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A high-resolution record of atmospheric ^{14}C based on Hulu Cave speleothem H82

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ABSTRACT

The development of a calibration of atmospheric radiocarbon ($\Delta^{14}C$) is a significant scientific goal because it provides the means to link the numerous ^{14}C dated paleoclimate records to a common timescale with absolutely dated records, and thereby improve our understanding the relationships between the carbon cycle and climate change. Currently, few calibration datasets that directly sample the atmospheric ^{14}C reservoir are available beyond the end of the dendro-dated Holocene tree ring record at 12.6 kyr BP (Before 1950 AD). In the absence of suitable true atmospheric records, ^{14}C calibrations beyond this age limit are based largely on marine data, that are complicated by the marine reservoir effect, which may have varied over the glacial cycle. In this paper, we present a high-resolution record of U–Th series and ^{14}C measurements from Hulu Cave speleothem H82, spanning 10.6–26.8 kyr BP. Corrections for detrital ^{230}Th are negligible, and the contribution of ^{14}C-free geologic carbon to the speleothem calcite is small (5–6%) and is stable across major climate shifts. The time series provides a 16 kyr record of atmospheric $\Delta^{14}C$ as well as an updated age model for the existing Hulu Cave $\delta^{18}O$ record. The ^{14}C data are in good overall agreement with existing marine and terrestrial ^{14}C records, but comparisons with the Cariaco Basin marine $\Delta^{14}C$ record through the deglacial interval reveal that the Cariaco reservoir age appears to have varied during parts of the Younger Dryas and Heinrich Stadial 1 cold events. This highlights the importance of developing extended high-resolution marine and terrestrial ^{14}C records as a means of detecting changes in ocean circulation over the glacial cycle.

1. Introduction

Reconstruction of a high-resolution radiocarbon (^{14}C) record that directly samples atmospheric CO_2 through the last glacial cycle, tied to a robust independent timescale, has been a long-time goal of the scientific community. Atmospheric concentrations of ^{14}C ($\Delta^{14}C$, expressed as per mil deviations from a modern reference standard) have varied over time due to changes in production and the partitioning of ^{14}C between reservoirs of the earth's carbon cycle, and must be calibrated against a calendar timescale for use as a chronometer. Independently dated ^{14}C calibration records provide the means to link the numerous ^{14}C dated paleoclimate records to a common timescale with absolutely dated archives such as layer counted ice cores. Additionally, when corrected for production variations, atmospheric ^{14}C records can be used to trace carbon cycle and ocean circulation changes via comparisons with archives of surface and deep ocean ^{14}C. Such comparisons can lead to an improved understanding of the history of the carbon cycle and a more precise knowledge of its role in climate change.

Few ^{14}C calibration data that directly sample the atmospheric ^{14}C reservoir are available beyond the end of the dendro-dated master tree ring record, which presently extends to 12.6 kyr BP calendar (Reimer et al., 2009). A recently published Huon pine ^{14}C record (Hua et al., 2009) bridges the gap between the master tree ring series and a 1400-year floating Allerød pine sequence (Kromer et al., 2004), extending the tree ring record to approximately 14 kyr BP. A few additional older floating sequences are available back into Marine Isotope Stage 3, most notably New Zealand kauris (Turney et al., 2007), but the distribution of ages for trees recovered so far is patchy (A. Hogg, pers. comm.) and it is unclear whether sufficient trees will be found to produce a continuous record. Terrestrial macrofossils in varve-counted cored sediments from Lake Suigestu in western Japan may ultimately fill this data gap (Nakagawa et al., 2011), but comparison of the existing Suigetsu data (Kitagawa and van der Plicht, 2000) with other records shows that varves are missing and/or that core recovery was incomplete (Staff et al., 2010).

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In the absence of suitable true atmospheric records, ^{14}C calibrations beyond 12.6 kyr are largely based on marine data. Several coral data sets with independent $^{234}U-^{230}Th$ (U–Th) chronologies exist (Bard et al., 1990, 1998, 2004; Edwards et al., 1993; Burr et al., 1998, 2004; Cutler et al., 2004; Fairbanks et al., 2005), but these are almost all "spot" measurements, and the records contain numerous gaps. In contrast, foraminifera records in marine sediments from the Cariaco Basin (Hughen et al., 2004, 2006) and Iberian Margin (Bard et al., 2004) are essentially continuous, but apart from the 10–15 kyr BP interval of the Cariaco record which has its own varve timescale (Hughen et al., 2004), they must be dated indirectly by correlation with other records via sediment color or $\delta^{18}O$ stratigraphy. This is particularly difficult for the period 15–24 kyr BP because the $\delta^{18}O$ records from the layer counted Greenland ice core (Grootes and Stuiver, 1997; NGRIP Members, 2004), which provide the chronostratigraphy for so many marine sequences, contain few high resolution features in this interval that can be convincingly correlated with other records.

These marine records are subject to possible variations in the ocean-atmosphere ^{14}C offset (marine ^{14}C reservoir age), which represents a ^{14}C balance between the effects of air-sea gas exchange and the upwelling and mixing of radiocarbon-depleted subsurface waters into the local mixed layer. Records for ^{14}C calibration are chosen from low-latitude locations thought to be least sensitive to possible reservoir age changes (Reimer et al., 2009). However, comparisons of early Younger Dryas ^{14}C data (Muscheler et al., 2008) suggest that the Cariaco record, and perhaps subtropical North Atlantic ^{14}C archives generally, may have been anomalously young when the Atlantic Meridional Overturning Circulation was weakened, as may have occurred in the early Younger Dryas (YD) and Heinrich Stadial 1 (HS1) (McManus et al., 2004). Modeling results (Butzin et al., 2005; Singarayer et al., 2008; Ritz et al., 2008) support this conjecture, though the effect observed in Cariaco is unexpectedly large. In addition, the presence of extremely ^{14}C-depleted waters at depths above 1500 m during the YD and HS 1, at various sites in the North Atlantic, Pacific and Indian Oceans (Voelker et al., 1998; Sikes et al., 2000; Robinson et al., 2005; Marchitto et al., 2007; Stott et al., 2009; Bryan et al., 2010) suggests that large increases in regional reservoir ages may have occurred at some locations if those waters reached the surface. These variations can potentially give valuable insights into past carbon cycle and ocean circulation changes, but their presence may confound the use of marine-based ^{14}C records for radiocarbon calibration for at least some intervals within the glacial.

This highlights the fact that in the absence of detailed knowledge of how ^{14}C offsets between different carbon reservoirs have varied over time, attempts to derive the history of atmospheric ^{14}C using archives that sample other carbon pools can only succeed for intervals where disparate records are in good agreement. Intervals of disagreement may ultimately provide valuable insights into changes in pool-to-pool ^{14}C gradients and therefore into ocean circulation and carbon cycle dynamics, but it is not possible to know definitively which (if any) of the apparently inconsistent radiocarbon records truly represents atmospheric ^{14}C. However, with a sufficiently large number of datasets it becomes easier to distinguish consensus values. Thus, a key to better understanding of the history of atmospheric ^{14}C, marine reservoir ages, and past carbon cycle dynamics, is the development of multiple records of ^{14}C from different carbon reservoirs with robust independently dated calendar timescales.

