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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.