20 percent of darker mare material. (iii) Bright craters and rays in the maria darken and redden in situ by vitrification of the ilmenite-rich basalt (by micrometeoroid impacts) and by mechanical mixing with preexisting dark fines. (iv) Bright craters in the highlands darken largely by the addition of material derived from the maria, which is mixed with highland material and is partially vitrified.

JOHN B. ADAMS
Caribbean Research Institute,
College of the Virgin Islands,
St. Croix 00820

THOMAS B. MCCORD
Planetary Astronomy Laboratory,
Department of Earth and Planetary
Sciences, Massachusetts Institute of
Technology, Cambridge 02139

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The Last Interglacial: Paleotemperatures and Chronology

Abstract. *The* O^{18}/O^{16} *analysis and* Th^{230}/Pa^{231} *dating of deep-sea cores showed that the last interglacial age, with an early major temperature maximum followed by two smaller ones, extended from 100,000 to 70,000 years ago and was preceded by a glacial age extending from 120,000 to 100,000 years ago. The* O^{18}/O^{16} *analysis and* Th^{230}/U^{234} *dating of speleothems confirm and refine these ages.*

The O^{18}/O^{16} analysis of deep-sea cores, together with absolute dating by C^{14} and by methods based on the decay products of the two uranium families, has changed drastically the classical picture of the Pleistocene as given, for instance, by Schuchert and Dunbar (*1*). Not only has postglacial time been reduced to 10,000 years but also the preceding several hundred thousand years have been shown to include rapidly alternating glacial and interglacial events exhibiting an average periodicity of about 50,000 years. High-temperature events in the deep-sea cores were identified by odd integers increasing with time, low-temperature events by even integers (*2*). The amplitude of the temperature oscillations of the surface seawater at low altitudes appears to have increased by about 10 percent toward the present, but age 3, the temperate age preceding the present interglacial, is unique in that it does not exhibit temperatures as high as those of the warm ages before or after [see (*3*) for a possible explanation]. These results were recently reviewed in *Science* (*4, 5*).

Because temperature did not reach fully interglacial values during age 3, the age closest to us in time which offers conditions most closely resembling the present ones is age 5. Twelve long deep-sea cores from the Atlantic Ocean and adjacent seas have been analyzed so far (*2, 3, 6–9*), all including stage 5 as well as the adjacent stages 4 and 6. The numerous isotopic curves thus available have been used to reconstruct a detailed generalized isotopic curve from which much of the stratigraphic noise is filtered out (Fig. 1). The time scale is provided by C^{14} and Th^{230}/Pa^{231} measurements (*9, 10*).

The generalized curve is very characteristic. From stage 7, the curve slopes down to the minimum of stage 6, dated at about 105,000 years before the present. Following a minor inflection, the curve rises rapidly to a major maximum dating from about 95,000 years B.P. This maximum, representing temperatures as high as those of the last hypsithermal, has a duration of only a few thousand years. The isotopic curve then drops to a minimum that is intermediate in value between interglacial maxima and glacial minima. This minimum, dating from about 90,000 years B.P., is followed by a similar minimum about 10,000 years later. Between the two minima and following the second one, the isotopic curve rises, but it reaches only half way up toward the value of the major maximum of 95,000 years B.P. For much of age 5, therefore, temperature was appreciably lower than today. This age came to an end about 70,000 years ago, when temperature began dropping toward the minimum of age 4. This time coincides with the extinction of the pelagic foraminiferal subspecies *Globorotalia menardii flexuosa*. The minimum of age 4 was reached about 10,000 years later, or 60,000 years ago. The characteristic isotopic trend of age 5 was noticed before (*3*) and has been discussed in some detail by Shackleton (*11*), who defined as substages the three isotopic maxima and the two intervening minima occurring within age 5.

The amplitude of the isotopic oscillations within age 5 increases from the Caribbean-equatorial Atlantic to the North Atlantic [core 280, see (*7*)] and the Mediterranean [core 189, see (*6*)].

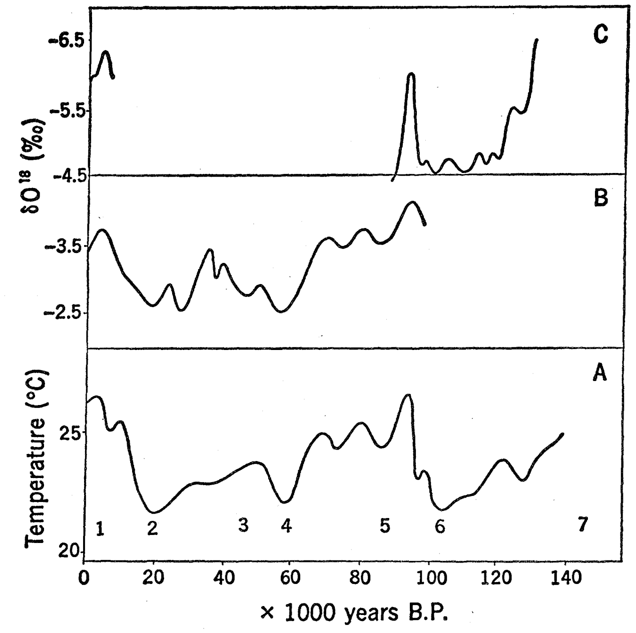

Fig. 1. (A) Isotopic paleotemperature curve from deep-sea cores (with age or stage numbers above abscissa); (B) O^{18}/O^{16} ratios (δ per mil) in New Zealand speleothems; and (C) O^{18}/O^{16} ratios (δ per mil) in speleothems from southern France. Curves are approximate tracings of original data.

