Reports

Paleotemperature Variations across the Plio-Pleistocene Boundary

Abstract. *Strong variations in the* O^{18}/O^{16} *and* C^{13}/C^{12} *ratios occur through the type section for the Plio-Pleistocene boundary, but the boundary itself is not characterized by unusual isotopic gradients.*

The beginning of the Calabrian age was defined by Gignoux (1913) as the time of the first appearance of a number of northern marine invertebrates in the late Cenozoic sections of southern Italy and Sicily (*1*). This age, designated by Gignoux as the last age of the Pliocene, was redefined by the 18th International Geological Congress (London, 1948) as the first age of the Pleistocene epoch. The beginning of the Calabrian, therefore, is also the beginning of the Pleistocene.

Many excellent sections of marine epicontinental Plio-Pleistocene sediments occur in Italy. Particularly impressive are the deposits of the Crotone basin in Calabria, ranging from shallow-water facies along the periphery to deep-water facies in the center. Post-Calabrian uplift truncated the basin so that sediments deposited near its center now outcrop along the modern shoreline. The exposed part of the basin measures 30 km east to west and 60 km north to south. The Plio-Pleistocene sediments in the central portion are essentially marly clays (Cutro clays) up to 1615 m thick (*2*), representing a single transgressive cycle ranging from middle Pliocene to late Calabrian time (*3*). The appearance of the northern marine invertebrates mentioned above and, therefore, the Plio-Pleistocene boundary, coincide with the transgressive maximum (*3*).

Particularly abundant and characteristic among the northern invertebrates are the shallow water pelecypod *Arctica* (*Cyprina*) *islandica* and the deeper water benthonic foraminifer *Hyalinea* (*Anomalina*) *baltica*. Because of the different habitats, the two species are generally not found together. Close to the margin of the Crotone basin, where water was shallower, the Plio-Pleistocene boundary is identified by the first appearance of *A. islandica*, while in sediments deposited offshore it is identified by the first appearance of *H. baltica*. Because the arrival of these two species in the Mediterranean may not have been synchronous (*4*), the 7th INQUA Congress (Denver, Colorado, 1965) redefined the Plio-Pleistocene boundary as the time when *H. baltica* appeared in the section at le Castella, Italy, 20 km southwest of Crotone (*5*). This definition, refining the original one by Gignoux, represents a well-defined event in time believed to date from either 0.7 to 0.9 or 1.8 million years ago (*6*).

Many authors since Gignoux's time have used different criteria to define the Plio-Pleistocene boundary, ranging from the inception of the first major glaciation (several million years ago in Antarctica, 300,000 to 400,000 years in Europe) to the appearance of the Villafranchian fauna (more than 3.2 million years ago) and to certain specific microfaunal changes in deep-sea sediments (either 0.7 or 1.8 million years ago). These diverging definitions entail diverging durations for the very same geological epoch, the Pleistocene, and should be abandoned in favor of the single definition adopted by the 7th INQUA Congress in order to avoid any further confusion.

In a recent study (*2*), 47 samples from the section at le Castella were analyzed isotopically. Variations in the oxygen isotopic composition of the shells of pelagic and benthonic Foraminifera, amounting to about 4 per mil, were noticed and taken to be related to early glacial-interglacial episodes of varying magnitudes. A close relationship between isotopic variations and variations in the shell morphology of the planktonic foraminiferal species *Globigerinoides rubra* was noticed (*2*, figure 2), which supports the conclusion that the isotopic variations are related to marked variations in temperature.

In the study in question (*2*), 15 samples of *G. rubra* ranged stratigraphically from approximately 10 m below the Plio-Pleistocene boundary to approximately 15 m above. The average sampling interval, 1.7 m, was considered too large and the results were presented as preliminary only (*2*, p. 687). This same section was later resampled and a total of 60 samples were obtained, reducing the average sampling interval to about 40 cm. Shells of *G. rubra* (including the subspecies *rubra rubra* and *rubra gomitulus*), and of *Globigerina bulloides*, were separated from each sample. The foraminiferal shells were analyzed by mass spectrometry to determine both the O^{18}/O^{16} and the C^{13}/C^{12} ratios. The results are shown in Fig. 1. The data point density of the isotopic curves of this figure indicates that sampling has been adequate and that additional sampling is not likely to produce additional major maxima or minima. The base of the Pleistocene corresponds to a 0.3-m thick sand layer, as noticed previously (*2*). Because of Bayliss's finding (*7*) that *H. baltica* is continuously present in the section at Santa Maria di Catanzaro and of Smith's contention (*8*) that it is continuously present also in the section at le Castella, all samples reported here were carefully scrutinized for this species. This examination has shown that *H. baltica* is absent from samples 1 to 24, with the exception of sample 22, in which a single specimen was noticed. The species is present (several specimens per gram of residue larger than 62 μ) in sample 25 from the bottom of the sand layer and remains present in varying quantities to the top of the section. As a result of these observations, the Plio-Pleistocene boundary, as officially defined (*5*), is placed at the base of the sand layer mentioned, in confirmation of our previous observations (*2*).

