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Assessing influences on speleothem dead carbon variability over the Holocene: Implications for speleothem-based radiocarbon calibration

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ABSTRACT

Recently, it has been shown that U–Th dated speleothems may provide a valuable archive of atmospheric radiocarbon (^{14}C), but the reliability of these records is dependent upon the stability of the dead carbon proportion (DCP) derived from the soil and bedrock. In order to assess climatic influences on speleothem DCP, we have investigated DCP variability over the Holocene interval where atmospheric ^{14}C is well known based on dendrochronologically dated tree rings by conducting ^{14}C measurements on a U–Th dated stalagmite (HS4) from Heshang Cave, Hubei Province, China (30°27′N, 110°25′E; 294 m) spanning 0.5–9.6 ka. We investigated climatic controls on DCP, and found that DCP in HS4 has an average value over the Holocene of 10.3 ± 1.5%, with an average age offset from atmospheric radiocarbon of 875 ± 130 years, and displays a response to both precipitation increases and decreases. HS4 DCP increases during the wetter mid-Holocene interval (~5.5–7.1 ka), likely reflecting a shift to more closed-system dissolution in response to increased soil moisture. DCP decreases during the 8.2 ka event, a time period of dry conditions at Heshang Cave, though the lower amplitude of this shift indicates that DCP may be less sensitive to dry events. Speleothems are potentially valuable archives of atmospheric radiocarbon, especially in older portions of the ^{14}C calibration curve where knowledge of atmospheric ^{14}C is limited, however minor climatic influences on DCP could introduce uncertainties of several hundred years to calibrated ages.

1. Introduction

1.1. Calibration of atmospheric radiocarbon

In order to study the causes and effects of past changes in Earth's climate, precise and accurate chronologies and chronometers are key. Many paleoclimate proxy records rely on measurements of the concentration of radiocarbon (^{14}C) in calcite ($CaCO_3$) or organic matter for construction of their calendar age chronologies. However, radiocarbon-based geochronology, which is theoretically possible to at least 50 ka, is complicated by changing atmospheric concentrations of ^{14}C, which are controlled by: (1) non-constant ^{14}C production rates in the upper atmosphere, which vary with geomagnetic field intensity and solar variations over a wide-range of timescales (Bard, 1998), and (2) changes in carbon cycling which redistributes carbon, including ^{14}C, between ocean, atmosphere, and biosphere reservoirs. In order to use ^{14}C as a chronometer, and investigate changes in carbon cycling, the ^{14}C timescale must be calibrated by reconstruction of records of atmospheric ^{14}C tied to robust independent chronologies.

Tree ring records of ^{14}C with calendar ages derived from dendrochronology are considered the most robust records of atmospheric ^{14}C because they directly incorporate atmospheric CO_2 during photosynthesis and have a high-resolution independent chronology. Tree ring records from central and northern Europe are the basis of the most recent IntCal13 radiocarbon calibration curve to 13.9 ka (Reimer et al., 2013). Before this point, regional climate conditions were less hospitable to trees, and the tree ring records are no longer the basis of ^{14}C calibration curves, although there are some floating tree ring chronologies covering earlier intervals (e.g. Turney et al., 2007; Muscheler et al., 2008; Kromer et al., 2004; Hua et al., 2009; Hogg et al., 2013).

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The only true non-tree ring record of atmospheric ^{14}C extending beyond 13.9 ka is a record from Lake Suigetsu, Japan, which is based on macrofossils paired with a varve counting chronology (Kitagawa and van der Plicht, 1998a, 1998b, 2000; Staff et al., 2010; Bronk Ramsey et al., 2012) and covers the interval 0–52.8 ka. The Lake Suigetsu record presented by Kitagawa and van der Plicht (1998a, 1998b, 2000) showed significant divergence from other atmospheric radiocarbon reconstructions prior to ~25 ka, which was found to be due to errors in the calendar chronology because of incomplete core retrieval during sampling (Staff et al., 2010). A new set of overlapping cores was taken and a new high-resolution record with an improved chronology has been constructed, though the record displays large scatter in the ^{14}C ages in the interval >28 ka due to small sample sizes, as well as large uncertainty in the layer-counting age model (Bronk Ramsey et al., 2012). Nonetheless, the Lake Suigetsu ^{14}C record provides a valuable "backbone" for the atmospheric ^{14}C record, which is refined by a variety of other ^{14}C records.

In the absence of true atmospheric records, the majority of calibration efforts have been focused on marine sediment records with a constant correction applied to account for the marine reservoir effect – the offset between the concentration of ^{14}C in the ocean and the atmosphere. The use of marine records for calibration of terrestrial radiocarbon dates is complicated by the potential for climatically driven variations in marine reservoir age. It is well known that large and rapid changes in climate occurred during the deglacial period, which were likely associated with changes in the Atlantic Meridional Overturning Circulation (McManus et al., 2004; Vellinga and Wood, 2002). These climatic changes were accompanied by large variations in surface ocean ^{14}C (Broecker and Barker, 2007; Hughen et al., 2000), consistent with the idea that they involved major shifts in the carbon cycle, which would have had large impacts on marine reservoir ages. Despite this complication, the agreement between these reservoir corrected marine records and the Lake Suigetsu record is very good to ~28 ka. Before 28 ka the divergence between records increases (Reimer et al., 2013), as does the variance in the Lake Suigetsu record (Bronk Ramsey et al., 2012), with differences between records on the order of thousands of years, leading to high uncertainty in the atmospheric ^{14}C record in the earlier intervals.

