

tives to a solution of **2** in  $\text{CDCl}_3$ , benzene- $d_6$  or *p*-xylene- $d_{10}$ , a second set of signals appears in the  $^1\text{H}$  NMR spectra: a new capsule species is formed (Fig. 2*b, e*). In addition to the second set of signals for the capsule (host), a new set of upfield signals for the encapsulated guests emerges. These appear in the region 0.5 to -0.5 p.p.m. for the adamantanes, and 3.5 to 2.5 p.p.m. for the ferrocenes (additional spectra are available as supplementary information). Integration shows that the ratio of the new hosts to the encapsulated guests is 1:1. Moreover, the widely separated and relatively sharp signals for free and encapsulated guest in the NMR spectra indicate that exchange of guests in and out of the capsule is slow on the NMR scale. The relative concentrations of the original (solvent-occupied) and new (guest-occupied) capsules can be determined by signal integration. These values can be obtained for various guests as a function of temperature (Fig. 2*c, f*); equilibrium constants and their thermodynamic parameters can be determined from this procedure (Table 1).

The most significant observation is that guest encapsulation increases with temperature. As most processes involving host-guest association are entropically unfavourable but enthalpically favourable, the trends for **2** are unexpected. Indeed, much has been written about the compensating effects of entropy and enthalpy in complex formation<sup>8-10</sup>, but for **2** the inclusion of guests involves an enthalpic cost, which is compensated by a larger entropic gain. This behaviour is reminiscent of the classical hydrophobic effect, in which release of bound water to the bulk solvent compensates for the association of solutes. In organic media, such behaviour is rarely encountered and generally unpredictable<sup>11-13</sup>, even though liberation of solvent is a universal feature of molecular recognition phenomena in solution. What is special about the case at hand?

It is proposed that for **2**, a single solvent molecule is too small to fill the cavity. Rather, more than one  $\text{CDCl}_3$  or *p*-xylene is required to maximize the intermolecular forces (van der Waals interactions) between the convex surfaces of the guests and the concave surface of the host's interior. Now single molecular guests that fill the cavity and offer chemical and structural complementarity are entropically preferred to multiple solvent molecules; one guest releases several solvent molecules. Consequently, the encapsulation of adamantanes or ferrocenes by **2** increases entropy, because more than one molecule of solvent is released to the bulk solution (Fig. 3*a*). Release of solvents on the surface of the guest as encapsulation proceeds will reinforce the observed increases in enthalpy and entropy. Spectra taken in mixtures of two solvents ( $\text{CDCl}_3/\text{CD}_2\text{Cl}_2$  and toluene- $d_6/p$ -xylene- $d_{10}$ ) showed only a single (rather than two<sup>14</sup>) capsule species. Apparently, the spectra of the variously occupied capsules in these solvents are not resolved at the 500 MHz of the spectrometer. However, in mixtures of fully deuterated benzene and fluorobenzene, three species of capsule can be observed, a result that confirms the occupancy of the capsule with two solvent molecules (Fig. 3*b-d*).

The ability of **2** to host more than one guest suggests that its cavity is roomy enough to act as a reaction chamber for bimolecular reactions. It will be interesting to determine whether catalysis of reactions with transition states of the appropriate size shape and functionality can be observed within the capsule<sup>15,16</sup>. □

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ACKNOWLEDGEMENTS. We are grateful for advice and experimental help from R. Meissner, and for financial support from the NIH.

CORRESPONDENCE and requests for materials should be addressed to J.R. at The Scripps Research Institute, 10550 N. Torrey Pines Rd., La Jolla, California 92037, USA.