Globigerinoides rubra and *Globigerina bulloides* remain generally abundant throughout the sampled section. The O^{18}/O^{16} and C^{13}/C^{12} curves for both species exhibit a number of oscillations that have an appreciable parallelism (Fig. 1). The isotopic maxima, minima, averages, and ranges are shown in

Table 1. The O^{18} and C^{13} isotopic minima are seen to correlate generally with tripoli-rich layers.

The isotopic curves of Fig. 1 must be interpreted in terms of the following factors: (i) depth habitats and seasonal growth of *G. rubra* and *G. bulloides*; (ii) secular and seasonal oxygen and carbon isotopic variations of the Crotone basin water; and (iii) environmental temperatures.

Globigerinoides rubra is a common pelagic foraminiferal species generally abundant at middle and low latitude in the Atlantic Ocean and adjacent seas. It has a shallow habitat, living mainly within 50 m from the surface in open oceanic waters, and it grows mainly during the summer (*9*, *10*). *Globigerina bulloides*, on the other hand, has a deeper habitat and grows mainly during the winter (*9*). The oxygen isotopic data shown in Fig. 1 are in agreement with these field observations. In fact, not only is the average oxygen isotopic composition of *G. rubra* 1.85 per mil lighter than that of *G. bulloides* (indicating an average temperature of shell deposition about 8.0°C warmer) but also the isotopic range is 0.97 per mil greater, which indicates a difference in depth habitat with *G. rubra* occupying the shallower habitat. The C^{13}/C^{12} ratios exhibit an opposite trend—the carbon isotopic composition of *G. rubra* is 1.44 per mil heavier than that of *G. bulloides* and the range is 0.84 per mil smaller.

The temperature-dependence of the fractionation factor between water and calcium carbonate is − 0.23 per mil per degree centigrade for O^{18} and + 0.07 per mil per degree centigrade for C^{13} (*11*). Because the two have opposite signs, the marked parallelism between O^{18}/O^{16} and C^{13}/C^{12} curves for both *G. rubra* and *G. bulloides* (Fig. 1) indicates that the C^{13}/C^{12} ratios were determined by the carbon isotopic composition of ions in solution in the Crotone basin water rather than by temperature, the temperature effect for carbon having been, in fact, reversed. The lighter carbon isotopic composition of

