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28. Supported by the Department of Energy, Mines and Resources and by the National Research Council of Canada. We thank W. G. Wahl for unpublished maps of the Magnetawan area, J. A. Hanes for assistance with the initial sampling, and W. F. Fahrig and J. H. Foster of the Geological Survey of Canada for making their paleomagnetic facilities available to us.

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28 February 1975; revised 20 June 1975

^{18}O Changes in Foraminifera Carbonates During the Last 10^5 Years in the Mediterranean Sea

Abstract. *The Mediterranean response to major climatic events during the Upper Pleistocene could be seen as an integration of the principal phenomena particular to oceans and of regional phenomena peculiar to the Mediterranean Sea. The magnitude of oxygen isotope changes in foraminifera tests suggests that the temperature variations between stadial and interstadial periods could not exceed 11°C and that the correction factor for isotopic changes of waters should be about twice the value used for the oceans, or 2.7 per mil.*

The first data on oxygen isotope analysis in the Mediterranean deep-sea sediments were published by Emiliani in 1955 (*1*) for the core 189 from the eastern basin. In the present work some of the conclusions of an isotopic study made on foraminifera carbonates from four deep-sea cores from the Mediterranean Sea are presented (*2–6*). The locations of these cores are shown in Fig. 1: core 68 from the Alboran Sea, core KS05 from the Balearic basin, and core C_3 from the Ligurian Sea in the western part of the Mediterranean and core $V_{10\text{-}67}$ from the Ionian basin in the eastern part.

Species having relatively higher abundance throughout the cores were chosen for the analysis: *Globigerinoides ruber* in all four cores, *Globigerina bulloides* in core C_3, and right-coiling *Globigerina pachyderma* in core 68. Today the habitat of the first two species in the Mediterranean is restricted to shallower depths. The third species can migrate in the water column; however, this migration does not indicate that *G. pachyderma* has varying temperature requirements, for this species appears in greatest abundance in winter, when the water column in the Mediterranean is homeothermal (around 13°C, which is the winter minimum). Analyses were carried out on samples of 100 to 150 specimens; thus individual variations were averaged out. Samples with organic matter were cleaned by using a 24-hour treatment with Clorox, while samples with sediment filling were given a 30-second ultrasonic treatment. The carbon dioxide was released through the action of 100 percent phosphoric acid at 25°C. The $^{18}O/^{16}O$ ratios are reported as δ values (per mil) relative to the Pee Dee belemnite standard (PDB-1) (Table 1 and Fig. 2).

Table 1. Magnitude of isotopic changes for major paleotemperature peaks in cores 68, KS05, C_3, and $V_{10\text{-}67}$, reported as δ values relative to the PDB-1 standard. Abbreviations: B.P., before the present; *G. ruber*, *Globigerinoides ruber*; *G. bulloides*, *Globigerina bulloides*; and *G. pachyderma*, *Globigerina pachyderma*. Dashes indicate no results.

Species	Cores							
	68		KS05		C_3		$V_{10\text{-}67}$	
	Depth of core (cm)	δ value	Depth of core (cm)	δ value	Depth of core (cm)	δ value	Depth of core (cm)	δ value
Age: 1.7 × 10^4 years B.P.								
G. ruber	380 to 250	≥ 3.3	180 to 10	4.3			58 to 35	4.1
G. bulloides	—	—	—	—	140 to 50	5.2	—	—
G. pachyderma	480 to 240	5.2	—	—	—	—	—	—
Age: 3 × 10^4 years B.P.								
G. ruber	—	—	—	—	340 to 300	2.8		
G. bulloides	—	—	—	—	360 to 300	3.9	—	—
G. pachyderma	—	—	—	—	—	—	—	—
Age: 5.5 × 10^4 years B.P.								
G. ruber	—	—	680 to 650	3.9	—	—	—	—
G. bulloides	—	—	—	—	720 to 660	4.3	—	—