Particularly strong are the variations in the Mediterranean core, with the subage minima of age 5 exhibiting relatively high O^{18}/O^{16} ratios.

All cores show that temperature rose very rapidly during anathermal 6/5 (*12*). A similarly rapid temperature rise occurred during anathermal 2/1, that is, during the last deglaciation. Because of continuous reworking by metazoans living on the sea floor, even an instantaneous change will be recorded as a gradient in deep-sea sediments of normal globigerina-ooze facies. Broecker *et al.* (*13*) showed that a major portion of the temperature rise leading from age 2 (Main Würm or Main Wisconsin) into age 1 (the present interglacial) could have taken place within a time interval as short as 1,000 years about 11,000 years ago. At least 70 percent of the glacial ice had disappeared by then (*14*), however, so that the rapid temperature change at 11,000 years may not have resulted from major continental deglaciation but, possibly, from a rapid decrease in albedo associated with thawing of the northern North Atlantic when northern summers came to coincide with terrestrial perihelion (*15*).

The resolution of rapid climatic events, which is not better than about 3,000 years in deep-sea sediments of normal globigerina-ooze facies, may be much greater in other deposits. Using marine shells (food refuse) from the Haua Fteah cave of Cyrenaica, Emiliani *et al.* (*16*) were able to reconstruct the trend of both summer and winter temperatures during the past 15,000 years and to show that much of the temperature rise during the anathermal 2/1 was very rapid indeed (see Fig. 2).

An excellent resolution may be offered also by speleothems, as noticed by Hendy and Wilson (*17*). Fornaca-Rinaldi *et al.* (*18*) and Duplessy *et al.* (*19*) discussed the various factors affecting the oxygen and carbon isotopic composition of speleothems. Fornaca-Rinaldi *et al.* (*18*) obtained an average oxygen isotopic composition of −5.8 per mil from a stalagmite grown upon a Roman tile in a cave near Siena, Tuscany; Labeyrie *et al.* (*20*) and Duplessy *et al.* (*19*) obtained values of about −6 per mil for modern stalagmites in caves in the region of Nîmes, southern France; and Hendy and Wilson (*17*) obtained values of −3.5 per mil for the modern layers of a stalactite from the Waitomo caves, about 30 km inland from the west coast of the North Island, New Zealand. These values, compared with the regional oxygen isotopic composition of atmospheric precipitation [−7, −7, and −4.5 per mil, respectively; see (*21*)] and the regional temperatures (average, 15°, 16°, and 15°C, respectively), clearly indicate that the speleothem calcite has been deposited at, or close to, isotopic equilibrium in all cases.

The speleothems from the Waitomo caves of New Zealand, analyzed by Hendy and Wilson (*17*), extend from modern time to the last interglacial, as shown by C^{14} and O^{18}/O^{16} analysis (*17*, figures 1, 2, and 3; this report, Fig. 1). The O^{18}/O^{16} ratio ranges from −3.7 per mil for the postglacial hypsithermal to −2.5 per mil for the maximum of the last glaciation. The difference is thus 1.2 per mil. A similar glacial-interglacial difference (1.3 per mil) is exhibited by the stalagmite from southern France analyzed by Duplessy *et al.* (*22, 23*). This stalagmite extends from the temperature peak of the last interglacial (age 5) to the end of the preceding interglacial (end of age 7), as shown by the O^{18}/O^{16} values and by Th^{230}/U^{234} dating (Fig. 1). A layer near the top, 77 cm thick and ranging in age from 91,000 to 97,000 years B.P., gave O^{18}/O^{16} values ranging from −5.5 to −6.3 per mil, with a weighted average of −5.9 per mil (*22*, table 1). This average is identical to the values mentioned above for the modern stalagmite from the same cave (*19*), indicating deposition under similar conditions. The underlying 1-m thick layer, ranging in age from 97,000 to about 122,000 years, has an O^{18}/O^{16} composition ranging from −4.5 to −5.2 per mil, with a weighted average of −4.6 per mil. This average is 1.3 per mil heavier than that of the layer above. In the bottom layer, about 32 cm thick and ranging in age from 122,000 to 130,000 years B.P., the O^{18}/O^{16} ratio increases