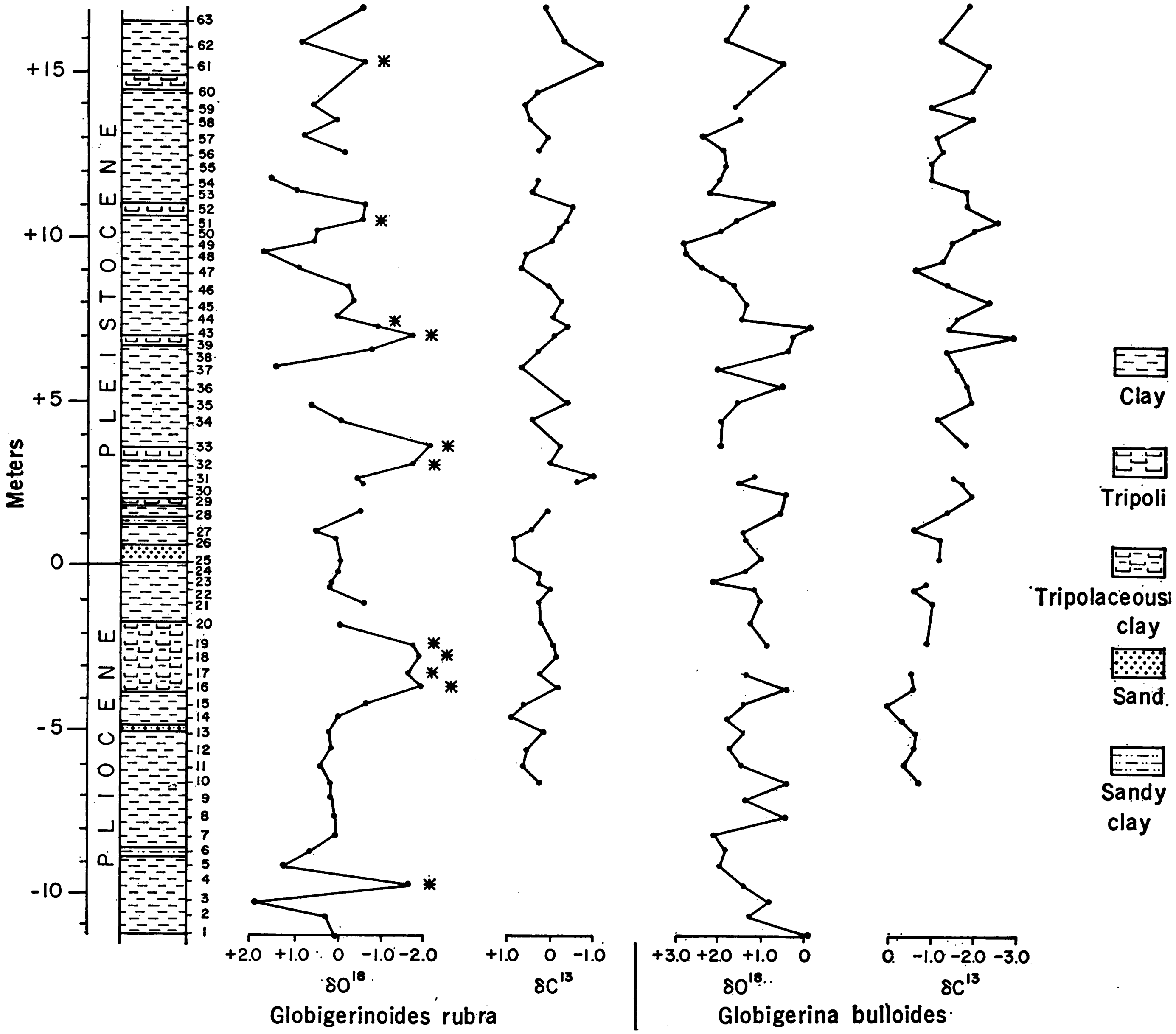

Fig. 1. Stratigraphy, lithology, and isotopic data from the section at le Castella, Calabria, southern Italy. Asterisks identify samples with predominant *Globigerinoides rubra rubra*. The isotopic values refer to the Chicago Standard PDB-1. Numbers to the right of the lithologic section are sample numbers.

Table 1. The O^{18}/O^{16} and C^{13}/C^{12} maxima, minima, averages, and ranges for *Globigerinoides rubra* and *Globigerina bulloides* at le Castella, Italy. The isotopic values refer to the Chicago Standard PDB-1 (PDB, Pee Dee belemnite).

Species	O^{18}/O^{16} (δ ‰)				C^{13}/C^{12} (δ ‰)			
	Maximum	Minimum	Average	Range	Maximum	Minimum	Average	Range
Globigerinoides rubra	+2.03	−2.03	−0.39	4.06	+1.01	−1.10	+0.21	2.11
Globigerina bulloides	+2.94	−0.15	+1.46	3.09	+0.08	−2.87	−1.23	2.95

G. bulloides, a winter species, indicates a greater influx of fresh water into the Crotone basin during the winter, as fully expected from the meteorological regime of the area. The lighter carbon isotopic composition of both *G. rubra* and *G. bulloides*, in correlation with lighter oxygen isotopic composition, suggests greater runoff during intervals of high temperature, which is in agreement with the known aridity of the Mediterranean during cold ages (*12*).