## Deglacial sea-level record from Tahiti corals and the timing of global meltwater discharge

Edouard Bard\*†, Bruno Hamelin\*, Maurice Arnold‡, Lucien Montaggioni§, Guy Cabioch||, Gérard Faure¶ & Francis Rougerie#\*☆

\* CEREGE, Université d'Aix-Marseille III, URA CNRS 132, Europôle de l'Arbois, BP 80, Aix-en-Provence cedex 4, France

† Institut Universitaire de France

‡ Centre des Faibles Radioactivités, CNRS-CEA, 91198 Gif-sur-Yvette cedex, France

§ Centre de Sédimentologie et de Paléontologie, Université de Provence-St-Charles, 3 Pl. V. Hugo, 13331 Marseille cedex 3, France

|| ORSTOM-TOA, UMR CNRS-ORSTOM GéoAzur (EP 1.25), BP 48, 06230 Villefranche-sur-Mer, France

¶ Laboratoire d'Hydrobiologie Marine, Université de Montpellier II, case 096, Pl. E. Bataillon, 34095 Montpellier cedex 5, France

# ORSTOM Centre de Papeete, Papeete, Tahiti, French Polynesia

THE timing of the last deglaciation is important to our understanding of the dynamics of large ice sheets<sup>1</sup> and their effects on the Earth's surface<sup>2,3</sup>. Moreover, the disappearance of the glacial ice sheets was responsible for dramatic increases in freshwater fluxes to the oceans, which probably disturbed the ocean's thermohaline circulation and, hence, global climate<sup>4-7</sup>. Sea-level increases bear witness to the melting of continental ice sheets, but only two such records—from Barbados<sup>8,9</sup> and New Guinea<sup>10,11</sup> corals—have been accurately dated. But these corals overlie active subduction zones, where tectonic movements are large and often discontinuous (especially in New Guinea), so the apparent sea-level records may be contaminated by a complex tectonic component. Here we date fossil corals from Tahiti, which is far from plate boundaries (and thus is likely to be tectonically relatively stable) and remote from the locations of large former ice sheets. The resulting record indicates a large sea-level jump shortly before 13,800 calendar years BP, which corresponds to meltwater pulse 1A in the Barbados coral records<sup>8,9</sup>. The timing of this event is more accurately constrained in the Tahiti record, revealing that the meltwater pulse coincides with a short and intense climate cooling event<sup>12-15</sup> that followed the initiation of the Bølling-Allerød warm period<sup>12-16</sup>, but preceded the Younger Dryas cold event by about 1,000 years.

The Barbados sea-level record<sup>8,9,17,18</sup> suggested that the last deglaciation was characterized by two brief periods of accelerated melting superimposed on a smooth and continuous rise of sea level with no reversals. These so-called MWP-1A and MWP-1B events (~14,000 and 11,300 calendar years BP, cal. yr BP) are thought to correspond to massive inputs of continental ice: for

Received 21 December 1995; accepted 29 May 1996.

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\* Present address: Observatoire Océanologique Européen de Monaco, Av. St Martin, MC-98000 Monaco.

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example,  $\sim 50\text{--}40\text{ mm yr}^{-1}$  is roughly equivalent to discharge rates of  $16,000\text{ km}^3\text{ yr}^{-1}$  for MWP-1A). A third meltwater pulse, smaller than the two other, was identified at  $\sim 7,600\text{ cal. yr BP}$  in a compilation of Caribbean corals together with the Barbados curve<sup>19</sup>.

Nevertheless, there are still some doubts concerning the reality of the meltwater pulses (see, for example, ref. 20). Indeed, the Barbados sea-level curve was obtained from three separate cores and within each core a nearly constant sea level rise is observed. Each of these segments is offset from the next, and these offsets constitute the two rapid meltwater surges. A similar problem arises for the third meltwater pulse<sup>19</sup> which corresponds to the junction between the data sets obtained for the Barbados drills and for other Caribbean corals collected by diving. In addition the sea-level jump evidenced in New Guinea ( $\sim 11,000\text{ cal. yr BP}$ ) is delayed by a few centuries when compared<sup>11</sup> to the one observed at Barbados. Furthermore, these two islands are located in active subduction zones where vertical movements result from discontinuous motion. Consequently, the assumption of constant uplift rates may only be a first-order approximation:  $0.34\text{ mm yr}^{-1}$  for Barbados<sup>8,9,18</sup> and  $1.9\text{ mm yr}^{-1}$  for the Huon peninsula in New Guinea<sup>10,11</sup>.