Speleothems are cave calcite deposits precipitated from drip water, that represent a potential source of temporally well constrained atmospheric ^{14}C records, because an absolute chronology can be assigned using U–Th series dating with a correction for any detrital Th initially incorporated into the crystal matrix. Meteoric waters above the cave react with soil CO_2, which is present at elevated concentrations (pCO_2) due to biological activity and is in isotopic equilibrium with the atmosphere on annual to decadal timescales (Trumbore, 2000). This reaction forms carbonic acid, which drives carbonate dissolution as the water percolates through the cave host bedrock. As drip waters enter the cave, CO_2 degassing occurs, due to the lower pCO_2 of cave air relative to the drip water, leaving excess carbonate alkalinity that is precipitated as speleothem carbonate. Drip waters will initially be close to saturation for soil CO_2, with ^{14}C values essentially those of the contemporary atmosphere, but as they interact with the host bedrock, they will accumulate a percentage of ^{14}C free or 'dead' carbon, which will be reflected in the radiocarbon ages of the speleothem calcite. If the drip waters equilibrate in a closed system, one mole of carbonate is required to neutralize one mole of dissolved CO_2, and the dead carbon fraction (DCF) is 50%; whereas under completely open conditions where drip waters continue to exchange CO_2 with an essentially infinite soil gas reservoir as carbonate dissolution takes place, the DCF approaches zero (Hendy, 1971). In practice, dissolution takes place under conditions that are intermediate between these end points.

A correction of the DCF can be determined in a similar manner to a reservoir age for a marine record, by comparing speleothem ^{14}C measurements on samples of known calendar age with the tree ring record of atmospheric ^{14}C during a period of overlap. The offset between the datasets is then subtracted throughout the remainder of the record to produce a DCF corrected atmospheric ^{14}C record. This procedure involves the implicit assumption that the correction has remained constant through time. As shown below, comparison with tree ring records indicates that the DCF correction in H82 did remain constant across the Allerød/Younger Dryas and Younger Dryas/Holocene transitions, though the reason for this stability is unclear. Despite the lack of a detailed explanation, the stability of the DCF correction across major climate shifts that likely involved significant changes in hydrology and soil carbon dynamics suggests empirically that a constant DCF correction may be valid for some speleothem records extending further back in time.

The first high-resolution speleothem-based record of atmospheric ^{14}C, spanning 11–45 kyr BP, was measured on speleothem samples from a now submerged cave in the Bahamas (Beck et al., 2001). This stalagmite exhibits relatively high levels of detrital thorium that create significant uncertainty in the absolute chronology, plus a large DCF of 1.5 kyr, and the record deviates significantly from the tree ring data during the Younger Dryas. Nevertheless, agreement with other ^{14}C records is typically within a few ^{14}C hundred years back to 25 kyr BP. Beyond 33 kyr BP, the record displayed very large ^{14}C excursions, whose origin was initially unexplained but ultimately traced to problems with subtraction of laboratory ^{14}C backgrounds (Hoffmann et al., 2010). A new record from the same cave with well characterized blank corrections displays much better agreement with other ^{14}C calibration data beyond 33 kyr BP (Hoffmann et al., 2010) but the uncertainties associated with the large Th and DCF corrections remain high, and the question remains of the precision with which speleothems can be used as meaningful sources of atmospheric ^{14}C records.

To investigate the efficacy of speleothem based reconstructions of atmospheric ^{14}C records, it is clear that studies must be made on speleothems of more pristine calcite. The Hulu Cave speleothems, which are from the region of Eastern China currently influenced by the East Asian Monsoon and have been used to create a high-resolution record of $\delta^{18}O$ as a proxy for monsoon strength (Wang et al., 2001; Wu et al., 2009), represent an excellent opportunity to carry out such a test. Here we present a new record of atmospheric ^{14}C based on the Hulu Cave speleothem, H82, spanning 10.7–26.6 kyr BP.

2. Material and methods

The Hulu Cave site at Tang Shan in eastern China near Nanjing (32°30′N, 119°, 90 m asl), is overlain by 30–40 m of limestone, with 30–40 cm of soil consisting mainly of weathered carbonate debris with a <5 cm upper layer of clays and organic matter, that currently supports subtropical C3 vegetation (Kong et al., 2005). 80% of the precipitation at the cave site occurs during the summer monsoon season (Wang et al., 2001), and monitoring by the Nanjing Normal University group has shown that drip rates respond rapidly to changes in rainfall. The 35 cm long speleothem H82 was collected from 35 m depth in Hulu Cave in two sections (A and B + C in Fig. 1) that were recovered on separate expeditions led by Y.W. The upper ~17 cm of the speleothem is cylindrically shaped with a flat top, and represents the upward extension of one of two fused adjacent stalagmites that together form the lower section. Both sections show wax luster, and well-preserved growth laminations are present from the top of the speleothem through 30 cm (Wu et al., 2009). Previous U–Th work on the upper part of the speleothem (Wang et al., 2001; Yuan et al., 2004; Wu et al., 2009) has shown that detrital thorium corrections are negligible, which allows a robust U–Th chronology to be constructed

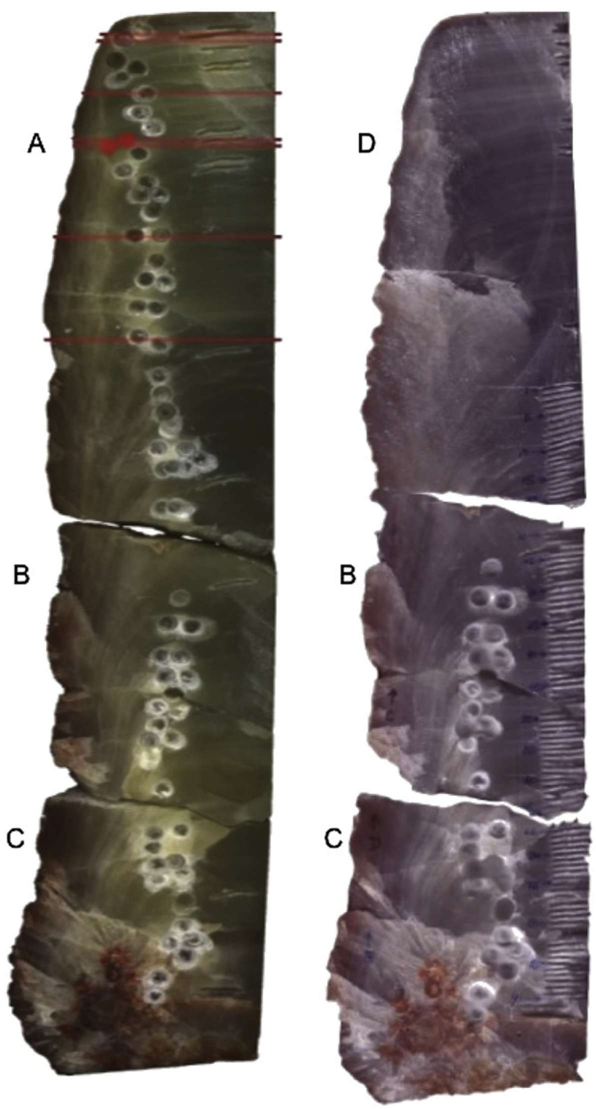

Fig. 1. The H82 speleothem: two photographs showing sampling done for this project. The speleothem was removed from Hulu Cave in two separate expeditions as Piece A and one continuous Piece B + C, which later broke into two sections. Piece D is a 1 cm slice taken from the right-hand side of piece A, as is evidenced by the matching scars. Pieces B, C, and D were sampled using a trench and wall method as described in the text. Trench and wall sampling for the upper 138 mm was carried out on a different quadrant (not shown). Pieces A, B, and C were also sampled off axis using a 3 mm ID coring drill.

