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ADRIATIC DEEP WATER FORMATION DURING
THE HOLOCENE: IMPLICATION FOR THE
REOXYGENATION OF THE DEEP EASTERN
MEDITERRANEAN SEA

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Abstract. Under modern conditions, the reoxygenation of eastern Mediterranean deep water is the result of the formation of dense bottom water in the southern Adriatic Sea. Oxygen isotopic records of planktonic foraminifera used as a paleosalinity tracer show that Po River and/or the alpine glaciers meltwater are not directly responsible of the inhibition of the deep water formation in the Adriatic, during sapropel (S1) formation at 9,000 years B.P.. Sedimentological evidence indicates that fully oxygenated conditions in the deep Adriatic occurred only by 1,650±100 years B.P., a long time after the total reoxygenation of the deep eastern Mediterranean. Organic carbon content and isotopic ratio indicate that persistence of a reduced sediment phase until 1,650 years B.P., does not result from increased primary productivity or large input of terrestrial organic matter.

INTRODUCTION

Organic-rich layers occur in Quaternary deep water sedimentary sequences from the Mediterranean Sea

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[Bradley, 1938; Olausson, 1961]. These sapropel layers, containing more than 2% organic carbon, have been attributed either to the stratification of the water column due to a large input of freshwater inhibiting the thermohaline convection [Bradley, 1938; Olausson, 1961; Kullenberg, 1951; Ryan, 1972; Muller, 1973; Vergnaud-Grazzini et al., 1977; Thunell et al., 1977; Rossignol-Strick, 1983, 1985], thereby leading to bottom water stagnation, or to a large increase in primary productivity [Calvert, 1983] which increased the flux of organic matter into the deep waters. However, these various hypotheses cannot be checked because of the uncertainties about the origin, beginning, and duration of freshwater input. Furthermore, the ways in which stagnation and consequently the inhibition of bottom water oxygen renewal occurred, have not been well documented. Under modern conditions, the reoxygenation of Mediterranean deep water is the result of the formation of dense bottom water in the southern Adriatic Sea [Pollack, 1951; Lacombe and Tchernia, 1960; Wüst, 1961] which overflows into the Ionian Sea over the Otrante sill. The formation of Adriatic bottom water presently depends on the wind strength and is directly related to the gradient of atmospheric pressure between northern Europe and the Mediterranean Sea [Zore-Armanda, 1973]. It is very sensitive to small increases in water temperature (0.7°C) or small decreases in salinity (0.2 ‰) which could cause stratification of water masses [Mangini and Schlosser, 1986]. In this context, either an increased flow of freshwater from the Po River and Dalmatian coastal rivers or of meltwater from alpine glaciers may inhibit the formation of deep bottom water. We show here, from a paleohydrological reconstruction of the southern Adriatic Sea and the adjacent Mediterranean Sea, that freshwater input from the northern Adriatic Sea cannot be responsible for a cessation of bottom water formation

during the last sapropel (S1) formation. The following reoxygenation of the eastern Mediterranean Deep Water was not related to new deep water production in the Otranto basin because sedimentological evidences indicates that fully oxygenated conditions in the deep Adriatic occurred only by 1,650±100 years B.P..

MATERIALS AND METHODS

Adriatic Bottom Water is now currently formed during winter in the southern Adriatic Sea due to the cooling of surface water induced by northeast winds (Bora). However, the formation of such water depends upon the intrusion of saline Levantine Intermediate Water near the Dalmatian coast which increases the density, thereby allowing the water to sink. To determine the impact of freshwater input during the Holocene, we have used variations in the $^{18}\text{O}/^{16}\text{O}$ ratio of planktonic foraminifera as a tracer of the variations of near-surface salinities. As freshwater is depleted in the heavy oxygen isotope compared with seawater, the $\delta^{18}\text{O}$ value of the calcite tests of planktonic foraminifera, such as *Globigerinoides ruber* (which is dependent upon the isotopic composition of seawater), will record the occurrence of freshwater input and the variation of the salinity gradient [Duplessy, 1982] between the Adriatic Sea and the northern Ionian Sea. However, the $\delta^{18}\text{O}$ of foraminifera also depends on the temperature of seawater in which the foraminifera lived, with a decrease of about 0.25 ‰ for every 1°C temperature increase. Fortunately, the surface temperature gradient between the southern Adriatic and Ionian seawater is small (Satmer, Bulletin mensuel de renseignements océanographiques obtenus à partir de mesures satellitaires météorologiques sur la Méditerranée et l'Atlantique nord-est, Vol. 29-53, published by Direction de la Météorologie Nationale, Boulogne-Billancourt, France, 1986-1987), and we have assumed that it was the same during the whole Holocene period.

