tives to a solution of 2 in CDCl₃, benzene-d₆, or p-xylene-d₈, a second set of signals appears in the ¹H NMR spectra: a new capsule species is formed (Fig. 2c, 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. 2c, f); equilibrium constants and their thermodynamic parameters could be determined from this procedure (Table 1).

The most significant observation is that guest encapsulation increases with temperature. As more 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, 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, 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 CDCl₃ 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. 3c). 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 (CDCl₃/CDCl₆ or toluene-d₈/p-xylene-d₆) showed only a single (rather than two) 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. 3b–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 biomolecular 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.

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

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The timing of the last deglaciation is important to our understanding of the dynamics of large ice sheets and their effects on the Earth’s surface. 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. Sea-level increases bear witness to the melting of continental ice sheets, but only two such records—from Barbados and New Guinea—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. 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 that followed the initiation of the Bolling–Allerød warm period, but preceded the Younger Dryas cold event by about 1,000 years.

The Barbados sea-level record 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

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example, ~50–40 mm yr⁻¹ is roughly equivalent to discharge rates of 16,000 km² yr⁻¹ for MWP-1A. A third meltwater pulse, smaller than the two others, was identified at ~5,600 cal. yr BP in a compilation of Caribbean coral reef age determinations with the Barbados curve [3].

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 [6] 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 (~7,000 cal. yr BP) is delayed by a few centuries when compared 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 mm yr⁻¹ for Barbados [3,10] and 1.9 mm yr⁻¹ for the Huon peninsula in New Guinea [11].

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 ~86–87 m depth. ²³⁰Th/²³⁴U 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 [22]. The 2σ precision of the ²³⁰Th/²³⁴U ages ranges from 30 to 60 years for ages between 8,000 and 14,000 cal. yr BP (²³⁰Th/²³⁴U ages are considered as equivalent to calendar ages [3]). 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 ~56 m depth). The five ²³⁰Th/²³⁴U ages agree with each other within the 2σ errors, with an overall error on the mean (11,005 cal. yr BP) of 12 yr and a maximum difference between replicates of ~30 yr.

Values of ³⁶Cl/³⁵Cl (that is, (initial ²³⁴U/²³⁸U – 1) × 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 measurements. This average is indistinguishable from the values measured on present-day sea water (144‰, standard deviation 4‰) [23] and recent corals [12,13,14]. This further confirms that the samples remained closed systems for U-Th in the past. The magnitude of the ¹³C/¹²C-Th age difference observed on the Tahiti corals agrees well with previous studies of corals [12,13,14] and varved sequences [24].

The species assemblages of several types of organisms (for example, corals, encrusting algae, sessile foraminifers and verm...
tidal 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 Barbados9,18 and New Guinea10,11. The small but systematic shifts can be attributed to different hydro-isostatic responses for the three sites9. 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 ~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 Barbados9,18 but is significantly older by ~400 yr than the one evidenced in New Guinea11. 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 thought9,18.

The last sample above the hiatus of the Tahiti record is dated at 13,750 ± 30 cal. yr BP and 11,790 ± 220 14C yr BP. New cores drilled in the Tahiti barrier reef confirm the presence of this discontinuity19. An Acroropa sample found just above the hiatus in a new core gives an age of 13,850 ± 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 ~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 ± 160 cal. yr BP was found just below a subaerial exposure overlaid by a continuous sequence starting at 13,730 ± 100 cal. yr BP and 11,780 ± 180 14C yr BP (refs 8, 9, 17, 18). The synchronism of the hiatuses in the Barbados and Tahiti cores provides strong support 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 level20. 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

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**FIG. 2** Sea-level history reconstructed for long drill cores from Tahiti (red triangles). Barbados (blue squares)9,10,17,18 and New Guinea (green dots)10,11. For clarity, samples dated by 14C only9,18 have been converted to calendar years by means of calibration formulas24 and are represented with open symbols. Local movements were corrected for the different sites: tectonic uplift for Barbados (~0.34 mm yr⁻¹; refs 8, 18) and New Guinea (~1.9 mm yr⁻¹; refs 10, 11) and subsidence for Tahiti (~0.2 mm yr⁻¹; refs 31, 32). The basalt found below the P7 carbonate sequence has been dated at 549 ± 11 ky (2σ) 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 ~0.25 mm yr⁻¹ similar to what has been obtained by other authors10,11. Arrows indicate the median ages of MWP-1A and MWP-1B, first evidenced for Bardados9,18.

**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 seaward26 seem to confirm this scenario: the contacts with the karstified Pleistocene reef and the oldest coral (~13,800 yr BP) are both deeper (~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 230Th and 14C 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 δ18O profiles13 and the δ18O record of deep-sea core S81-1827. 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 recently21 but criticized by Clark22. In fact, MWP-1A probably corresponds to the first major cooling event of the Bolling–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 period22. The same cooling is also very clear at 14,000–14,100 cal. yr BP in the GISP2 II time series of δ18O22, ice accumulation rate23 and electrical conductivity24.

The effect of an abrupt meltwater discharge on the temperature of the North Atlantic was recently studied with a coupled ocean–atmosphere general circulation model3. During the modelled meltwater pulse the thermohaline circulation and the North 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 δ18O profiles obtained for the Bolling–Allerød/Younger Dryas section of the GRIP ice core13. 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 GISP2 II 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.

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

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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 core2. Tomographic models of mantle compressional-wave velocity (vP) have their worst resolution in D’, owing to limited ray sampling3–4, but have hinted at large-scale lateral variations there. Here I use a new technique, which has its greatest resolution within D’, to produce