Prior to the work described here, the H82 stalagmite had already been sectioned into quadrants and extensively sampled for stable isotope analysis and U–Th dating (Wang et al., 2001; Wu et al., 2009). Most of the sampling for this study was carried out for stalagmite depths 1–138 mm and 131–311 mm in two separate campaigns at University of Minnesota, using a 'trench and wall' method that produced series of closely interleaved U–Th and ^{14}C dates (Tables S1 and S2). Parallel trenches several mm deep by ~1 cm long, separated by 1 mm thick walls, were drilled perpendicular to the growth axis using a Dremel tool, to sample over approximately 1 mm of stalagmite depth (Fig. 1). Powdered calcite samples weighing between 100 and 200 mg from the trenches were used for U–Th measurements. The ^{230}Th dating work was performed on a multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS, Thermo-Finnigan Neptune) in the Minnesota isotope laboratory, University of Minnesota. The chemical procedures used to separate the uranium and thorium for ^{230}Th dating are similar to those described in Edwards et al. (1987). Uranium and thorium isotopes were analyzed on the multiplier behind the retarding potential quadrupole (RPQ) in peak-jumping mode. Instrumental mass fractionation was determined by measurements of a ^{233}U–^{236}U spike. The details of the technique are similar to those described in Cheng et al. (2000, 2009a,b), and half-life values are described in Cheng et al. (2008).

Intervening calcite walls between the trenches were removed as wafers for ^{14}C measurements at University of California Irvine in the Keck Carbon Cycle Accelerator Mass Spectrometry (AMS) Laboratory. Chips from the wafers were used for ^{14}C because we found that drilled powder from the dense H82 calcite gave ^{14}C ages that are systematically younger. This effect has been seen in work on some other speleothems and may be due to pickup of atmospheric CO_2 due to local overheating during drilling (W. Beck, T. Guilderson pers. comm.). A lower resolution wet coring method was used for an earlier ^{14}C sampling series covering the entire stalagmite length, with samples removed as cores 3 mm in diameter, drilled some distance from the growth axis (Fig. 1). ^{14}C results from the cores, plus a few measurements on leftover calcite chips sampled for some of the early U–Th work, are given in Table S2.

Aliquots of calcite wafers or cores for AMS measurements were crushed into sub-millimeter pieces to achieve a desired mass of carbon (typically 12–14 mg of calcite), and pretreated by leaching away 30% of the material in weak HCl. Sample were then hydrolyzed in 85% H_3PO_4 and graphitized by iron catalyzed hydrogen reduction following standard AMS protocols. Prior to graphitization, all sample reactors were baked at 500 °C for 45 min with ~ 1 atm. of ^{14}C-free CO_2 to reduce any memory effects from modern carbon (Southon, 2007). ^{14}C measurements were carried out on an NEC Compact (1.5 SDH) AMS system, using six aliquots of Oxalic Acid 1 as the normalizing standard. Each mg-sized carbon sample was measured multiple times (typically 8 to 15 runs) over a 24 h period, and 41 samples out of a total of 260 are duplicate aliquots. Geologic calcite and aliquots of Hulu Cave speleothem MSX (U–Th dated at 135 kyr), of similar size to the H82 samples and similarly processed, were used as procedural blanks. Leftover portions of calcite wafer and core samples taken for ^{14}C were measured for stable isotopes to allow detailed correlations to be made between high-resolution stable isotope records measured previously (Wang et al., 2001; Wu et al., 2009) and the densely dated records from the present study. Measurements were carried out at UC Irvine on samples of ~100 μg of powdered calcite, using a Finnigan Delta Plus IRMS equipped with a Kiel IV Carbonate Device.

3. Results

3.1. H82 age model

The U–Th results from the trench and wall samplings for this study, plus earlier lower resolution measurements (Wang et al., 2001; Yuan et al., 2004; Wu et al., 2009, plus unpublished data) are shown in Table S1 and Fig. 2. Data have been corrected for detrital thorium on the basis of an assumed initial $^{230}Th/^{232}Th$ atomic ratio of $4.4 \pm 2.2 \times 10^{-6}$ (Wang et al., 2001) and are shown as ages BP (before 1950 AD) with 2σ uncertainties. Fig. 2A and B shows, respectively, the speleothem age model before and after small depth adjustments explained in detail section 3.2, required for consistency between samples from different slabs and quadrants of calcite. No significant age reversals are present, and corrections for detrital Th are a few years above 300 mm, rising to a few decades near the speleothem base. The record displays two periods of very slow stalagmite growth or hiatus: one short gap at 263 mm between ~19.5 and 20.0 kyr BP and a second longer hiatus at 295 mm, between ~22.5 and 24.5 kyr BP. The latter corresponds with a hiatus previously identified by Wu et al. (2009) at 305 mm in a column cut from another quadrant of H82: the depth difference reflects the irregular nature of the growth surfaces in the bottom few cm. This hiatus occurs during Heinrich Event 2, which appears in the Hulu Cave $\delta^{18}O$ record (Wang et al., 2001) as a spike to less negative values. To the extent to which this can be interpreted as a period of especially low summer monsoon intensity, the extreme reduction in growth rate in H82 is consistent with the inferred reduction in precipitation.

3.2. Depth adjustments

Depths measured from the top of H82 to the center of each sample (mid depths) are shown in Tables S1 and S2. The samplings presented here were done on several different quadrants or slabs of calcite, and comparisons of U–Th and stable isotope ($\delta^{18}O$) data showed that several small adjustments were required to bring the data sets to a common depth scale on the quadrant cutting axis. We stress that these were not required for construction of the ^{14}C record, for which all calendar ages are based on direct interpolation between ^{230}Th ages measured on the same pieces of calcite. Instead, they were used to show consistency between the different samplings, and for placing published high-resolution stable isotope results (Wang et al., 2001; Wu et al., 2009) on the densely dated age model from the present study. These adjusted depths are also shown in Tables S1 and S2, and the unadjusted and adjusted age models are shown in Fig. 2. The three adjustments required are as follows:

