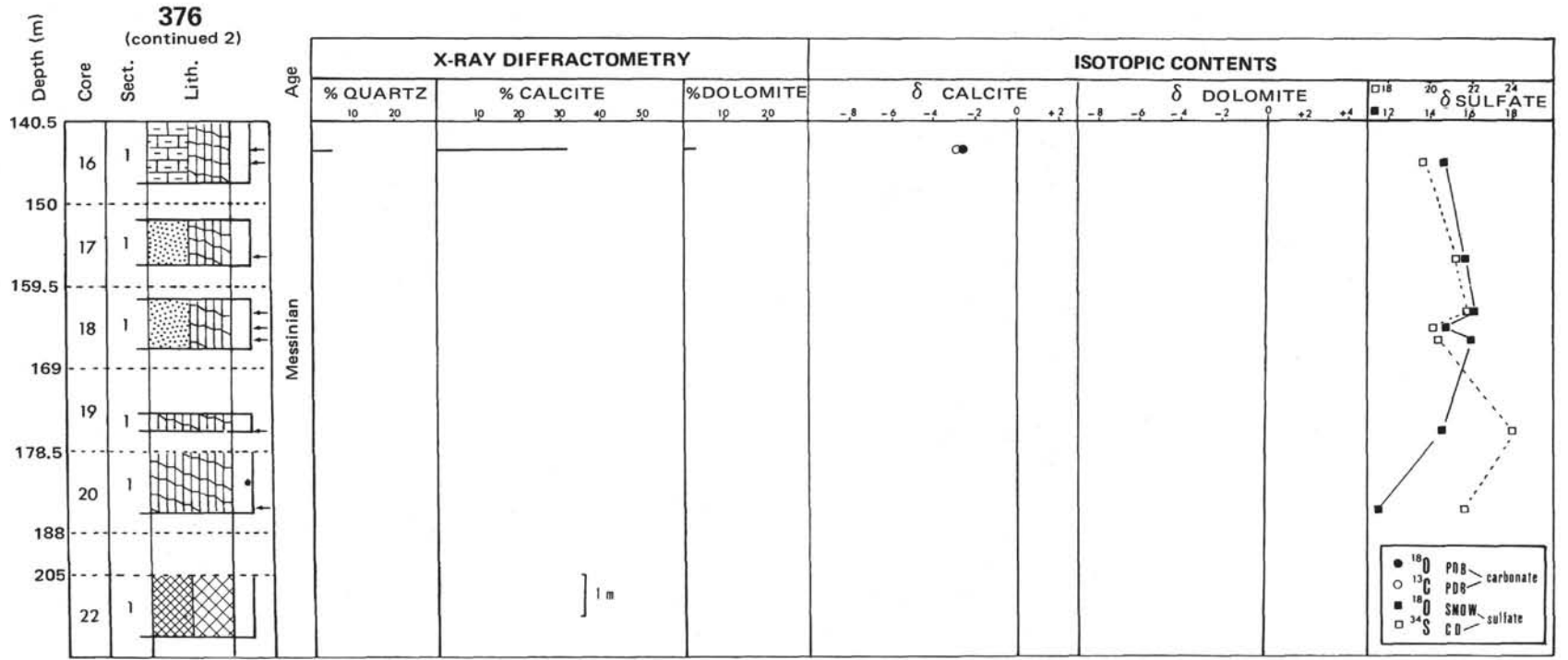


Figure 4. (Continued).