Reef cores recently taken by the French ORSTOM team at Tahiti provided an opportunity to obtain a new sea-level record in a completely different tectonic and hydro-isostatic setting than Barbados and New Guinea. Long vertical cores (drill holes P6 and P7, separated by 700 m) taken from the outer barrier reef flat protecting Papeete harbour show a sequence of reef carbonates overlying the basaltic substratum at 114 m core depth (that is, below the present sea level, Fig. 1). The P7 carbonate sequence is divided into two subunits separated by a clear unconformity with evidence of subaerial exposure at  $\sim 86\text{--}87\text{ m}$  depth.

$^{230}\text{Th}/^{234}\text{U}$  ages (Fig. 1) were measured with a VG-54-30 mass spectrometer fitted with an ion-counting Daly detector (CEREGE/Aix-en-Provence). The chemical and mass spectrometric techniques are similar to those previously described<sup>21,22</sup>. The  $2\sigma$  precision of the  $^{230}\text{Th}/^{234}\text{U}$  ages ranges from 30 to 60 years for ages between 8,000 and 14,000 cal. yr BP ( $^{230}\text{Th}/^{234}\text{U}$  ages are considered as equivalent to calendar ages<sup>17</sup>). The precision of the ages has been checked by measuring numerous replicates (Fig. 1; also see Supplementary Information). In particular, we performed five analyses of different pieces of the same coral specimen (sample P7-7 at  $\sim 56\text{ m}$  depth). The five  $^{230}\text{Th}/^{234}\text{U}$  ages agree with each other within the  $2\sigma$  errors, with an overall error on the mean ( $11,005\text{ cal. yr BP}$ ) of 12 yr and a maximum difference between replicates of  $\sim 30\text{ yr}$ .

Values of  $\delta^{234}\text{U}_i$  (that is,  $(\text{initial } ^{234}\text{U}/^{238}\text{U} - 1) \times 1,000$ ) obtained on the Tahiti corals are between 142 and 150‰ with a mean value of 147‰ and a standard deviation of 1.5‰ on 40 measure-

ments. This average is indistinguishable from the values measured on present-day sea water (144‰, standard deviation 4‰)<sup>23</sup> and recent corals<sup>11,17</sup>. This further confirms that the samples remained closed systems for U–Th in the past. The magnitude of the  $^{14}\text{C}$ – $^{230}\text{Th}$  age difference observed on the Tahiti corals agrees well with previous studies of corals<sup>11,17,24</sup> and varved sequences<sup>25</sup>.

The species assemblages of several types of organisms (for example, corals, encrusting algae, sessile foraminifers and verme-