i) The trench and wall sampling for depths 1–138 mm was taken somewhat off axis, where curvature of growth surfaces distorts the on-axis age vs depth relationship. These adjustments become significant for depths below 40 mm where the flat-topped region of H82 rather abruptly becomes significantly smaller and off-axis growth surfaces begin to crowd together and extend down the flanks of the speleothem (Fig. 1). The H82-A (^{14}C and $\delta^{18}O$) and H82-B (U–Th) records required compression by 8% below 40 mm to achieve consistency with the upper portions of the old U–Th chronology and the published high resolution $\delta^{18}O$ record (Wang et al., 2001).
ii) The H82-2 trench and wall samples for depths 130–310 mm were taken on axis, and the depths shown for off-axis core samples in Table S2 are equivalent on-axis depths determined by visually tracing growth surfaces back to the speleothem axis, hence similar adjustments are not required for these series. However, comparisons of $\delta^{18}O$ data from this study and from Wu et al. (2009) with a new high-resolution $\delta^{18}O$ record (R.L. Edwards pers. comm.) showed that the calcite pieces in Fig. 1 and the calcite column sampled by Wu et al. (2009) were both missing ~3 mm at a depth of 172 mm. This represents the break between the upper and lower sections of H82, that were collected from Hulu Cave at different times and sectioned independently, and in retrospect it is not surprising that some of the pieces thought to be contiguous were actually missing a few mm of calcite near the break. The 3 mm of missing calcite was inserted at 172 mm into all of the records used in this study, to ensure consistency with the upcoming new $\delta^{18}O$ data.
iii) Similar $\delta^{18}O$ comparisons suggested that the calcite column sampled for the lower portions of the old U–Th chronology and for the high-resolution Wu et al. (2009) $\delta^{18}O$ record was also compressed by 3 mm between 245 and 248 mm (248–251 mm after the initial adjustment at 172 mm). Detailed comparisons between the different $\delta^{18}O$ records across this interval

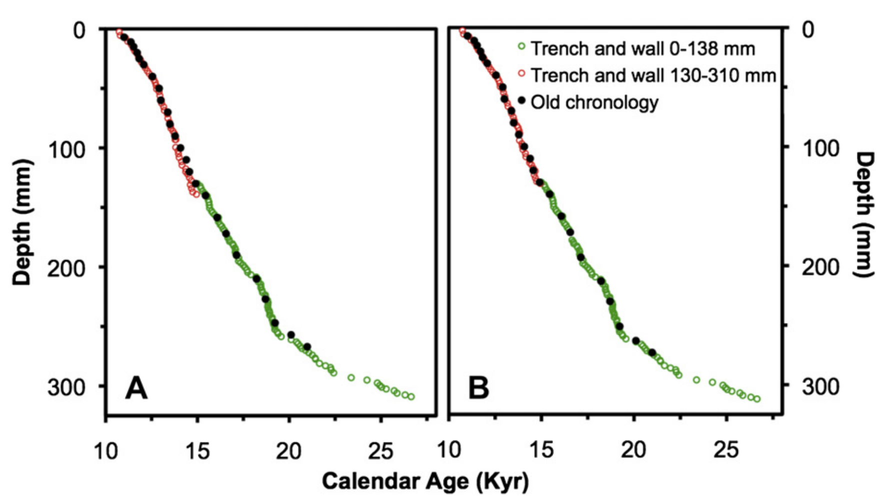

Fig. 2. A. Age model for H82 based on U–Th measurements from this study (Trench and wall sampling) plus earlier work (Old chronology) – see text. B. Age model after depth adjustments for consistency between samples from different quadrants and slabs of H82 calcite as described in the text.

suggested that it represents a period where different parts of the speleothem grew at very different rates, rather than actual missing calcite. The cause(s) for such differential growth remain unclear, but might be related to a small change in the drip line. The 245–248 mm interval in the published $\delta^{18}O$ record has been linearly expanded to 6 mm, and depths for the oldest three samples from the old chronology are increased by 3 mm.

3.3. ^{14}C ages

^{14}C results are shown in Table S2, as conventional radiocarbon ages (Stuiver and Polach, 1977). Uncertainties are shown at 1σ and include contributions from background corrections, normalization to standards, and the scatter in repeated measurements on each sample, as well as counting statistics. A $\pm 30\%$ uncertainty was used for all background subtractions, based on scatter between results on different background materials and separate aliquots of the same material, and background variations between measurement runs on different days. Initial ^{14}C ages for three of the samples were significantly older than adjacent data points. The samples were remeasured and the duplicates returned ages consistent with other results, indicating that the aliquots run initially were somehow contaminated with old carbon. These results are retained in Table S2 but have not been used in the subsequent analyses. Anomalous results on two other samples were traced to mislabeling, and Table S2 shows the corrected samples ID's. Two pairs of duplicates from regions of very slow growth disagree, probably because the calcite subsamples represented chips of different age.

3.4. Interpolated ^{230}Th ages and uncertainties

Interpolated ^{230}Th ages for the ^{14}C record are shown in Table S2. We stress that the calendar ages for the ^{14}C data are derived exclusively from U–Th measurements on the same pieces of calcite and are completely independent of the depth adjustments discussed above, ^{14}C measurements on the chip series (Table S2a) were carried out on aliquots of the same samples used for the old U–Th chronology, and the calendar ages and uncertainties for those samples are those of the corresponding ^{230}Th measurements from Table S1. Calendar ages for the closely spaced H82-A and H82-2 ^{14}C series are averages of the ^{230}Th ages for adjacent powder samples, and the uncertainties are taken as the standard errors in the means of the bracketing ^{230}Th ages. For the core samples, equivalent on-axis depths found by tracing growth surfaces were used to interpolate among ^{230}Th ages measured on-axis on the same H82 quadrant. For depths below 130 mm, the means of the bracketing H82-2 U–Th series ages were used, and the uncertainty assigned to the calendar age for each ^{14}C datum is once again the uncertainty in the mean ^{230}Th age. However, above 130 mm, linear interpolations between the old chronology ^{230}Th ages spaced 5–10 mm apart were required, because the denser H82-B U–Th series was measured on a different H82 quadrant. Given this coarse spacing, we assumed that the calendar age uncertainties for the interpolated points were comparable with those of the endpoints, and used the means of the uncertainties in the endpoint ages, rather than the more precise uncertainty in the mean.

3.5. Depth-based calendar age uncertainties

In addition to the analytically based calendar age uncertainties described above, we also incorporated age uncertainties due to the finite depth ranges spanned by samples taken for ^{14}C (allowing for the possibility of non-uniform sub-sampling for a given ^{14}C measurement) and we also considered possible errors in tracing growth surfaces. Trench and wall ^{14}C samples were approximately 1 mm wide, from which we adopt a maximum depth uncertainty of ± 0.5 mm for the on-axis H82-2 samples. Similarly, we took the maximum uncertainty for the larger chip samples as ± 1 mm. For the off-axis H82-A trench and wall series we increased the depth range by 30% below 40 mm stalagmite depth to take account of the crowding together of curved growth surfaces, which increases the amount of equivalent on-axis depth (and time) represented in each sample. For the 3 mm core samples we assumed a maximum possible error due to finite sample size of ± 1.5 mm above 40 mm and ± 2 mm below that depth, and also factored in an additional uncertainty in tracing growth surfaces back to the stalagmite axis of ± 1 mm above 40 mm and ± 2 mm below 40 mm. For simplicity, and given the relatively coarse sample spacing, we assumed that these tracing errors were uncorrelated between adjacent core samples. Adding these components in quadrature, rounding, and approximating an equivalent 1σ uncertainty as half the maximum possible error, we derive overall 1σ depth uncertainties for the core samples of ± 1 mm from 0–40 mm depth and ± 1.5 mm below 40-mm. Similarly, depth uncertainties for the trench and wall samples are ± 0.25 mm, rising to ± 0.33 mm below 40 mm for the off-axis H82-A series; and ± 0.5 mm for the chips.