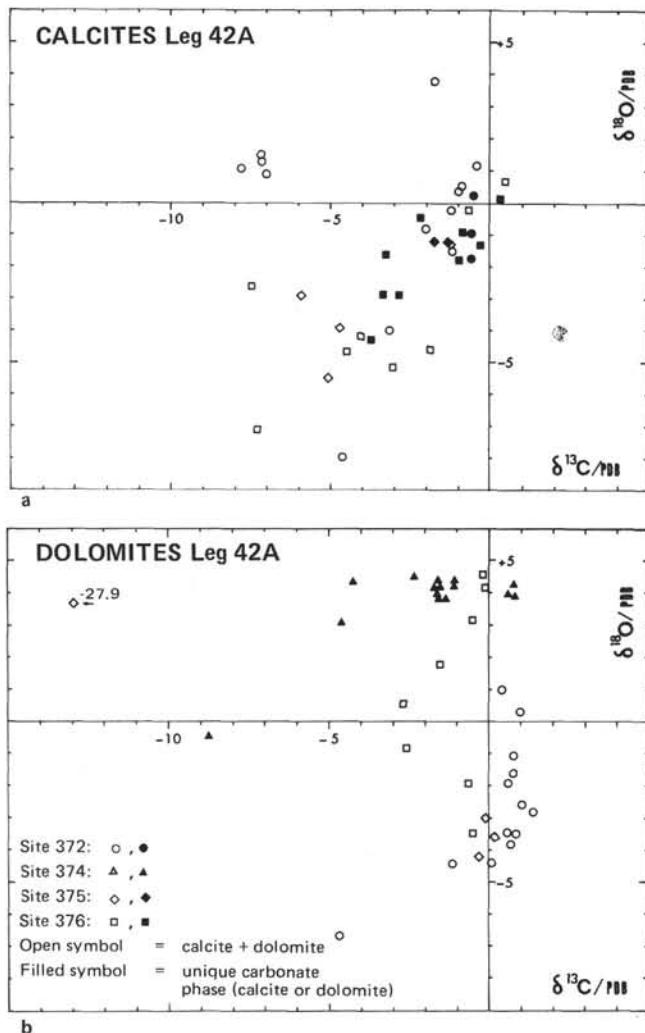


Figure 5. Plot of $\delta^{18}\text{O}$ against $\delta^{13}\text{C}$ of the carbonates of Leg 42A.

successive phases of dissolution and partial crystallization leads to an isotopic enrichment of the solid sulfate. The largest variations in the isotopic content of sulfates are a result of bacterial activity. In sulfate reduction the bacteria preferentially extract the light isotopes; the remaining fraction of sulfate is therefore enriched in heavy isotopes (Nakai and Jensen, 1964; Kemp and Thode, 1968; Mizutani and Rafter, 1969, 1973). The ratio of the ^{34}S and ^{18}O enrichments is close to 4 (Mizutani and Rafter, 1969). However, in a more recent work, Mizutani and Rafter (1973) note variations in this ratio which is mainly related to the kinetics of the bacterial reduction.

In sulfide oxidation 32% of the oxygen is given by air ($\delta^{18}\text{O} = +23.5\text{‰}$; Kroopnick and Craig, 1972) and 68% by water (Lloyd, 1968). The $\delta^{18}\text{O}$ of the resulting sulfate reflects the ^{18}O content of the water in which the oxidation takes place (Rafter and Mizutani, 1967).

The $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of the solid sulfates obtained from Leg 42A (gypsums and anhydrites) vary considerably among the sites sampled.

At Site 374 eight pairs of $\delta^{18}\text{O}$ - $\delta^{34}\text{S}$ values (Figure 6) lie on a straight line with a slope $s = 1.28$. If the correlation is confirmed by further analysis, it could be interpreted as follows: The slope of the correlation line is intermediate between that of a single reduction process ($s' = 4$) and that of a multistage process of crystallization-dissolution in an open system ($s'' = 0.66$).² The latter process leads to the slope of 0.66 *only* in the case of dissolution of solid sulfate by nonsulfate-bearing waters, followed by crystallization in a drained basin, i.e., in a continental environment. Consequently, the resulting sulfate, such as at Site 374, would have a double origin.

At the other sites (372, 375, 376) and for two points in the Site 374 data, no correlation exists because of a variable contribution of secondary sulfate. This sulfate came from reoxidized bacterial sulfide. The reoxidization occurred in a water body enriched in heavy isotopes by evaporation as shown by the high ^{18}O content of the sulfates.

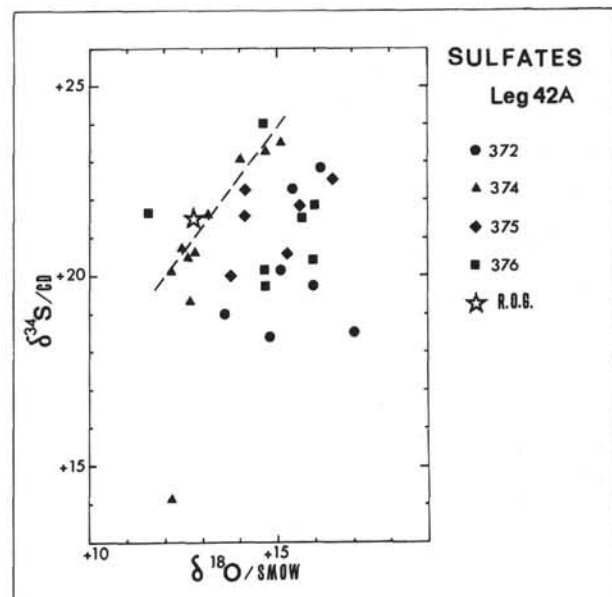


Figure 6. Plot of $\delta^{34}\text{S}$ against $\delta^{18}\text{O}$ in solid sulfates (gypsums and anhydrites) from Sites 372, 374, 375, and 376. R.O.G.: recent oceanic gypsum.