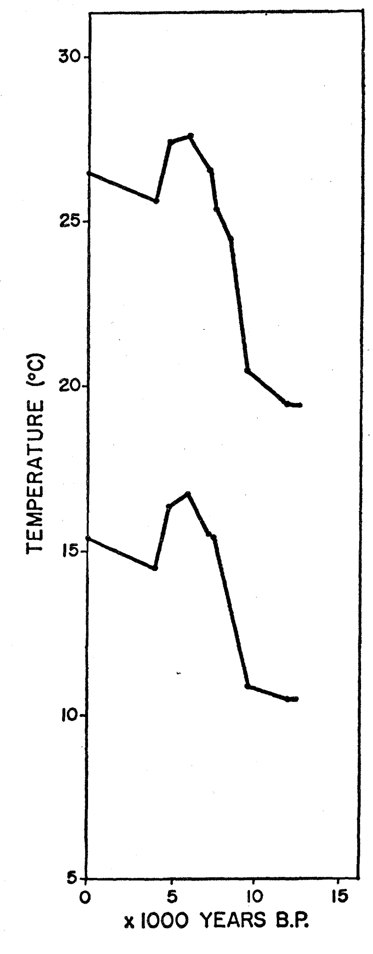

Fig. 2. Changes in summer (upper curve) and winter (lower curve) temperatures during the last deglaciation in the Mediterranean [from (*16*)].

back in time to a value of -5.9 per mil, again identical to the modern value. It is apparent that the bottom layer of this stalagmite was deposited toward the end of age 7, the intermediate layer during age 6, and the top layer during the temperature maximum of age 5. The oxygen isotopic trend of the speleothems from both southern France and New Zealand parallels closely that of the generalized paleotemperature curve (Fig. 1) obtained from the deep-sea cores.

The Th^{230}/U^{234} analysis of the stalagmite from southern France, which is discussed by Duplessy *et al.* (*22*) and which is apparently quite accurate (*24*), dates a temperature decline from 130,000 to 120,000 years ago (end of age 7); a major glaciation from 120,000 to 97,000 years B.P. (age 6); and a major interglacial maximum from 97,000 to 91,000 years B.P. (temperature maximum of age 5). This chronology is identical to that of the deep-sea cores and provides an important, independent verification. In addition, it pinpoints the age of anathermal 6/5 at 97,000 years B.P. and the age of the stage 5 hypsithermal at 95,000 years B.P.

Absolute dating of this stalagmite also shows a considerable variation in calcite precipitation rates [see (*24*)], averaging 3.2 cm per 1000 years between 120,000 and 100,000 years ago (glacial age 6) and 14.5 cm per 1000 years from 100,000 to 92,000 years B.P. (mostly interglacial age 5). Particularly high rates (60 cm per 1000 years) seem to have occurred between 93,000 and 92,000 years B.P., during the first minor temperature minimum immediately following the temperature maximum of age 5. In maritime regions such as southern France, Italy, and New Zealand, it seems likely that, judging from the generally dry state of the caves today (partly produced by regional deforestation, however), speleothem accumulation was maximum during minor interglacial temperature decreases, minimum during glacial ages (*25*), and intermediate otherwise.

The particular significance of the work on speleothems discussed above is threefold: (i) it reveals very clearly the major glacial-interglacial climatic variations; (ii) it affords a greater time resolution than deep-sea deposits; and (iii) it provides an absolute time scale independent of the one obtained from the deep-sea sediments. The results presently available confirm that age 7 ended about 120,000 years ago; age 6 extended from 120,000 to 97,000 years ago; and the major temperature maximum of age 5 dates from 95,000 years ago. Thus, the time scale of Rosholt *et al.* (*9*) and of Rona and Emiliani (*10*) is closely verified for this important time interval.

C. EMILIANI

School of Marine and Atmospheric
Sciences, University of Miami,
Miami, Florida 33149

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Protein–Metal Ion Binding Site: Determination with Proton Magnetic Resonance Spectroscopy

Abstract. *Proton magnetic resonance spectra of aqueous gelatin were analyzed with respect to composition and molecular interactions. Aqueous gelatin complexes cobaltous ions in the* pD *range of ~3.5 to 7.5. Glutamyl and aspartyl side chains are shown to be the sites of binding.*

Proton magnetic resonance (PMR) has become increasingly used in the study of macromolecular systems. Attempts have been made to understand the discouragingly broadened, still "high-resolution," spectrum which is often typical of the proton resonance of proteins in solutions (*1*). I now report a technique which has enabled the unambiguous identification of metal-binding sites of a biological polyelectrolyte and which may have promise in the study of metal-activated enzymes and other metallo-proteins.

I have obtained a rather promising fit to the 100-Mhz PMR spectrum of a random-coil protein (*2*) (gelatin) solution. This has been achieved by considering the superposition of the side-chain resonances which were determined by examining the PMR spectra of model compounds such as homopolypeptides, protein derivatives, and amino acids (*3*). Briefly, with a knowledge of the amino acid composition, the integrated intensity of each resonance pattern is scaled relative to a known reference peak from the spectrum (the unresolved methyl resonances of leucine, isoleucine, and valine at highest