These depth uncertainties were converted to age errors using H82 growth rates approximated by piecewise linear fits to short sections of the U–Th age vs. depth record. The resulting age uncertainties were then added in quadrature with those derived from the ^{230}Th ages to produce the total calendar age uncertainties shown in Table S2. The average growth rate for H82 is approximately 6 mm/kyr from the base of the stalagmite to 260 mm, and increases to an average of 30 mm/kyr above 260 mm. Depth-derived age uncertainties are therefore most significant near the base of the stalagmite, and are especially large during the periods of hiatus. They dominate the overall calendar age uncertainties for the large core samples below 130 mm and contribute significantly over the entire depth range of H82; but only become significant for the much smaller trench and wall samples in the bottom few cm of the speleothem.

3.6. DCF correction

The DCF correction was determined by comparing ^{14}C results from the uppermost section of H82 with IntCal09 tree ring data (Reimer et al., 2009), represented by the continuous blue line in Fig. 3. The overlap period extends from the start of the German Pine dataset in the mid-YD at 12.6 kyr BP to the end of growth for H82 at 10.7 kyr BP. For simplicity, the H82 data were compared with the smoothed IntCal data rather than the raw tree ring results; and since the ^{14}C calibration curve is relatively flat over most of this interval, the fit is insensitive to small errors in the calibrated ages and no attempt was made to account for uncertainties in the U–Th age model. A DCF correction of 452 yrs was derived from the average of the differences between equivalent H82 and IntCal measurements. Those differences showed substantially greater scatter (± 62 years at 1σ) than the ± 33 years expected from the quoted uncertainties in the H82 and IntCal09 data, suggesting that analytical errors may have been underestimated or that short term DCF variations are present. We have treated the extra variance as arising from rapid DCF variations and therefore assign a value of 450 years for the DCF correction, with an uncertainty $\sim\sqrt{(62^2 - 33^2)}$ or ± 50 years.

In Fig. 3 the H82 data are also compared with an extended tree ring record that includes the floating Allerød pine sequence (Kromer et al., 2004), and the recently published Huon pine series (Hua et al., 2009). The positions of the Huon pine and Allerød pine relative to the master series are based on ^{14}C wiggle matching, and are believed to

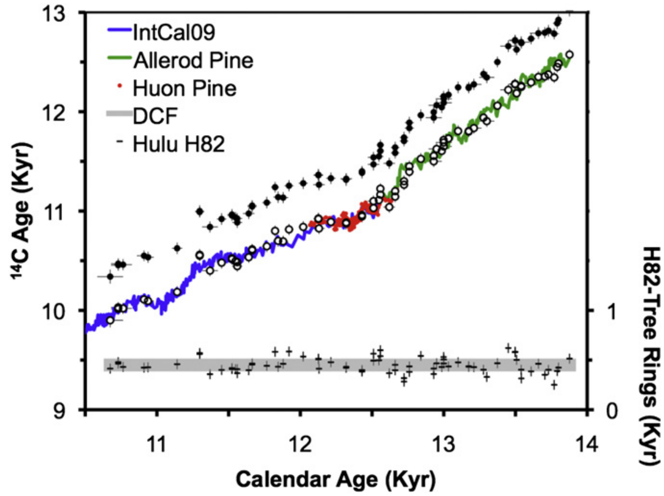

Fig. 3. ^{14}C measurements on the H82 speleothem plotted with and without DCF correction against an extended tree ring data set: IntCal09 tree rings (Reimer et al., 2009) plus Huon Pine (Hua et al., 2009) and Allerød Pine (Kromer et al., 2004). Tree ring − H82 age differences are shown at the base of the plot, with a grey bar representing the ±50 year DCF uncertainty derived from the H82 − IntCal09 comparison.

be accurate within decades. This comparison yields a DCF of 450 ± 70 years, which is slightly more variable than the DCF calculated using only the well-established master series. The agreement with the extended tree ring data indicates that H82 faithfully records atmospheric ^{14}C with a stable DCF across both the Allerød/Younger Dryas and the Younger Dryas/Holocene transitions, i.e., through major monsoonal shifts that correspond to transitions both into and out of a Greenland stadial (Wang et al., 2001). This constancy through significantly different climate regimes is the basis for our working assumption that the H82 DCF is unchanged throughout the entire H82 record.

3.7. Comparison with H82 high-resolution δ^{18}O records

High resolution stable oxygen isotope records from H82 and other Hulu speleothems (Wang et al., 2001; Wu et al., 2009) have provided a valuable proxy record of changes in the East Asian monsoon on times scales ranging from years to glacial-interglacial cycles. The δ^{18}O data are highly correlated with summer insolation on Milankovich timescales, and with the record of centennial to millennial Greenland stadial/interstadial variations (Wang et al., 2001; Yuan et al., 2004), consistent with a strong linkage between speleothem δ^{18}O and summer monsoon intensity that is further supported by pollen and other paleoclimate proxy data (Sun and Li, 1999; Xu et al., 2010; Zhu et al., 2010; Xiao et al., 2004). However, the details of precisely what monsoon parameters are recorded in the stable isotopes are less clear. The coherence of the records over thousands of km in eastern and southern Asia (Wang et al., 2001; Yuan et al., 2004; Sinha et al., 2005) argues against the idea that speleothem δ^{18}O responds primarily to local variations in temperature or precipitation amount, whether via changes in calcite-water fractionation or in δ^{18}O of meteoric water. Alternative hypotheses attribute δ^{18}O shifts to variations in the summer/winter precipitation ratio (Wang et al., 2001) or changes in the progressive removal of moisture from air masses during transport from tropical Indo-Pacific moisture source regions to sites in Asia (Yuan et al., 2004). Both mechanisms involve relatively direct connections between δ^{18}O and variations in the dominant summer monsoon rainfall, but a recent analysis of δ^{18}O in modern precipitation (Dayem et al., 2010) suggests that the cave δ^{18}O archives may record other effects – variations in the duration of seasonal precipitation regimes or in moisture source regions or transport pathways – that are less directly connected to changes in monthly or total precipitation.

The Hulu δ^{18}O data have played a significant role ^{14}C calibrations, as a means of tying radiocarbon-dated records from other locations (Bard et al., 2004; Hughen et al., 2006) to the Hulu U–Th timescale. The published high resolution H82 δ^{18}O data were sampled from a different quadrant of H82 from that used here (Wu et al., 2009), and used an earlier U–Th chronology based on ^{230}Th dates at ~750 year spacing. Stable isotope data from the present study are shown in Table S2, in standard delta notation relative to Vienna PDB. Instrumental precisions (1σ) are ~0.06‰ and 0.02‰ for δ^{18}O and δ^{13}C, respectively, based on long-term repeatability for the NBS19 standard. Missing data represent cases where insufficient material remained after the ^{14}C measurement. In Fig. 4 we compare δ^{18}O data from our discrete samples with the continuous high resolution records of Wang et al. (2001) and Wu et al. (2009), having transferred those δ^{18}O datasets to the densely dated U–Th age model from the present investigation with minor depth adjustments as described in Section 3.2. Agreement between the data sets is generally very good, though the high resolution data appear to be offset slightly older than our discrete sample measurements beyond 20.5 kyr BP. Growth surfaces in the bottom few cm of H82 are distinctly more irregular than those higher in the speleothem, so the relationships between depths in different calcite pieces are less obvious and more variable. However, any offsets are less than ~150 years; and pending availability of high resolution δ^{18}O data extending closer to the speleothem base (R.L. Edwards pers. comm.) we have not attempted additional depth adjustments or δ^{18}O wiggle-matching in this region.