Oxygen 18 and Deuterium in Crystallization Waters of Gypsums and Interstitial Water

Crystallization Waters of Gypsums

Within the range of sedimentary temperatures, the water of crystallization of the gypsum is enriched by about 4‰ in ^{18}O (Gonfiantini and Fontes, 1963) and depleted by about 16‰ in ^2H (Fontes and Gonfiantini, 1967), with respect to the mother water.

² Open system means here that the isotopic content of the solid phase does not depend upon the molar ratio between aqueous and solid sulfate. In the case of gypsum, this implies that in each stage, gypsum precipitation occurs in the same interval of saturation, i.e., with the same ionic strength.

The analyzed gypsum samples show different facies: laminated, saccharoidal (Figure 7) recrystallized, alabaster.

In a diagram $\delta^2\text{H}-\delta^{18}\text{O}$, the mother waters of these gypsums do not indicate a marine origin and generally do not show any tendency to an isotopic enrichment as a result of evaporation. Seven pairs $^2\text{H}-^{18}\text{O}$ lie on a line whose slope is 8 and fall in between the meteoric water line of Craig (1961) and the meteoric water line of the present eastern Mediterranean Basin (Nir, 1967). Two samples from Site 375 are out of the range $^2\text{H}-^{18}\text{O}$ of the previous samples. The points lie on a line whose slope is lower than 8 which corresponds to evaporated precipitations (Craig et al., 1963).

The high heavy isotope contents of these waters are similar to those of present-day tropical and equatorial rain in an oceanic field (Midway and Truk islands in the Pacific Ocean, Diego Garcia Island in the Indian Ocean) and to those of Bahrain in Persian Gulf (I.A.E.A., 1968, 1969).

The isotopic enrichments which occur during evaporation of water and successive condensation are $+1.6\text{‰}$ in ^{18}O and $+21\text{‰}$ in ^2H , if we assume evaporation at 35°C and a condensation at 15°C . The respective enrichments are $+1\text{‰}$ in ^{18}O and $+11\text{‰}$

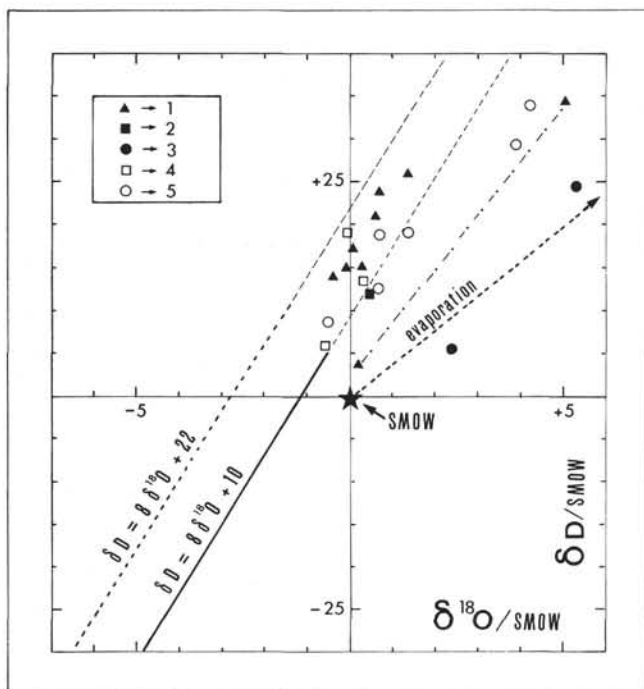


Figure 7. Deuterium versus oxygen 18 contents of waters.

1 = Mother water (i.e., crystallization water corrected for isotopic fractionation according to Fontes and Gonfiantini, 1967, and Gonfiantini and Fontes, 1963) of gypsum from Sites 372, 374, 375, and 376; 2 = Interstitial water from Sample 376-9-3, 140-150; 3 = Mother water of emerged Messinian gypsum from Sicily; 4 = Heavy isotope-rich precipitations from tropical and equatorial oceanic islands (Midway, Truk, Diego Garcia); data from I.A.E.A., 1968-1969; 5 = Rains at Bahrain (Persian Gulf); data from I.A.E.A. 1968-1969.

in ^2H for evaporation at 25°C and condensation at 15°C (Bottinga and Craig, 1969; Merlivat et al., 1963). The first estimation of the temperatures ($t^{\circ}_{\text{evap.}} = 35^\circ\text{C}$, $t^{\circ}_{\text{cond.}} = 15^\circ\text{C}$) is compatible with the $^{18}\text{O}-^2\text{H}$ contents of the mother waters of the analyzed gypsums.