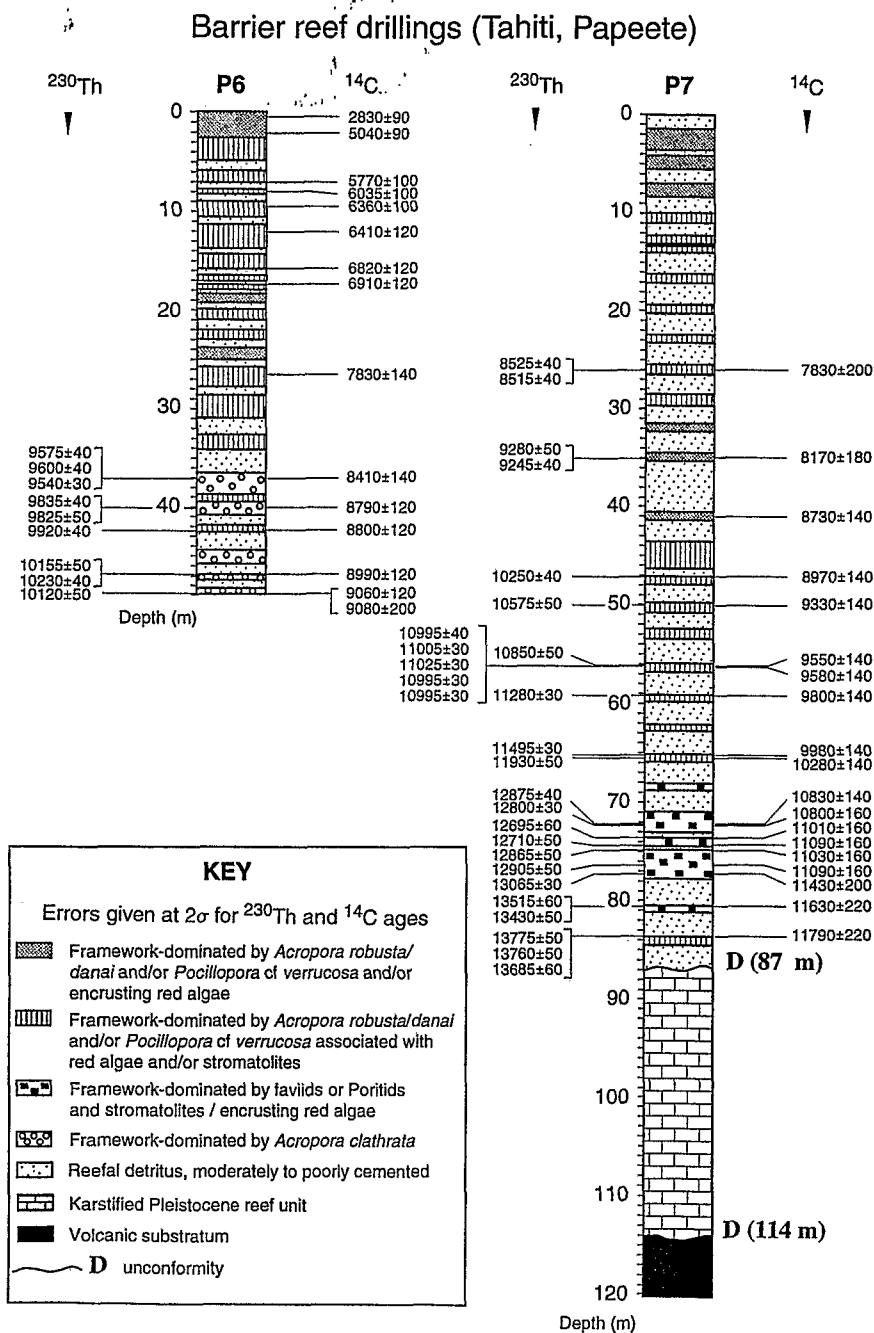


FIG. 1 Simplified representation of cores P6 and P7 from Papeete outer barrier reef flat. Details of the reef sedimentology and palaeoecology will be published elsewhere (L.M. *et al.*, manuscript in preparation). Below the unconformity ('D' at 86–87 m), the Pleistocene subunit exhibits freshwater-induced diagenetic features: karstified reef and the presence of 100% low magnesium calcite rock. In the upper subunit, corals are well preserved and devoid of secondary high magnesium calcite infilling. U–Th and conventional  $^{14}\text{C}$  ages are indicated on the left and right sides, respectively. (The  $^{14}\text{C}$  ages were measured on the Tandemron accelerator installed at Gif-Sur-Yvette). Errors are given at  $2\sigma$ . The replicates are indicated by vertical lines. U–Th ages have been calculated with the following  $^{234}\text{U}$  and  $^{230}\text{Th}$  decay constants:  $\lambda_{234} = 2.835 \times 10^{-6}\text{ yr}^{-1}$  and  $\lambda_{230} = 9.195 \times 10^{-6}\text{ yr}^{-1}$ .  $2\sigma$  uncertainties on these values are about 2‰ and 8‰, respectively<sup>30</sup>. The tabulated data are available as Supplementary Information.

tid gastropods) have been studied in detail on P7 and P6 cores and will be presented elsewhere (L.M. *et al.*, manuscript in preparation). By analogy to the modern biotic reef zonation and ecology, these assemblages are diagnostic of a high water-energy reef front or upper fore-reef zone, at depths less than 6 m below mean sea level.

