Earth and Planetary Science Letters 458 (2017) 58–68

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Atmospheric pCO_2 control on speleothem stable carbon isotope compositions

Daniel O. Breecker

Department of Geological Sciences, The University of Texas at Austin, Austin, TX, 78712, United States

ARTICLE INFO

Article history:
Received 11 July 2016
Received in revised form 15 October 2016
Accepted 21 October 2016
Available online 9 November 2016
Editor: H. Stoll

Keywords:
speleothems
carbon isotopes
LGM
atmospheric CO_2
C_3 plants

ABSTRACT

The stable carbon isotope compositions of C_3 plants are controlled by the carbon isotope composition of atmospheric CO_2 ($\delta^{13}C_a$) and by the stomatal response to water stress. These relationships permit the reconstruction of ancient environments and assessment of the water use efficiency of forests. It is currently debated whether the $\delta^{13}C$ values of C_3 plants are also controlled by atmospheric pCO_2. Here I show that globally-averaged speleothem $\delta^{13}C$ values closely track atmospheric pCO_2 over the past 90 kyr. After accounting for other possible effects, this coupling is best explained by a C_3 plant $\delta^{13}C$ sensitivity of $-1.6 \pm 0.3‰/100$ ppmV CO_2 during the Quaternary. This is consistent with 20th century European forest tree ring $\delta^{13}C$ records, providing confidence in the result and suggesting that the modest pCO_2-driven increase in water use efficiency determined for those ecosystems and simulated by land surface models accurately approximates the global average response. The $\delta^{13}C$ signal from C_3 plants is transferred to speleothems relatively rapidly. Thus, the effect of atmospheric pCO_2 should be subtracted from new and existing speleothem $\delta^{13}C$ records so that residual $\delta^{13}C$ shifts can be interpreted in light of the other factors known to control spleleothem $\delta^{13}C$ values. Furthermore, global average speleothem $\delta^{13}C$ shifts may be used to develop a continuous radiometric chronology for Pleistocene atmospheric pCO_2 fluctuations and, by correlation, ice core climate records.

1. Introduction

The magnitude of carbon isotope fractionation during photosynthesis (i.e., discrimination) increases with decreasing water stress resulting in lower $\delta^{13}C$ values as mean annual precipitation (MAP) increases (Diefendorf et al., 2010; Kohn, 2010). Experimental evidence suggests that carbon isotope discrimination also varies with atmospheric pCO_2, following a hyperbolic relationship (Schubert and Jahren, 2012), which accurately reconstructs pCO_2 from 0–30 kyr BP (Schubert and Jahren, 2015). In the hyperbolic model, carbon isotope discrimination increases with pCO_2, resulting in lower $\delta^{13}C$ values as pCO_2 increases. In contrast, MAP-corrected $\delta^{13}C_{plant}$ records from various time periods spanning the Cenozoic suggest that either there is no pCO_2 effect or that it is small enough to be ignored (Diefendorf et al., 2015; Kohn, 2016). Additional uncertainty regarding the pCO_2 effect arises from the absence of statistically significant European conifer tree ring $\delta^{13}C$ sensitivity to 20th century atmospheric pCO_2 increase (Frank et al., 2015; Saurer et al., 2004). Conversely, broadleaf tree ring $\delta^{13}C$ records suggest that there is a pCO_2 effect (Frank et al., 2015) and both broadleaves and conifers follow the hyperbolic relationship in greenhouse experiments (Schubert and Jahren, 2012). Does pCO_2 control C_3 plant $\delta^{13}C$ values in nature? Speleothems offer a unique perspective on this question.

Speleothems have several advantages for evaluating the pCO_2 control on C_3 plant $\delta^{13}C$ values. Speleothems are well-dated and provide long, continuous and globally distributed records across the late Quaternary, allowing precise comparison with ice core CO_2 records. In addition, the $\delta^{13}C$ values of cave CO_2, drip water and calcite experimentally harvested in caves are dominantly controlled by C_3 plants, even in mixed C_3–C_4 ecosystems, perhaps because C_3 plants tend to have deeper roots than C_4 plants (Breecker et al., 2012; Meyer et al., 2014). Thus, speleothem $\delta^{13}C$ values may be relatively insensitive to C_3–C_4 shifts that might otherwise be conflated with changes in pCO_2. Furthermore, speleothem $\delta^{13}C$ values integrate numerous individual plants, evening out inherent variabilities (Graham et al., 2014; Kohn, 2016). Indeed, it has been recently suggested that speleothem $\delta^{13}C$ values record atmospheric pCO_2 (Wong and Breecker, 2015). There are also challenges associated with using speleothems to evaluate the pCO_2 control on C_3 plant $\delta^{13}C$ values. Most importantly, the effects of changes in climate on the belowground processes controlling speleothem $\delta^{13}C$ values are complex. These processes include respiration, carbonate