4. Discussion

4.1. Stability of the H82 dead carbon fraction

Comparisons of the H82 ^{14}C record with tree ring data in the interval 10–14 kyr BP, and with several other calibration records discussed below over the period 14–16 kyr BP (Figs. 5–7), suggest that any changes in the H82 DCF were less than 100 years, perhaps as small as a few decades. This lack of variation in the DCF may be at least partly a consequence of the small absolute magnitude of the correction, determined by the local environment above the cave. The weak soil development and high infiltration capacity at the

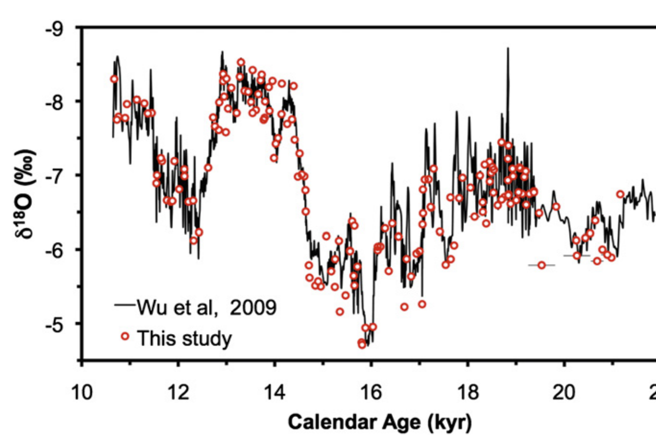

Fig. 4. High resolution H82 δ^{18}O record from Wu et al. (2009), which incorporates the earlier dataset of Wang et al. (2001), plus "spot" H82 δ^{18}O data from this study, on a timescale based on the age model shown in Fig. 2B.

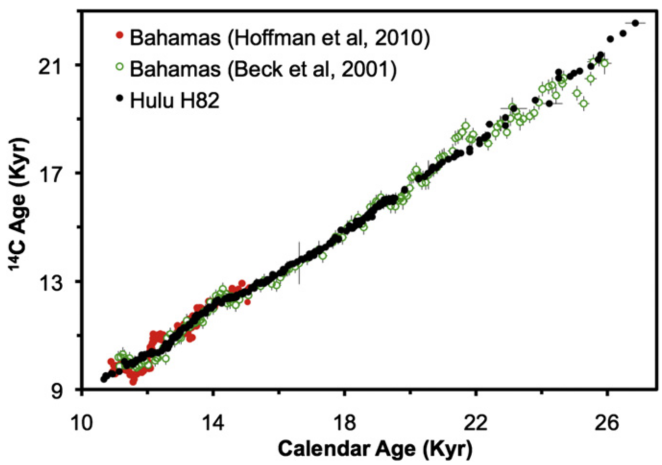

Fig. 5. Bahamas speleothem (Beck et al., 2001; Hoffmann et al., 2010) and H82 ^{14}C records.

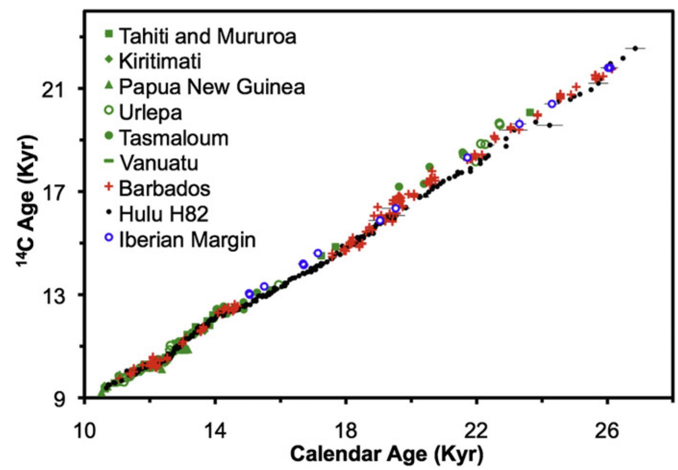

Fig. 7. All coral ^{14}C records included in IntCal09 (Reimer et al., 2009) plus ^{14}C data from the Iberian Margin sediments (Bard et al., 2004) and H82. Pacific coral records are indicated by green symbols (see legend for details); Atlantic (Barbados) corals are shown in red (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Hulu site, and the predominance of carbonate debris in the lower soil horizons (Kong et al., 2005) are consistent with water-carbonate equilibration occurring primarily at shallow depths in an environment that is seldom completely saturated, i.e., under predominantly open system conditions where continuing exchange between meteoric water and soil CO_2 dilutes any geologic carbon contribution

Nevertheless, the exceptional stability of the H82 DCF remains a puzzle. Pollen records from central and southeastern China (Sun and Li, 1999; Xu et al., 2010; Zhu et al., 2010; Zhou et al., 2004) show that the deglacial period encompassed major vegetation shifts that are broadly consistent with the record of summer monsoon changes inferred from the speleothem $\delta^{18}O$ data, though in some cases more gradual and prolonged. Widespread increases in broadleaf arboreal taxa indicating shifts to warmer and wetter conditions occurred after 15 kyr and 11.5 kyr BP, consistent with a strengthening of the summer monsoon. The responses to the onset of the YD (weakened summer monsoon) are mixed in the pollen data, with indications of a shift to cooler and wetter climate in southern and eastern China (Sun and Li, 1999; Zhou et al., 2004; Xu et al., 2010), whereas montane central China experienced cooler and drier conditions (Zhu et al., 2010). The warming and increased precipitation trends from 15 kyr and 11.5 kyr probably acted together to increase soil moisture; and these variations and the associated vegetation shifts to a more subtropical flora would likely have also altered soil carbon turnover and soil gas pCO_2 at the Hulu site, leading in turn to changes in ^{14}C in soil gas, groundwater, and speleothem calcite. In light of the varied wet/dry responses in the pollen data to the initiation of the YD at 13 kyr BP, it is unclear whether overall rainfall varied at Hulu Cave at that time. However, given the weakening of the summer monsoon indicated by the speleothem $\delta^{18}O$, YD cooling at Hulu was certainly accompanied by changes in the seasonality of precipitation, which again must have influenced the local vegetation cover, hydrology, and soil carbon dynamics. While the small overall magnitude of the H82 DCF probably contributed to the lack of variation, the mechanisms by which effects of the various environmental changes on speleothem ^{14}C were attenuated or canceled each other out remain unclear.