Figure 2 shows the relative sea-level history derived from the new Tahiti U–Th data and from the other published studies on Barbados<sup>8,9,18</sup> and New Guinea<sup>10,11</sup>. The small but systematic shifts can be attributed to different hydro-isostatic responses for the three sites<sup>2,3</sup>. The Tahiti sea-level curve can also be used to study in detail the timing of the last deglaciation and in particular to assess the existence of sea level jumps.

There is no detectable meltwater pulse at  $\sim 7,600$  cal. yr BP, but all three curves exhibit a change of deglaciation rate between 11,500 and 11,000 cal. yr BP, that is, at the time of MWP-1B. The age of the small sea-level step at Tahiti corresponds to the one observed at Barbados<sup>9,18</sup> but is significantly older by  $\sim 400$  yr than the one evidenced in New Guinea<sup>11</sup>. However, a straight line fits the Tahiti sea-level curve equally well when taking into account the uncertainty on the palaeodepths of sea-level indicators. This suggests that MWP-1B, if real, was smaller than previously thought<sup>8,18</sup>.

The last sample above the hiatus of the Tahiti record is dated at  $13,750 \pm 30$  cal. yr BP and  $11,790 \pm 220$   $^{14}\text{C}$  yr BP. New cores drilled in the Tahiti barrier reef confirm the presence of this discontinuity<sup>26</sup>. An *Acropora* sample found just above the hiatus in a new core gives an age of  $13,850 \pm 40$  cal. yr BP which further supports the results obtained in P7 (the contact with the karstified Pleistocene reef and the oldest coral are both deeper by  $\sim 7$  m than in core P7). These ages correspond precisely to the end of the first jump observed on the Barbados sea-level curve (MWP-1A). Indeed, a similar hiatus was also found in core RGF-12 from the Barbados collection, where a coral dated at  $30,230 \pm 160$  cal. yr BP was found just below a subaerial exposure overlaid by a continuous sequence starting at  $13,730 \pm 100$  cal. yr BP and  $11,780 \pm 180$   $^{14}\text{C}$  yr BP (refs 8, 9, 17, 18). The synchronism of the hiatuses in the Barbados and Tahiti cores provides strong support

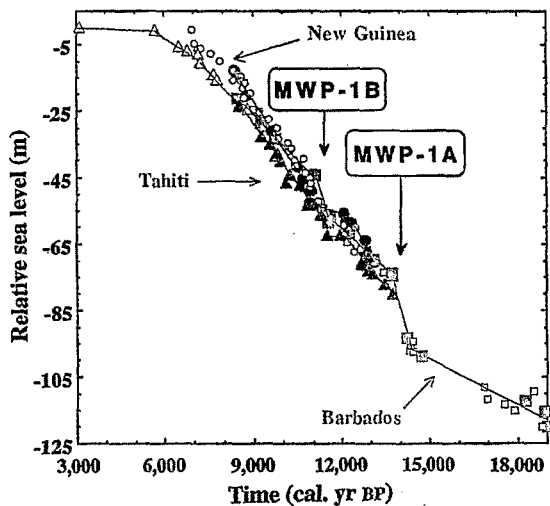


FIG. 2 Sea-level history reconstructed for long drill cores from Tahiti (red triangles), Barbados (blue squares)<sup>8,9,17,18</sup> and New-Guinea (green dots)<sup>10,11</sup>. For clarity, samples dated by  $^{14}\text{C}$  only<sup>10,18</sup> have been converted to calendar years by means of calibration formulas<sup>24</sup> and are represented with open symbols. Local movements were corrected for the different sites: tectonic uplift for Barbados ( $\sim 0.34$  mm yr<sup>-1</sup>; refs 8,18) and New Guinea ( $\sim 1.9$  mm yr<sup>-1</sup>; refs 10,11) and subsidence for Tahiti ( $\sim 0.2$  mm yr<sup>-1</sup>; refs 31,32). The basalt found below the P7 carbonate sequence has been dated at  $549 \pm 11$  kyr ( $2\sigma$ ) by K–Ar (H. Guillou, personal communication). The K–Ar age of the sample belonging to an aerial lava flow is compatible with a subsidence rate of  $\sim 0.25$  mm yr<sup>-1</sup> similar to what has been obtained by other authors<sup>31,32</sup>. Arrows indicate the median ages of MWP-1A and MWP-1B, first evidenced for Barbados<sup>8,9</sup>.