The greater secular ranges in O^{18}/O^{16} ratios for both *G. rubra* and *G. bulloides* with respect to the C^{13}/C^{12} ratios is a measure of the added temperature effect affecting predominantly the O^{18}/O^{16} ratios. In fact, if secularly varying runoff were the only factor, C^{13}/C^{12} ranges should be equal to or greater than the O^{18}/O^{16} ranges [compare (*11*)].

That the O^{18}/O^{16} minima represent high temperatures is also shown very clearly by the shell morphology of *G. rubra*. In the equatorial Atlantic and the Caribbean, this species is represented by the subspecies *G. rubra rubra* (the classical *G. rubra* of d'Orbigny) during both glacial and interglacial ages (*13*). In the North Atlantic *G. rubra rubra* occurs only during the interglacial ages and is replaced by the more compact *G. rubra gomitulus* during the glacial ages (*13*). In the eastern Mediterranean core 189, *G. rubra rubra* is narrowly restricted to the highest temperature intervals of the interglacial ages, while *G. rubra gomitulus* remains abundant through the rest of the core (*14*). In the section at le Castella under discussion here, *G. rubra rubra* predominates in the intervals having highly negative O^{18}/O^{16} ratios (sample Nos. 4, 16 to 19, 32, 33, 39 to 43, 52, and 61), while *G. rubra gomitulus* predominates in all others. There is strong micropaleontological evidence, therefore, that the O^{18}/O^{16} minima of Fig. 1 represent temperature maxima and not only greater influx of fresh water.

The observed coincidence of O^{18}/O^{16} minima with tripoli-rich layers appears to result from a common cause, namely, higher temperatures and greater fresh water influx. A direct causal relationship between high productivity of diatoms and radiolaria and low O^{18}/O^{16} ratios in the foraminiferal calcite is not supported by the C^{13}/C^{12} ratios, unless one were to believe that productivity is directly proportional to temperature secularly but inversely proportional to it seasonally (lower C^{13}/C^{12} ratios are given by *G. bulloides*, a winter species, than by *G. rubra*, a summer species; see Table 1).

Because of the uncertainty in the oxygen isotopic composition of the Crotone basin water, it is not possible to calculate absolute temperature values from the data of either Table 1 or Fig. 1. Nevertheless, it appears rather well established on both isotopic and micropaleontological grounds that the O^{18}/O^{16} variations represent marked climatic variations occurring while the sediments of the Plio-Pleistocene section at le Castella were being deposited. As previously noticed (*2*), no major temperature change occurs at the Plio-Pleistocene boundary. The amplitude of the O^{18}/O^{16} variations is about 0.7 per mil smaller than that noticed in the late Pleistocene core 189 from the eastern Mediterranean (*14*).

Six major temperature maxima are evident on both isotopic and micropaleontological grounds. If the resulting five major cycles had an average duration similar to that of the temperature cycles of the later Pleistocene [about 50,000 years each (see *15*)], the stratigraphic section of Fig. 1 would represent a time interval of 250,000 years and would have been deposited at an average rate of 10 cm per 1000 years.

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16. I am grateful to R. Selli for having made available the samples. Supported by NSF grant GA-15226. Contribution No. 1299 from the School of Marine and Atmospheric Sciences, University of Miami.

1 June 1970

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Amorphous Ice: Density and Reflectivity

Abstract. *Amorphous ice prepared under a wide range of conditions has a density, determined from its buoyancy in liquid oxygen, of 0.94 ± 0.02 gram per cubic centimeter, the same as that of ordinary hexagonal ice, with no indication of the glassy superdense ice (2.32 grams per cubic centimeter) reported recently. The diffuse reflectivity shows a small increase as the ice crystallizes at 153°K. This increase is followed by a much larger increase (probably associated with crystal growth) as the sample warms, and the reflectivity reaches a maximum well below the melting temperature. Although the ice deposits appear translucent, the specular reflectivity is low, thus indicating a dull rather than a glassy surface.*

Ice prepared by the condensation of water vapor on a surface cooled to 140°K or below gives only broad bands in its x-ray diffraction and is generally considered to be amorphous (*1*). Recently Delsemme and Wenger (*2*) reported the preparation of "glassy" amorphous ice with a density of 2.32 g/cm^3. This very high density was determined by computing the volume of a known weight of ice from photographs of a copper cone with and without the ice deposit. We have visually examined the crystallization of many samples of amorphous ice and have seen no change in volume or other indication of an abnormally high density.