We have also estimated the fraction of marine and terrestrial organic matter in the sediments by determining the $^{13}\text{C}/^{12}\text{C}$ ratio of organic matter and applying a simple mixing relationship [Sackett and Thompson, 1963; Fontugne and Duplessy, 1986; Calvert and Fontugne, 1987; Fontugne and Jouanneau, 1987]. The origin of the organic matter within the sapropel or protosapropel layers in the Adriatic Sea is unknown because of the enclosed nature of the basin.

The timing of sapropel S1 deposition and reoxygenation of the bottom water has been determined by the identification of ash layer by geochemical methods which has been correlated with a terrestrial deposit dated by classical radiometric methods [Paterne et al., 1986, 1988] and by ^{14}C measurements of planktonic foraminifera by accelerator mass spectrometry (AMS).

Core Sampling and Sedimentology

Four cores were selected for this study, one in the south Adriatic Sea (KET 8216, 41°31'N, 17°59'E, 1166 m) and three in the Ionian Sea (KET 8222, 37°56'N, 16°53'E, 1691 m; and RC 9-191, 38°11'N, 18°02'E, 2345 m; and MD 84658, 35°02'N, 17°38'E, 2020 m) (Figure 1). Sedimentological and micropaleontological data were obtained only from the Adriatic core KET 8216. This core contains five sedimentary units which are from top to bottom: light brown oxidized mud (0-8 cm), brown-grey mud (10-30 cm), grey-brown mud (30-48 cm), sapropelic mud (S1) (48-72 cm), and light grey mud (72-170 cm). Dark grey layers occur between 48 and 50 cm, at 55 cm and between 66 and 72 cm. Cores KET 8222 and RC 9-191 show the same sequence, the sapropel (S1) being divided in two parts; in core MD 84658 it appears as a single level because of the very low sedimentation rate in this core [Murat and Got, 1987]. The stratigraphy of core RC 9-191 has been published by Ryan [1972]; however, some discordance may appear between our depth scale and that of Ryan due to dessication of the core since collection. Nevertheless, the sedimentary sequences observed in cores KET 8222 and MD 84658 (grey-mud-sapropel-oxidized level just above the sapropel) are in good agreement with those observed throughout the eastern Mediterranean Sea [Murat, 1984; Murat and Got, 1987].

Analytical Procedure

Samples of *Globigerinoides ruber* were selected every 10 cm (or every 2 to 3 cm within the sapropel), and the $\delta^{18}\text{O}$ values were determined by mass spectrometry

Fig. 1. Core locations.

following the procedure described by Duplessy [1978]. Organic carbon contents were determined by combustion under oxygen flow and by measuring the evolved CO₂ with a Strolheim-Coulomat 702 carbon analyzer, and the carbon isotopic composition of organic matter was determined following the techniques described by Fontugne and Duplessy [1981]. Results of carbon and oxygen isotopic analyses (Table 1) are expressed versus PDB, in per mil, following the conventional fashion as δ values. AMS radiocarbon dating was performed on mixed planktonic foraminifera when *G. ruber* was not sufficiently abundant, following the method described by Arnold et al. [1987].

RESULTS AND DISCUSSION

Stratigraphy

The stratigraphy of the cores was determined from the $\delta^{18}\text{O}$ variations of *Globigerinoides ruber*, tephrochronology, and ¹⁴C AMS dating. The time scale is reported in Table 2 for each core. All four cores show the same features, similar to those observed in the open ocean, and they demonstrate a complete oxygen isotopic record extending at least to stage 2 as defined by Emiliani [1955]. Core to core correlations were made from the $\delta^{18}\text{O}$ peaks according to the time scale defined by Bard et al. [1987] for the deglaciation period in the North Atlantic Ocean. The $\delta^{18}\text{O}$ variations are represented versus time in Figure 2; the beginning of the sapropel S1 event is assumed to be synchronous for the four cores.

Origin of the Organic Matter in Core KET 8216

The proportion of marine and terrestrial organic matter in core KET 8216 has been estimated assuming a value of -27‰ (the modal value of C3 plants of temperate zone [Dienes, 1980]) which characterizes the terrestrial end member, and -21‰ is typical of the marine plankton [Sackett et al., 1965; Fontugne, 1983; Descolas-Gros and Fontugne, 1985; M. R. Fontugne and S. E. Calvert, unpublished manuscript, 1989].