Sedimentation rates. Radiocarbon datings on core KS05 [C. Evin, in (*5*)], on core $V_{10\text{-}67}$ [Lamont-Doherty Geological Observatory and J. Thommeret, in (*2*)], and on sediments cored near core 68 (*4*) lead to the following estimations for sedimentation rates: (i) in core 68 sedimentation rates vary between 26 and 30 cm per thousand years; (ii) in core KS05 they vary between 10 cm per thousand years in the upper part and 15 cm per thousand years in the lower part (an average value of 12 cm per thousand years could be used); and (iii) in core $V_{10\text{-}67}$ the sedimentation rate ranges from 4.5 to 13 cm per thousand years. Core C_3 was dated by the uranium series method [Larmande-Renou and Martin (*7*)], giving an average sedimentation rate of 13.5 cm per thousand years. However, since no correction for detritic contamination had been done on the core, one must assume the rate is less.

In Fig. 2 a correlation represented by a dashed line is proposed for the 1.7 × 10^3 year "cold" isotopic peaks (peaks toward the positive values of δ) and the 5.5 × 10^3 year "warm" isotopic peaks (peaks toward the negative values of δ). Five major climatic stages can be distinguished in the last 10^5 years. These may correspond to the isotopic stages 1 to 5 of the generalized paleotemperature curve (Fig. 2).

$\delta^{18}O$ changes recorded by planktonic foraminifera (Table 1). Variations in measured paleotemperatures in planktonic foraminifera are caused both by changes in the ocean surface temperature and by glacially controlled changes in the isotopic composition of the ocean water. Most workers believe now that the last is the dominant factor (*8, 9*) and have even suggested that the existence of any residual temperature effect remains to be demonstrated. An isotopic change of 1.2 to 1.6 per mil is generally admitted for ocean waters between glacial and interglacial periods.

Isotopic fluctuations recorded by planktonic foraminifera from Mediterranean sediments within the period covered by isotope stages 1 to 5 amount at least to 2.8 per mil and can reach magnitudes of 5.2 per mil (Table 1). These variations seem extremely high when compared with that shown by Pleistocene foraminifera from Atlantic or Pacific cores: variations from 0.9 to 2.0 per mil for both oceans are reported by Van Donk (*10*). Isotopic changes

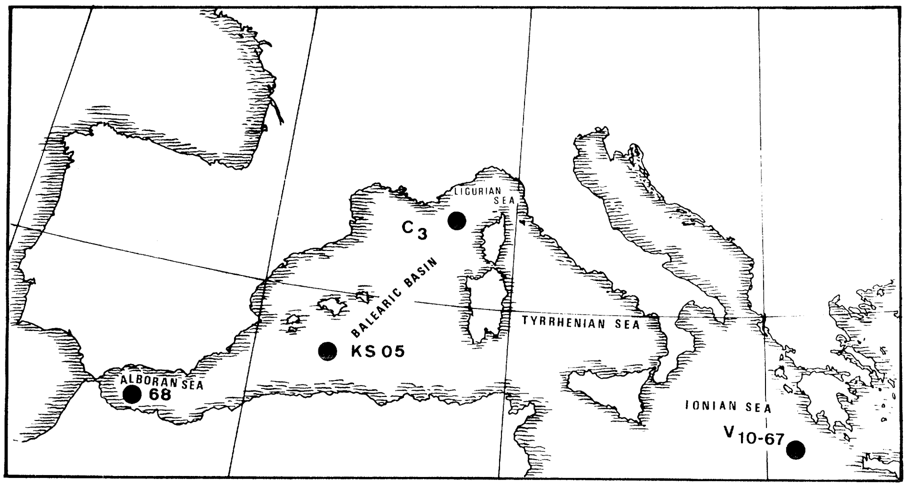

Fig. 1. Location of the cores in the western and eastern Mediterranean basins.

Table 2. Comparison between isotopic composition of benthic and planktonic foraminifera during glacial and postglacial phases. Symbol: σ, standard deviation.