for the existence and importance of MWP-1A. At both locations older sections ( $>14,000$  cal. yr BP) of the sea-level records have to be looked for in cores further offshore. The jump is thus not an artefact due to using different cores to reconstruct sea level<sup>20</sup>. We show below that the core break at about  $14,000$  cal. yr BP should be merely considered as an additional argument for a major sea level jump.

We used a numerical model simulating the reef building in order to study the effect of a sea-level jump on the reef geometry. This simple modelling allows qualitative assessment of the effect of sea-level fluctuations on the reef shape and age–depth relationships. For the sake of simplicity, we used a constant slope for the initial topography and a simplified sea-level curve including a major sea-level jump at  $14,000$  cal. yr BP. Age–depth records in drill holes are calculated by the model. Deglaciation records provided by a series of cores have been simulated for different

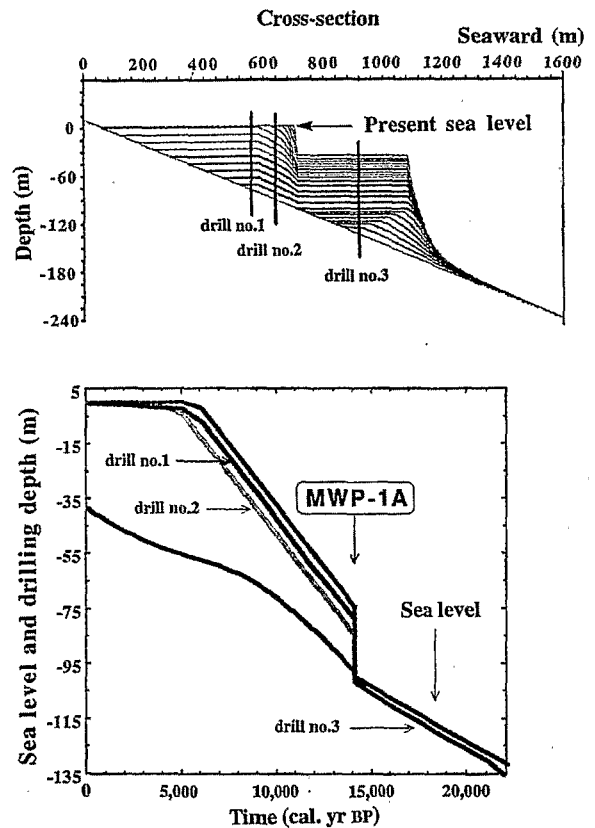


FIG. 3 Top panel, two-dimensional cross-section of a reef accreted on a simple topography (red line ramp) during the past 22,000 cal. yr BP. The x-axis is the distance seaward, and the y-axis is the depth (for graphical clarity the two scales are different). The input sea-level curve is shown on the lower panel (thick red curve). Each curve within the cross-section represents an isochron topography (the time step being 1,000 yr). For clarity, there is a colour code to distinguish the oldest from the youngest corals (green, 22,000–17,000; dark blue, 16,000–11,000; pink, 10,000–5,000; light blue, 4,000 cal. yr BP to the present). Equations of the model are similar to those in ref. 33. Details of the simulations will be presented elsewhere (E.B. *et al.*, manuscript in preparation). Vertical black lines show the positions of three vertical drills simulated by the model (drill no. 1 to drill no. 3). The coral age versus depth relationships in the drill holes are shown on the lower panel (drill no. 1, dark blue, drill no. 2, light blue, drill no. 3, green). Note that the palaeodepth of corals increases when the location of the drill is progressing seawards (drill nos. 1 and 2) but that the hiatus will always be at  $14,000$  cal. yr BP. Preliminary data on a new Tahiti drill deviated seaward<sup>26</sup> seem to confirm this scenario: the contacts with the karstified Pleistocene reef and the oldest coral ( $\sim 13,800$  yr BP) are both deeper ( $\sim 7$  m) than in core P7. In addition, preliminary data on biological assemblages suggest an increase of palaeodepth, as in the model. In simulation, drill no. 3 recovers deeper-living corals in the reef section corresponding to the past  $14,000$  cal. yr BP. In reality, these deeper living corals do not form continuous blankets and the chance of recovery is weak.