Figure 3 and Table 1 show that the sapropelic horizon contains between 0.7 and 1.1% organic carbon, whereas the other sediments have low amounts (0.2–0.3%). From the $\delta^{13}\text{C}$ values, terrestrial organic matter constitutes less than 10% of the total during the terminal Holocene. During the sapropelic event, however, the terrestrial input increased sharply, varying between 30 and 50 %; it remains stable around 30% between 10,000 and 15,000 years B.P.. The glacial period records a high contribution (reaching 50%) except that low values occur just before the first phase of the deglaciation (Termination Ia). The rather low carbon content during the sapropelic phase together with a low

TABLE 1a. Carbon Isotopic Composition and Content of Organic Matter Versus Depth in Core KET 8216

Depth, cm	Organic carbon %	Organic carbon $\delta^{13}\text{C}$
3	0.30	-21.08
13	0.29	-21.49
23	0.26	-21.87
33	0.24	-21.56
43	0.33	-22.36
53	0.70	-24.30
54	0.64	
58	0.60	
61	0.67	
63	0.72	
64	0.95	-23.30
68	1.10	
73	0.36	-23.62
83	0.33	-22.71
93	0.25	-23.33
103	0.33	-23.03
113	0.33	-22.94
123	0.23	-23.03
133	0.26	-23.08
143	0.24	-23.15
153	0.23	-22.94
163	0.22	-22.31
173	0.19	-22.63
183	0.26	-23.07
193	0.28	-23.06
203	0.18	-23.52
213	0.08	-23.81

marine organic matter contribution suggests that primary productivity was probably not responsible for sapropel S1 formation in the Otrante basin.

Sapropel S1 Formation and the Origin of the Stagnation

During the sapropelic phase the $\delta^{18}\text{O}$ values of *G. ruber* reach values as low as -0.2 ‰ in the Otrante basin and -0.80 to -0.85‰ in the Ionian Sea core. *G. ruber* mainly lives during summer and autumn in the central Mediterranean Sea and the Adriatic [Emiliani, 1969; Vergnaud-Grazzini et al., 1986] and consequently may record the input of freshwater mainly from the Po River to the Adriatic Sea. Similarly, cores RC 9-191 and KET 8222 are located near the Calabrian and Sicilian coasts where the surface water outflow from the Adriatic occurs [Barale et al., 1984]. Consequently, $\delta^{18}\text{O}$ values in these cores will be representative of the input and/or the output of freshwater in the Adriatic Sea. Figure 2 shows that Termination I in the Adriatic Sea occurs

TABLE 1b. Values of $\delta^{18}\text{O}$ of *Globigerinoides ruber* Versus Depth in Cores KET 8216, KET 8222, MD 84658 and RC 9-191

Depth, cm	$\delta^{18}\text{O}$
Core KET 8216	
1	0.79
10	0.77
20	0.85
30	0.53
40	0.60
50	-0.03
52	-0.14
57	-0.02
60	-0.20
63	-0.18
67	0.00
70	0.73
80	1.31
90	2.19
100	2.16
110	2.15
120	2.25
129	2.32
140	2.97
150	3.53
170	3.38
Core KET 8222	
0	0.03
10	-0.59
20	-0.05
30	-0.05
40	-0.78
50	-0.47
60	0.55
70	0.89
80	1.19
90	1.14
100	1.59
110	2.56
120	2.40
130	2.87
140	2.61
150	2.26
160	2.55
Core MD 84658	
2	0.58
6	-0.21
9	-0.45
14	2.83
17	3.10
22	3.26
28	3.00
36	2.72

TABLE 1b. (continued)

Depth, cm	$\delta^{18}\text{O}$
Core MD 84658 (continued)	
42	2.40
Core RC 9-191	
15	0.72
20	0.71
30	0.60
43	0.32
50	-0.22
51	-0.59
55	-0.69
56	0.05
62	-0.16
64	0.22
68	-0.54
74	-0.86
84	0.99
100	1.63
113	2.70
128	2.78
136	3.16
145	3.13
156	3.09
164	2.93

following the two steps found in the North Atlantic [Duplessy et al., 1981]. Within core KET 8216, the $\delta^{18}\text{O}$ values during Termination Ib and during the sapropel phase are markedly higher than those of the Ionian Sea cores which exhibit rather constant values from north to south. During the terminal Holocene and the glacial maximum, no $\delta^{18}\text{O}$ gradient occurs between the southern Adriatic Sea and the Ionian Sea. If we assume that, at the end of Termination I, during the sapropel formation, the sea surface temperature gradient during summer was the same as today (about 1°C), the observed gradient in $\delta^{18}\text{O}$ values shows that there was no large input of freshwater or meltwater from the Po River or coastal rivers of the Dalmatian or Italian coasts. This eliminates the Po River as a significant source of low-density water which could lead to vertical density stratification. However, the low $\delta^{18}\text{O}$ values show that somewhat less saline water was present in the Adriatic at this time. The decrease observed since the beginning of the sapropel would correspond to a 4.4 °C decrease of sea surface temperature since the end of Termination Ib which is not reflected in faunal changes. Hence, these changes are assumed to be due to reduced salinity confirming the stagnation and the slackening of