$\delta^{18}O$ per mil		$\delta^{18}O$ differences between benthic and planktonic	Mean
Planktonic	Benthic		
Living forms			
1.0	1.5	0.5	0.5
Age: 12 × 10³ years B.P.			
3.5	4.7	1.2	1.03
3.1	4.2	1.1	[σ = 0.17]
Age: 22 × 10³ years B.P.			
2.2	3.0	0.8	

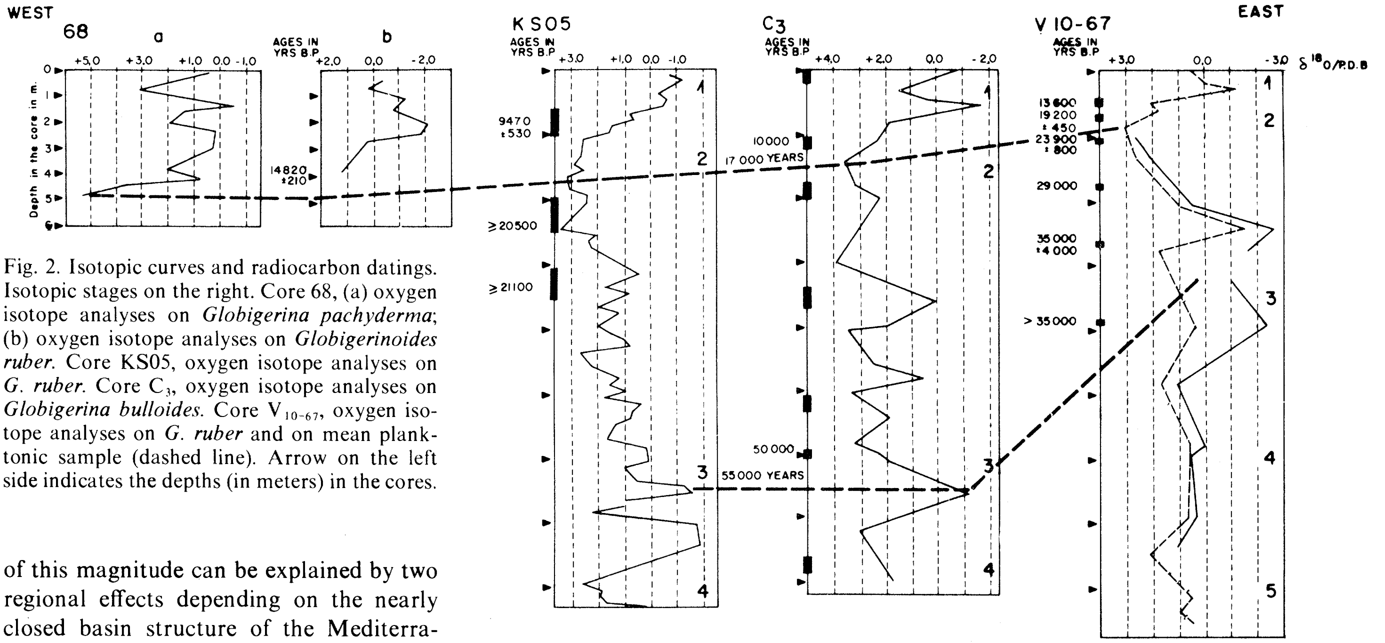

Fig. 2. Isotopic curves and radiocarbon datings. Isotopic stages on the right. Core 68, (a) oxygen isotope analyses on *Globigerina pachyderma*; (b) oxygen isotope analyses on *Globigerinoides ruber*. Core KS05, oxygen isotope analyses on *G. ruber*. Core C_3, oxygen isotope analyses on *Globigerina bulloides*. Core $V_{10\text{-}67}$, oxygen isotope analyses on *G. ruber* and on mean planktonic sample (dashed line). Arrow on the left side indicates the depths (in meters) in the cores.

of this magnitude can be explained by two regional effects depending on the nearly closed basin structure of the Mediterranean Sea.

The first effect may have been a thermic effect. Let us take the example of the ^{18}O variations corresponding to the last glacial and postglacial periods. If one assumes that the isotopic changes in Mediterranean waters were similar to those of the oceans and thus that a correction of at least 1.2 per mil is to be used for temperature calculations, then the δ variations that can be ascribed to temperature fluctuations range between 4.2 and 1.2 per mil for the autumnal species *G. ruber* and 5.2 and 1.2 per mil for the two winter-spring species *G. bulloides* and *G. pachyderma*. These variations correspond to temperature drops of 13° and 17°C, respectively. As far as the superficial species *G. bulloides* is concerned, the higher value is most improbable since present-day winter temperatures are around 13°C and since surface glacial temperatures could not have been lower than 0°C in the Mediterranean.