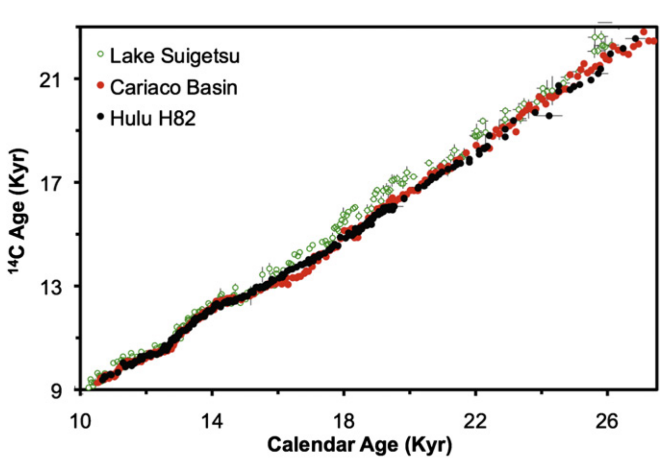

Fig. 6. ^{14}C from H82, plus sedimentary ^{14}C records from the Cariaco Basin (Hughen et al., 2006) and Lake Suigetsu (Kitagawa and van der Plicht, 2000).

4.2. *Comparison with other ^{14}C calibration data*

^{14}C data from H82 are compared with several existing large-scale calibration datasets in Figs. 5–7. There is good overall agreement between the Beck et al. (2001) Bahamas speleothem ^{14}C record and the Hulu Cave data (Fig. 5), though some differences are present, notably before 21 kyr BP. The concordance between the two records for the period 15–21 kyr BP is striking, and indicates that the Bahamas record is accurate over this interval despite the large uncertainties associated with the large DCF and initial thorium corrections. The consistency between the two speleothem records, despite their large differences in location and geochemistry, suggests that there are no major variations in DCF in either record, and that both datasets provide good records of atmospheric ^{14}C over this period. The Hulu record is essentially monotonic over the entire 15–26 kyr BP interval, but the Bahamas record shows some structure around 20 kyr BP and again around 21.5 and 22.5–24.5 kyr BP. Given the large uncertainties in the Bahamas data, these "wiggles" might be statistical artifacts, but since most of them correspond to the periods of hiatus in H82, the Hulu data cannot confirm or refute these results. Before 24.5 kyr BP, the Bahamas data show a large shift to younger ages that is not reproduced in H82.

The overall agreement between the Hulu Cave and Cariaco Basin records shown in Fig. 6 is also good, but there are clear systematic differences between 16 and 17 kyr BP, corresponding to part of

Heinrich Stadial 1 (HS1). Since the agreement between the Hulu Cave and Bahamas speleothem records in this interval is excellent, the offset between the Hulu Cave and Cariaco records is probably not due to changes in the H82 DCF. The existing Hulu chronology for the Cariaco record (Hughen et al., 2006) is based on correlation of the sediment color record with an earlier lower resolution H82 $\delta^{18}O$ dataset (Wang et al., 2001), but comparisons with the new higher resolution H82 $\delta^{18}O$ (Wu et al., 2009) data suggest that the Cariaco Basin calendar age chronology is accurate and hence that the offset is not due to an erroneous "warping" of the Cariaco data to older calendar ages. The younger Cariaco ^{14}C ages in this interval are therefore most likely explained by a remarkable decrease of 300–400 years in the marine reservoir age of the Cariaco Basin during this period.

Whether this was due to local effects within the basin or represents a regional response to ocean circulation changes during HS1 is unclear. A large decrease or total shutdown of North Atlantic Deep Water (NADW) formation associated with HS1 (Seidov and Maslin, 1999; Meissner et al., 2002; McManus et al., 2004) would likely lead to decreased subsurface turbulence and increased stratification in the North Atlantic, which might allow for air–sea mixing to become the dominant influence on the ^{14}C age of equatorial Atlantic and Caribbean surface waters. However, since the observed drop in Cariaco reservoir age is substantially larger than models predict (Butzin et al., 2005; Ritz et al., 2008; Singarayer et al., 2008) any regional changes may have been augmented by local effects. Sea level during HS1 was 100–110 meters lower than at present (Peltier and Fairbanks, 2006), reducing the basin sill depths to just 45–35 meters and limiting water exchange with the open Caribbean, though a recent modeling study shows persistent mixing under even shallower LGM conditions (Lane-Serff and Pearce, 2009). Sediment reflectance and Fe and Ti concentration data indicate dry and windy conditions within the basin during HS1 (Peterson et al., 2000), suggesting that increased air–sea gas exchange coupled with reduced input of Caribbean water could have biased local reservoir ages to low values. Recent comparisons of Cariaco data with tree ring data from the early Younger Dryas (Muscheler et al., 2008; Hua et al., 2009) suggest that a similar (but much briefer) reduction in reservoir age may have occurred at the Allerød/Younger Dryas transition, at a time when sill depths were 60–70 m.

Three other radiocarbon records shown in Figs. 6 and 7 and discussed below all contain data that are systematically older than the H82 results over portions of the record beyond 15 kyr BP. One possible explanation is that the H82 DCF was significantly lower in glacial time, so that the plotted H82 ages are too young. However, two lines of evidence suggest that the discrepancies are mostly due to other causes, likely involving changes in marine reservoir ages or questions about the independent timescales for the other records. First, for intervals where the Bahamas and H82 results agree well, this explanation would require equally large shifts in DCF's for two speleothems in very different locations and geochemical environments, which seems unlikely. Second, in several of these cases the implied decrease in H82 DCF is so large that it would require an extraordinarily low (essentially zero) input of geologic carbonate to Hulu Cave drip waters. However, despite the stability of the H82 DCF over the later period covered by the comparison with the dendro records, the possibility remains open that modest (~100–200 year) DCF reductions occurred in H82 during the glacial and contributed to these discrepancies.

^{14}C dates on macrofossils from varved Lake Suigetsu (Kitagawa and van der Plicht, 2000) are several hundred years older than our new data over most the period before 16 kyr BP (Fig. 6), but this is probably due to problems with the Lake Suigetsu timescale, as opposed to reflecting true carbon cycle changes or a change in H82 DCF. The Lake Suigetsu chronology was based on varve counting in cores from a single borehole and this coring method may have led to the loss of material, particularly from the base of each core section (Staff et al., 2010). New cores were taken from Lake Suigetsu in 2006, using overlapping sections from multiple boreholes to insure continuous coverage, and varve counting and ^{14}C analyses are underway (Nakagawa et al., 2011).

^{14}C results from the Iberian Margin foraminiferal ^{14}C record (Bard et al., 2004) are offset from the new H82 data between 15 and 17 kyr BP (Fig. 7), probably due to an increase in Iberian Margin surface reservoir age by ~350 ^{14}C yr or an offset in calendar timescale of ~400 yrs younger relative to H82. The latter scenario is possible because the lack of structure in the low-resolution Hulu Cave $\delta^{18}O$ record on which the published Iberian Margin calendar timescale is based limits the number of tie points available for correlation in this interval. Correlation to the new high resolution H82 $\delta^{18}O$ record is underway (E. Bard, pers. comm.) and this question should be resolved shortly. Alternatively, the Iberian Margin reservoir age may have increased as proposed by Skinner (2008), though other studies suggest that any large increases in N.E. Atlantic reservoir ages during HS1 were confined to more northern sites (Waelbroeck et al., 2001).