positions progressing towards the shore (Fig. 3). Up to a threshold, the age–depth relationship of a core always stops, with a hiatus, at a maximum age which corresponds precisely to the major sea-level step (drill holes 1 and 2). Only off-shore drilling enables to recover corals deposited before 14,000 cal. yr BP (drill hole 3). This simple approach clearly illustrates that a major sea-level jump creates a strong unconformity in the reef structure which is in turn responsible for the presence of a synchronous hiatus in cores drilled at different positions on the same reef. The presence of such an unconformity is thus an adequate explanation for the exact synchronism (with both  $^{230}\text{Th}$  and  $^{14}\text{C}$  chronometers) of the hiatuses observed for Barbados and Tahiti which cannot be accidental. The final step of this project should be to organize an expedition to drill off-shore Tahiti in order to sample corals which were living during the period between the Last Glacial Maximum and MWP-1A.

The existence of a major meltwater pulse shortly before 13,800 cal. yr BP must have dramatically changed the sea surface salinity and temperature distribution of the Atlantic Ocean and hence the thermohaline circulation which maintains a rather mild climate on the European continent. To evaluate the role of the melting history on the North Atlantic climate it is enlightening to plot the meltwater pulses on the same timescale as the Greenland ice  $\delta^{18}\text{O}$  profiles<sup>12</sup> and the  $\delta^{18}\text{O}$  record of deep-sea core SU81-18<sup>27</sup>. Figure 4 demonstrates that the sharp temperature rise at ~14,700 cal. yr BP cannot be a consequence of MWP-1A at ~14,000 cal. yr BP, as proposed recently<sup>19</sup> but criticized by Clark<sup>28</sup>. In fact, MWP-1A probably corresponds to the first major cooling event of the Bølling–Allerød period evidenced at ~13,800–13,900 cal. yr BP in the GRIP core. This event may be equivalent to the Older Dryas climate period<sup>29</sup>. The same cooling is also very clear at 14,000–14,100 cal. yr BP in the GISPII time series of  $\delta^{18}\text{O}$ <sup>15</sup>, ice accumulation rate<sup>13</sup> and electrical conductivity<sup>14</sup>.

The effect of an abrupt meltwater discharge on the temperature of the North Atlantic was recently studied with a coupled ocean–atmosphere general circulation model<sup>5</sup>. During the modelled meltwater pulse the thermohaline circulation and the North