These gypsums are not "primary" gypsums precipitated from solutions concentrated in calcium sulfate by evaporation, but are recrystallized in meteoric waters. Except for samples of Site 375, the recrystallization may have occurred after the gypsum formation, but more probably occurred after anhydrite formation with groundwater preserved from evaporation.

The gypsums of Site 132 (Leg 13) were interpreted as rehydrated anhydrites (Ryan, Hsü, et al., 1973, p. 425; Friedman, 1973, p. 700). The ^{18}O content of the mother waters of four gypsum samples from Site 132 ($-1.7 < \delta^{18}\text{O}/\text{SMOW} < +0.2$) was in agreement with a secondary origin (Pierre, 1974). Such diagenetic mechanisms of hydration of anhydrite and dehydration of gypsum have been described by Shearman (1966), Butler (1969), and Kinsman (1969, 1974) in Persian Gulf sabkhas.

The ^2H and ^{18}O contents of two samples collected in the Messinian sequence which outcrops in Sicily (Erculea section) are given for comparison in Table 5. The mother waters show ^{18}O and ^2H contents consistent with their formation in a marine evaporitic environment.

Interstitial Water

One sample was available from 376-9-3, 140-150 cm. In the diagram (Figure 7) $\delta^2\text{H}-\delta^{18}\text{O}$, the representative point of this interstitial water lies on the general meteoric water line. This is consistent with the low isotope contents obtained for the carbonates (see Site 376 discussion, this paper). This continental water was not evaporated and its residence time in the sediments was long enough to induce recrystallizations in sulfate and carbonate phases. Consequently, its presence must be attributed to existence of a permanent aquifer which was recharged on the margin of the basin. This aquifer was probably present in the sediment even when the basin was momentarily invaded by the sea.

CONCLUSIONS

In general, the isotopic studies show drastic changes in the Messinian water salinities and environments: pure continental water to highly evaporated brines with episodes of incursions of open marine water. Each site, however, had specific depositional environments induced by local physiographic conditions.

Instead of a unique evaporitic basin, we are dealing with an evaporitic system of coalescent units. This system was open to marine transgression and was drained during or after evaporitic episodes. This drainage, evidenced by the variations of the isotope content of the sulfates, led to segregation in the K-Mg hypersaline brines which were collected into the deepest parts of the system. This possible mechanism for formulation of the Messinian evaporites was previously suspected by workers as a result of the isotopic and mineralogical

TABLE 5
 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ Values from Interstitial Water and Mother Waters of Gypsum,
 Leg 42A and Samples from the Eraclea Section of Sicily

	Sample (Interval in cm)	$\delta^{18}\text{O}/\text{SMOW}$	$\delta^2\text{H}/\text{SMOW}$	
Interstitial Water Leg 42A	376-9-3, 140-150	+0.52	+12.1	
Mother waters of gypsum of Leg 42A	372-7, CC	-0.08	+15.0	Alabaster
	372-8-1, 119-121	+0.60	+20.9	Laminated
	374-16-1, 87-91	-0.41	+13.8	Recrystallized
	374-19-1, 92-93	+0.06	+16.8	Laminated
	374-20-1, 42-45	+0.34	+14.9	Recrystallized
	375-1-1, 144-148	+5.05	+34.3	Recrystallized
	375-2-1, 119-122	+0.20	+4.2	Alabaster
	376-16-1, 101-104	+1.42	+26.1	Alabaster
Mother waters of Sicilian gypsums	376-19-1, 146-150	+1.23	+23.8	Saccharoidal
	Si 59	+2.40	+5.5	"Balatino"
	Si 65	+5.30	+24.3	Selenite

studies of Leg 13 (Fontes et al., 1973 a,b; Pierre, 1974).

Within each type of paragenesis or early diagenesis (continental, marine, or evaporitic) large variations occurred in the hydraulic regime as evidenced by the changes in the redox potentials.

The influence of continental waters was both a result of direct influx of water bearing detrital deposits into the basins, and to ground-water supplies which induced recrystallization and epigenesis within the unconsolidated sediments.

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26.2. STABLE ISOTOPIC INVESTIGATION OF CARBONATE SAMPLES RELATED TO THE MESSINIAN SALINITY CRISIS FROM DSDP LEG 42A, MEDITERRANEAN SEA

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ABSTRACT

The oxygen-18 and carbon-13 ratios were measured on a series of carbonate samples selected from two different Messinian sequences: the marine deposits of the intra-Messinian and the Lago Mare deposits at the end of the Messinian. The intra-Messinian

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