There is good agreement between the Hulu Cave ^{14}C record and published U–Th dated coral data from the end of the Hulu Cave record at 9.5 kyr back to 19.5 kyr BP (with a gap from 16 to 17.5 kyr BP where coral data are absent) but Vanuatu coral data (Cutler et al., 2004) are 350–500 ^{14}C yrs older than equivalent measurements from H82 beyond 19.5 kyr BP (Fig. 7). Additionally, Atlantic corals from Barbados (Fairbanks et al., 2005) are systematically ~100–250 ^{14}C yrs older than the H82 data in the interval 19.5–21 kyr BP. This disagreement could indicate either a decrease in H82 DCF, or increased marine reservoir ages in the LGM continuing into early deglacial time. Since a decrease in DCF of the magnitude implied by the Vanuatu data is unlikely, at least some of the discrepancy is probably due to reservoir age variations.

These centennial scale differences between calibration records remain difficult to characterize and explain, particularly in the older portions of the records where uncertainties in both ^{14}C and calendar ages are larger, and especially for intervals that lack robust agreement between any of the datasets. Given current uncertainties concerning glacial ocean circulation and the likelihood of significant hydrologic changes in the tropics during Isotope Stage 2, we cannot rule out the possibility of changes in ^{14}C offsets for both cave and marine systems. More precise apportionment of any changes in marine reservoir ages and speleothem DCF's will rely on the development of other high-resolution records of terrestrial and marine ^{14}C in these intervals.

4.3. The timing and origin of the deglacial pCO_2 increase

Identifying the magnitude and timing of any changes in ^{14}C offsets between different carbon pools is of particular interest in the so-called Mystery Interval (Broecker and Barker, 2007) between about 15 and 18 kyr BP, which was characterized by a drop of almost 200‰ in atmospheric and surface ocean $\Delta^{14}C$ (Beck et al., 2001; Fairbanks et al., 2005; Hughen et al., 2006) and a rise of 40 ppm in atmospheric pCO_2 (Monnin et al., 2001). Marchitto et al. (2007) linked these changes with a low-$\Delta^{14}C$ excursion in eastern North Pacific intermediate waters, and hypothesized that they represented the ventilation via the Southern Ocean of a previously isolated glacial deep water mass (Adkins et al., 2002), with massive release of sequestered CO_2. Evidence for such a ^{14}C -depleted water mass in the deep glacial Pacific remains elusive (Broecker and Barker, 2007), and the circulation pathways by which any newly ventilated low-^{14}C waters reached intermediate depths in the North Pacific (Marchitto et al., 2007), eastern tropical Pacific (Stott et al., 2009) and Arabian Sea. (Bryan et al., 2010) have not

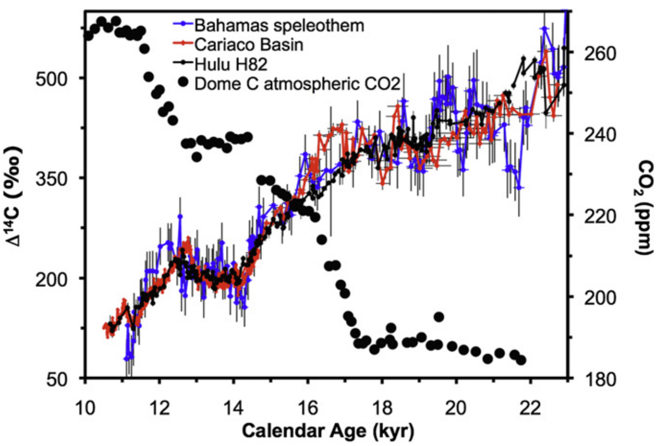

Fig. 8. $\Delta^{14}C$ for the H82, Bahamas and Cariaco records, plus pCO_2 data from Dome C, Antarctica (Monnin et al., 2001) placed on the layer-counted GISP2 Greenland ice core timescale via synchronization of methane records (Marchitto et al., 2007).

been found (De Pol-Holz et al., 2010). However, if mechanism proposed by Marchitto et al. (2007) is correct, the ^{14}C drop is directly related to the problem of glacial–deglacial pCO_2 variations, which are presently poorly understood and are not well simulated by current climate models. Recent studies show intensified upwelling and enhanced biological productivity (Anderson et al., 2009) and a rise in deep ocean $\Delta^{14}C$ (Skinner et al., 2010) within the Southern Ocean, that are coeval (within large uncertainties) with the pCO_2 increase, consistent with the recoupling of a previously isolated deep reservoir with the surface.

The H82 ^{14}C record displays the same ~200‰ atmospheric $\Delta^{14}C$ drop, and the exceptionally high resolution absolute dating of H82 allows for more precise constraints on the timing of the decrease. Fig. 8 shows $\Delta^{14}C$ data from the Bahamas, Cariaco and H82 records, plus pCO_2 data from trapped air in the Dome C (Antarctic) ice core (Monnin et al., 2001) plotted on the absolutely dated GISP2 ice core layer counted timescale. The $\Delta^{14}C$ drop in the H82 and Bahamas data begins more than 1 kyr earlier compared with the Cariaco record, coincides within uncertainties with the atmospheric pCO_2 rise, and closely tracks $\Delta^{14}C$ decreases at intermediate depths in the eastern North Pacific (Marchitto et al., 2007) and the Arabian Sea (Bryan et al., 2010). The new chronology is therefore consistent with the recoupling hypothesis outlined above (though this remains unproven) and underscores the requirement that any hypothesis seeking to explain the glacial-interglacial rise in atmospheric CO_2 must involve strong linkages between atmospheric pCO_2 and terrestrial and marine ^{14}C.

4.4. High-resolution $\delta^{18}O$ data

The present study provides a well-constrained age model for the high resolution H82 $\delta^{18}O$ data spanning the deglacial period (Wang et al., 2001; Wu et al., 2009), with U–Th dates at centennial spacing rather than every 750 years as previously (Table S3). This places the stable isotope data on a more solid chronological framework, though the old and new age models differ very little, typically by 100 years or less. Minor changes primarily reflect "kinks" in the growth rate that were hidden in the lower resolution chronology. The new age model has implications for ^{14}C calibration during early deglaciation, since the rich structure of the high resolution $\delta^{18}O$ data over this interval attests to significant centennial scale monsoon changes (Wu et al., 2009) that provide numerous potential tie points for correlating other climate proxy records with the detailed Hulu chronology.

5. Conclusion

This new record of atmospheric ^{14}C is in good overall agreement with existing marine and terrestrial ^{14}C records, suggesting that any changes in the DCF in the H82 speleothem are small, even across major climate transitions that likely involved large perturbations to the tropical hydrologic cycle. This in turn suggests that the Hulu Cave speleothems may be useful for reconstructing atmospheric ^{14}C back to the radiocarbon detection limit of ~50 kyr BP. The agreement between the H82 and Bahamas speleothem data over the 15–21 kyr BP interval shows that at least some records with large DCF can provide meaningful records of atmospheric ^{14}C and they should not be *a priori* excluded from consideration as calibration datasets. The high precision of this Hulu Cave record makes it particularly valuable for recognizing small changes in the paleo-carbon cycle. Comparison with the Cariaco Basin record through the deglacial interval reveals that the marine reservoir age of Cariaco Basin has varied, highlighting the importance of extending high-resolution marine and terrestrial ^{14}C records back to the radiocarbon detection limit to be able to detect changes in ocean circulation over the glacial cycle.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.quascirev.2011.11.022.

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