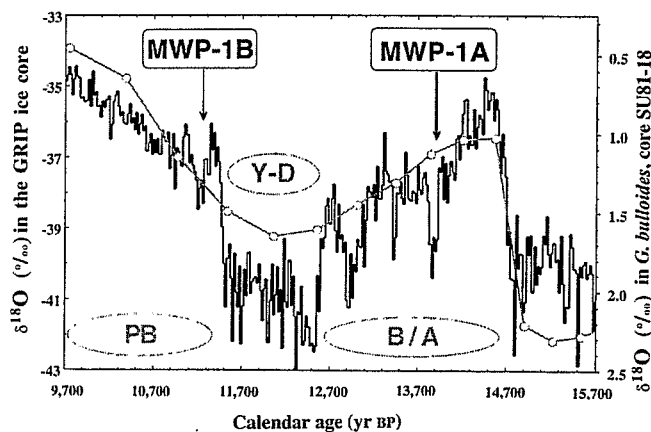


FIG. 4 The solid line represents the  $\delta^{18}\text{O}$  variations measured in the GRIP ice core<sup>12</sup> (numerical data provided by S. Johnsen, updated chronology from C. Hammer, personal communication) and the open dots show the planktonic foraminifera  $\delta^{18}\text{O}$  record of deep sea core SU81-18 raised at about 38° N in the Northeast Atlantic<sup>27</sup>. The SU81-18 chronology is based on more than 22 AMS- $^{14}\text{C}$  ages<sup>27</sup> converted to calendar years by means of calibration formulas<sup>24</sup>. The strong warming ( $\delta^{18}\text{O}$  increase at ~14,700 cal. yr BP in the Greenland ice) at the beginning of the Bølling–Allerød (B/A) period is synchronous with the sharp warming in core SU81-18 ( $\delta^{18}\text{O}$  decrease in the planktonic foraminifera which cannot be due to MWP-1A as proposed previously<sup>8</sup>). MWP-1A dated at ~14,000 cal. yr BP is significantly younger than the strong warming at 14,700 cal. yr BP. It corresponds to the first cold reversal of the Bølling–Allerød observed in the GRIP core (13,800–13,900 cal. yr BP<sup>12</sup>) and GISPII core (14,000–14,100 cal. yr BP<sup>13–15</sup>). MWP-1B (if real) could correspond to a small and abrupt cooling at about 11,300 cal. yr BP in the GRIP ice core<sup>12</sup>.

Atlantic surface temperatures weaken abruptly, then exhibit a complex transient behaviour consisting of an abrupt increase and decrease followed by a gradual recovery to the initial state. Similar transient oscillations can be observed (Fig. 4) in the  $\delta^{18}\text{O}$  profiles obtained for the Bølling–Allerød/Younger Dryas section of the GRIP ice core<sup>12</sup>. Although MWP-1A occurred about a millennium earlier than the start of the Younger Dryas cold period (~12,700 and ~12,900 cal. yr BP in the GRIP and GISPII chronologies), it could have acted as the initial trigger of transient perturbations of the thermohaline circulation of the North Atlantic: decadal–centennial oscillations ultimately leading to a millennium-long cold period, that is, the Younger Dryas event. □

Received 8 January; accepted 29 May 1996.

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ACKNOWLEDGEMENTS. We thank P. Clark, M. Field, H. Guillou, J. Guiot, S. Johnsen, J. Jouzel, M. Maia, D. Peteet and J. Récy for fruitful discussions and/or for critical review of the manuscript; B. Angeletti, W. Barthelemy, K. Claverie, P. Dejaradin, E. Kaltnecker, B. Laude, A. Laurenti, J. J. Motte, N. Tisnerat and K. Van de Velde for technical help; S. Johnsen for numerical data of  $\delta^{18}\text{O}$  in the GRIP ice core; H. Guillou for communicating his unpublished K/Ar age on the basalt in core P7. This study was supported by ORSTOM (Endo-Upwelling Program) and PNR. CEA and CNRS supported the AMS measurements.

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CORRESPONDENCE should be addressed to E.B. (e-mail: [ebard@arbois.cerege.fr](mailto:ebard@arbois.cerege.fr)).

## Large-scale structure at the core–mantle boundary from diffracted waves

Michael E. Wysession

Department of Earth and Planetary Sciences, Washington University, St Louis, Missouri 63130, USA

At the base of the Earth's mantle is a region, called  $D''$ , which serves as a thermal and chemical boundary layer between the silicate mantle and the liquid-iron outer core<sup>1,2</sup>. Tomographic models of mantle compressional-wave velocity ( $v_p$ ) have their worst resolution in  $D''$ , owing to limited ray sampling<sup>3–5</sup>, but have hinted at large-scale lateral variations there. Here I use a new technique, which has its greatest resolution within  $D''$ , to produce