1.2. Speleothem-based records of atmospheric radiocarbon

Recently, there has been interest in using speleothems to create records for radiocarbon calibration, in part because they have many features which may make them valuable sources of records which resolve the calibration curve in older intervals (e.g. Beck et al., 2001; Weyhenmeyer et al., 2003; Dorale et al., 2008; McDermott et al., 2008; Hoffmann et al., 2010; Southon et al., 2012). Speleothems hold some key advantages over floating tree rings, varved chronologies, and marine records: (1) They can be precisely and absolutely dated using U–Th methods (Richards and Dorale, 2003); (2) Their fast growth rates, highly resolvable stratigraphy, and excellent preservation allow for often continuous high-resolution ^{14}C measurement over the entire ^{14}C dating range; (3) they are widely used for paleoclimate reconstruction (Fairchild et al., 2006) so access to numerous U–Th dated samples is possible and will allow for replication of records and direct comparison with climate proxy data. There are, however, several complicating factors affecting speleothem-based radiocarbon calibrations stemming from the way that speleothems are formed.

Formation of speleothem calcite is driven by CO_2 degassing of cave drip water that has accumulated carbon from the soil and bedrock. Meteoric waters equilibrate with soil CO_2 to form carbonic acid, which drives carbonate dissolution as drip water percolates through the limestone cave host bedrock. Consequently, ^{14}C in speleothem calcite is offset from contemporaneous atmospheric ^{14}C because a proportion of speleothem carbon comes from old soil organic matter (SOM) and radiocarbon-free "dead carbon" from the bedrock. To date, the offset between speleothem ^{14}C and contemporaneous atmospheric ^{14}C has been referred to in a variety of different ways across the literature, often using the same acronym to refer to different metrics, which has been a source of some confusion. In this manuscript we will refer to the dead carbon proportion (DCP) as a percentage as defined by Genty and Massault (1997), but we also refer to the DCP as a "correction" or "offset" with units of ^{14}C years.

Hendy (1971) considered two end member scenarios under which dissolution of carbonate bedrock can occur: open and closed system dissolution. In open-system dissolution, the solution dissolving the bedrock is continually in contact with soil CO_2, which leads to speleothem $\Delta^{14}C$ compositions dominated by a soil CO_2 signature, as isotopic equilibrium with soil C and the dissolved inorganic carbon (DIC) pool is maintained during dissolution. In closed system dissolution, dissolution of the bedrock takes place in isolation from soil CO_2, leading to $\Delta^{14}C$ compositions shifted towards a bedrock ^{14}C isotope signature. Therefore, completely open-system dissolution, where soil CO_2 ^{14}C values are identical to atmospheric values would lead to an apparent DCP = 0%, whereas a completely closed-system dissolution wherein one mole of carbonate is required to neutralize one mole of dissolved CO_2 would lead to a theoretical DCP = 50%. However, soil gas $^{14}CO_2$ is rarely equal to atmospheric $^{14}CO_2$, because soil CO_2 is a mixture of atmospheric CO_2, root respiration, and CO_2 from decomposition of aged SOM, leading to the potential for a DCP > 50%, and making a DCP = 0% unlikely. In natural systems, carbonate dissolution usually falls somewhere between the two end member scenarios, with average DCP around $15 \pm 5\%$ (Genty et al., 1999). Despite the potential for variable DCP to complicate speleothem-based reconstructions of atmospheric ^{14}C, speleothem radiocarbon records have been used to provide valuable constraints on the calibration curve during intervals where true atmospheric ^{14}C data is limited (Beck et al., 2001; Hoffmann et al., 2010; Southon et al., 2012).

The speleothem-based records of atmospheric ^{14}C that have been included in IntCal13 are a record spanning 10.6–26.8 ka from Hulu Cave, China (Southon et al., 2012), and a record spanning 11.1–44.1 from the Bahamas (Beck et al., 2001; Hoffmann et al., 2010). These records were constructed using a trench-and-wall sampling technique, where ^{14}C measurements on intact chips of calcite from the walls are interleaved with U–Th measurements on powder from drilled trenches, resulting in a robust and well-constrained calendar chronology for the ^{14}C record. The record from Hulu Cave, based on speleothem H82, has a very low and stable DCP of $5.4 \pm 0.7\%$ (450 ± 50), calculated from the period of overlap between H82 with the master tree ring records spanning 10.7–12.6 ka, which covers the Younger Dryas/Holocene transition – a period of rapid climate change which is likely to have altered cave hydrology (Southon et al., 2012). The Bahamas speleothem record based on GB-89-24-1 spanning 11–45 ka was initially published in Beck et al. (2001) and showed extremely large variations in ^{14}C in the interval 41–44 ka. These variations were found to be an analytical artifact, and a new sampling of GB-89-24-1 covering 41–44 ka as well as a new record based on speleothem GB-89-25-3 spanning 28–44 ka and 11–15 ka to establish the DCP, was constructed by Hoffmann et al. (2010). GB-89-25-3 has a high DCP of $22.7 \pm 5.9\%$ (2075 ± 540), while GB-89-24-1 has a slightly lower DCP of $16.5 \pm 4.7\%$ (1450 ± 470).

There has been some hesitation in using speleothems for ^{14}C calibration, because of the potential for undetected variations in DCP, as well as the large variations in DCP seen in the Bahamas speleothem records. However, even with this additional