TABLE 2. Tephra and ^{14}C AMS chronology for cores KET 8216, KET 8222, MD 84658 and RC 9-191

Depth, cm	Estimated Age kyr B.P.	^{14}C AMS Age kyr B.P.	Geochemical Grouping	Correlation
10	1.50		TLP	Pollena eruption 472AD
11		1.65±0.10		
32		4.40±0.15		
49		6.27±0.11		
54	7.00		R	Rhyolite Eolian island E-1
70		8.61±0.11		
73		9.38±0.14		
89		9.99±0.16		
90	9.76		T(B)	Tuff de Agnano
117	12.30		T(B)	Napolitan yellow tuff
125		13.05±0.15		
145		13.78±0.18		
169		16.70±0.30		
189		16.30±0.26		
48-72	Sapropel			
Core KET 8222				
10-17	Sapropel S1a			
34-55	Sapropel S1b			
Core RC 9-191				
63	7.00		R	Rhyolite Eolian island E-1
50-75	Sapropel			
Core MD 84658				
8-10	Sapropel			

Abbreviations are defined as follows: TLP is tephrite-leucite-phonolite series; T(B) is trachyte; and R is rhyolite.)

the Adriatic bottom water formation in the Otrante basin.

Time Scale for the Reoxygenation of the Bottom Adriatic Sea

The sediment sequences in the eastern Mediterranean and in the Adriatic Sea are somewhat different. The sapropel S1 is not clearly marked in the Adriatic, and the transition above the sapropel to the oxidized level is gradual, while in the eastern Mediterranean the sapropels are clearly delineated and the transition to the oxidized sediment above is very abrupt (M. Arnold, unpublished data, 1989). The sapropelic phase is not well marked within core KET 8216 due to the relatively low carbon content (0.7 to 1.1%), while in the Ionian and Levantin basin cores the organic carbon content exceeds 2% [Murat, 1984]. The reduced phase between 10 and 48 cm cannot result from increased productivity because of the low sediment organic carbon content (0.08 to 0.2%).

On the other hand the $\delta^{13}\text{C}$ values of the organic matter show a marine fingerprint, thereby excluding large amounts of terrestrial organic material. The occurrence of the oxidized level 40 cm above the sapropelic phase in core KET 8216 indicates that full reoxygenation of the deep bottom water in the Otrante basin occurred at $1,650 \pm 100$ years B.P., more than 4,000 years after the end of the sapropelic phase. This indicates that the production of Adriatic bottom water, during this period, was weak. This observation is also supported by the benthic faunal record; the genus *Uvigerina*, which lives in oxygenated water, occurs in large abundance only in the terminal oxidized level. Its occurrence follows an increasing abundance of *Hoeglandina elegans* (10–40 cm) above the sapropel which is followed by the reappearance of benthic fauna at 40 cm. The preservation of pollen abundance also supports the hypothesis of progressive reoxygenation; the pollen number decreases regularly from the sapropel to the top of the core and parallels the increase in oxidation-proof pollen such as spores (M. Rossignol-Strick and N.

Fig. 2. Variations of $\delta^{18}\text{O}$ values of *Globigerinoides ruber* versus time in the cores KET 8216, KET 8222, MD 84658 and RC 9-191.

Planchais, unpublished manuscript, 1989). The sapropel S1 level over the whole eastern Mediterranean Sea is followed directly by a light brown oxidized sediment, suggesting a complete and abrupt reoxygenation of the Mediterranean deep waters [Murat and Got, 1987]. This is in contrast to the progressive reoxygenation of the southern Adriatic Sea which is now the location of the formation of deep water responsible for the oxygenation of the whole eastern Mediterranean. Such observations agree with those of Jorissen et al., [1988] on benthic foraminifera distributions and paleoproductivity which show major changes in surface circulation in the northern Adriatic Sea at about 2,000 years B.P.. The whole set of observations is consistent with the deduced difference in the time of bottom water renewal in the deep eastern Mediterranean and Adriatic seas and indicates at the same time that another source of deep water formation (probably the southern Aegean Sea) was active in the Mediterranean Sea, suggesting a time transgressive reoxygenation of the eastern basins.

Fig. 3. Variations of organic carbon content and isotopic composition of organic matter versus depth in core KET 8216.

Important changes in the deep ocean water circulation have thus even occurred during the Holocene period.

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