Thus, in the case of isotopic changes of high magnitude, a second factor is involved; it is supposed to be a higher variation of the isotopic composition of Mediterranean waters. This second regional effect could be related to the evaporation-precipitation balance (*11*). (i) During cold dry climatic stages, a "dry effect," resulting from lower precipitation or higher evaporation, or both, could have led to higher isotope and higher salt concentrations in the water. Such a dry effect can be observed now in very cold winter weather in both the eastern and western basins. In such circumstances one may observe a sinking to the bottom of the denser surface waters that have undergone extreme evaporation. (ii) During the deglaciation phases (under a humid and warm climate) a rapid dilution (higher output of rivers, meltwater adding, and higher inflow of surface Atlantic waters through the Strait of Gibraltar), which compensated for the evaporation effect, might have induced a lowering in the isotope concentration.

$\delta^{18}O$ changes recorded by benthic foraminifera (Table 2). Benthic foraminifera from core C_3 taken at glacial levels (stage 2) show $\delta^{18}O$ values higher by about 1 per mil than those for planktonic foraminifera from the same levels. In living forms, this difference does not exceed 0.5 per mil (*6*). A higher difference may have been caused by a thermal effect of 2°C: temperature changes in deep waters could have been 2°C greater than those of surface waters. Since deep temperatures could not have dropped more than 13°C, one may conclude that surface temperatures could not have varied more than 11°C. This temperature change corresponds to an isotopic change of about 2.5 per mil. Thus, the minimum change in isotopic composition of Mediterranean waters, corresponding to the highest isotopic peaks on the paleotemperature curve was 5.2 − 2.5 per mil = 2.7 per mil, in other words, twice the variations generally admitted for ocean waters.

In conclusion, the magnitude of paleotemperature changes in the Mediterranean basin suggests that the temperature drop during glacial phases was higher than in the oceans but could not exceed 11°C and that the correction factor for isotopic changes of the water should be about twice the value used for the oceans, or 2.7 per mil. The combined effects of temperature and of changing isotopic composition of water on the paleotemperature curve give rise to very sharp isotope peaks; but it is still possible to correlate isotopic stages observed in the Mediterranean area with that of the generalized paleotemperature curve for the last 10^5 years.

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14 February 1975

Phosphine on Jupiter and Implications for the Great Red Spot

Abstract. *A study of the chemistry and photochemistry of the recently discovered phosphine in the atmosphere of Jupiter suggests that the red colorations on this planet result from photochemical production of red phosphorus particles. Chemical-dynamical models of this red phosphorus haze imply that the intensity of the red coloration is a strong function of the strength of vertical turbulent mixing in the atmosphere. If the Jovian Great Red Spot is a region of considerable dynamical activity our model provides a self-consistent explanation for the redness of this region in comparison to the rest of the planet.*

Phosphine (PH_3) has recently been discovered in the atmosphere of Jupiter by Ridgway (*1*), who used a high-resolution Fourier transform interferometer-spectrometer in the wavelength region 8 to 13 μm; it has been reported more tentatively in the atmosphere of Saturn by Gillett and Forrest (*2*), who used a medium-resolution filter-spectrometer in the same wavelength region. These discoveries add an important new dimension to our understanding of the chemistry and photochemistry of these atmospheres.

In some respects the detection of PH_3 on these planets is surprising. Until this discovery, the thermochemical equilibrium models of Jupiter proposed by Lewis (*3*) had been remarkably successful in explaining the observed composition of its visible atmosphere. This model indicated that phosphorus should be present as PH_3 only below the 800°K level in the deep unobservable portion of the atmosphere. Between the 800° and 300°K levels PH_3 is oxidized by H_2O to form P_4O_6, while above the 300°K level P_4O_6 is condensed out as aqueous H_3PO_3. A reasonable explanation for the observation of PH_3 is possible if atmospheric vertical mixing is much faster than the thermochemical reactions converting PH_3 to P_4O_6. Alternatively, if the H_2O volume mixing ratio on Jupiter is as low as 10^{-6}, as recently reported by Treffers *et al.* (*4*), then there may be insufficient oxygen to oxidize PH_3 above the 800°K level.

Some time ago Lewis and Prinn (*5*) proposed that the yellow and brown colorations in the Jovian atmosphere resulted from rapid ultraviolet (UV) dissociation of H_2S and UV irradiation of NH_4HS particles to form elemental sulfur and ammonium and hydrogen polysulfides (*6*). On the other hand, the red coloration of certain regions, in particular the Great Red Spot, has been attributed to colored organic material produced from CH_4 photodissociation (*7*). However, photodissociation rates of PH_3 are about 1000 times greater than those of CH_4, and most of the products of CH_4 dissociation suggested by studies of Jovian aeronomy are colorless (*8*). We argue here that red phosphorus produced from PH_3 dissociation is the dominant red chromophore on Jupiter.

For our study we have utilized a model atmosphere for Jupiter (Fig. 1) which is composed primarily of H_2 and He in their solar abundance ratio of 7 to 1, with a PH_3 volume mixing ratio of 4×10^{-7} (*9*). At pressures less than 800 mbar we have used the temperature profile inferred by Wallace *et al.* (*10*) from the observed infrared emission in methane bands. At pressures exceeding 800 mbar we have adopted an adiabatic lapse rate as implied by the radiative-dynamical equilibrium calculations of Trafton and Stone (*11*).

Phosphine is dissociated by UV of wavelengths less than 2350 Å. Halmann (*12*) and Kley and Welge (*13*) found that its absorption spectrum in the region 1800 to 2350 Å is continuous with a peak at about 1900 Å. The primary photolysis products appear to be PH_2 and H. Becker and Welge (*14*) also detected absorption in the region 1165 to 1470 Å with a peak at 1250 Å, and the primary products here appear to be PH and H_2. We are not concerned with this shorter wavelength absorption here (*15*).

From Tomasko (*16*) and Anderson *et al.* (*17*) we estimate that the column abundance of H_2 above the effective level for penetration of 2068-Å radiation is about 2.7 km amagat (*18*). This level lies at a pressure of 80 mbar, where the temperature is 112°K (Fig. 1). To a sufficient approximation we can take the atmosphere above this level as optically thin to radiation in the region 1850 to 2200 Å while assuming negligible penetration of these wavelengths into the atmosphere below this level (*19*). The photodissociation rate constant, J_1, of PH_3 above the 80-mbar level is then obtained by convolving the incident solar UV radiation intensities at Jupiter (*20*) with the absorption cross sections of PH_3 in the region 1850 to 2200 Å (*12, 13*) and dividing by 4 for a planetary average. This yields $J_1 = 6 \times 10^{-7}$ sec^{-1} above the 80-mbar level, and as discussed above we take $J_1 = 0$ below this level.

The products of photodissociation of PH_3 were first studied by Melville (*21*) and most recently by Norrish and Oldershaw (*22*). These studies suggest the following reaction sequence

$$PH_3 \rightarrow PH_2 + H \tag{1}$$

$$PH_2 + PH_2 \rightarrow PH + PH_3 \tag{2}$$

$$PH + PH \rightarrow P_2 + H_2 \tag{3}$$

$$H + H + M \rightarrow H_2 + M \tag{4}$$

$$P_2 + P_2 + M \rightarrow P_4 + M \tag{5}$$

$$P_4 \rightarrow P_4(s) \tag{6}$$

where M is any background molecule. This sequence appears valid for pressures in the range 0.1 to 1000 mbar and for temperatures ranging from 290° to perhaps as high as 600°K. The products are exclusively red phosphorus [$P_4(s)$] and H_2. Diphosphine (P_2H_4) is not detectable, and in this respect photodissociation of PH_3 differs significantly from that of NH_3, where hydrazine (N_2H_4) is an important product (*23*).

The quantum efficiency of red phos-