E-mail address: breecker@jsg.utexas.edu.

http://dx.doi.org/10.1016/j.epsl.2016.10.042
0012-821X/

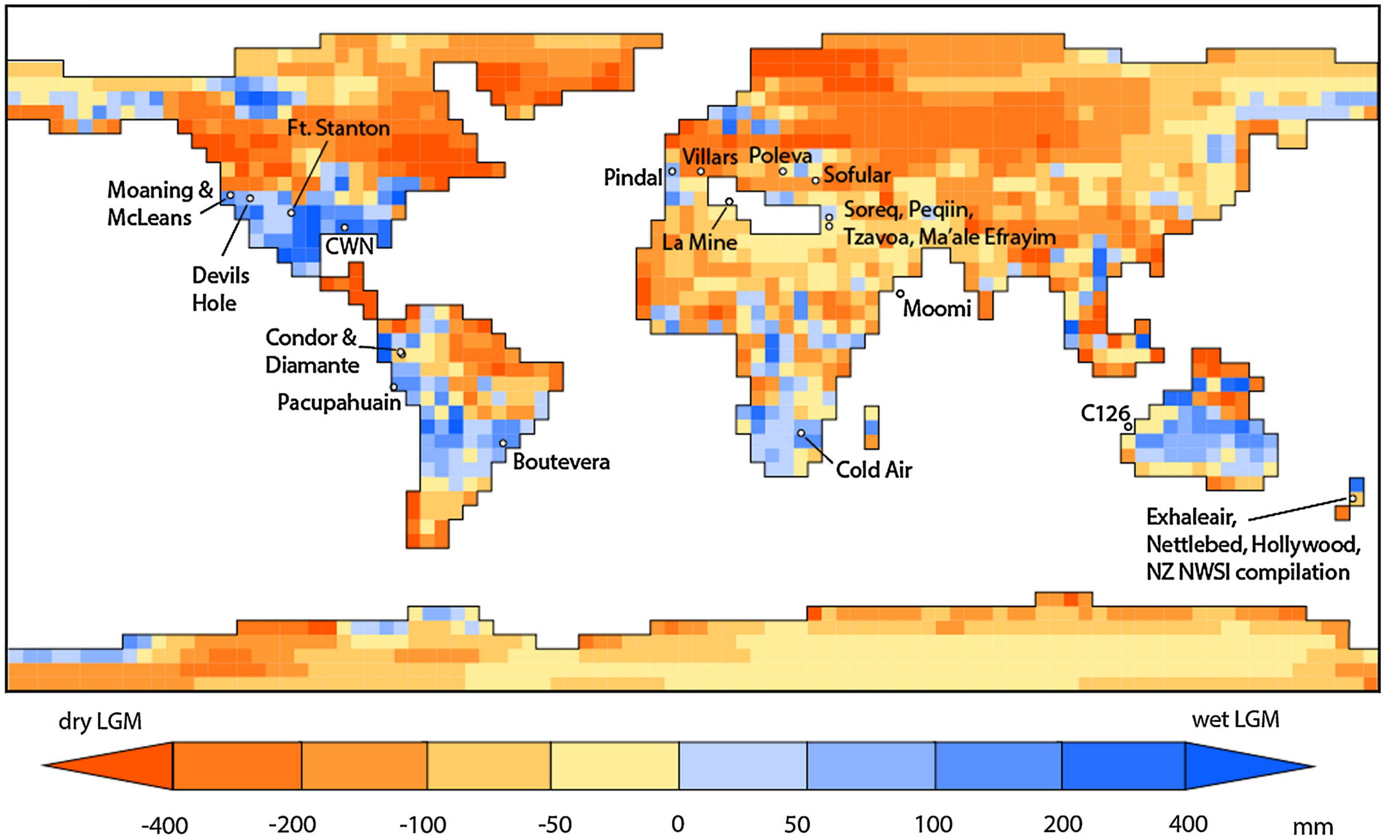

Fig. 1. Location of the last deglacial speleothem $\delta^{13}C$ records compiled in this study. Colors represent Last Glacial Maximum (LGM)–Holocene mean annual precipitation anomalies simulated using GENMOM (Alder and Hostetler, 2015). Modified from Alder and Hostetler (2015). References for records shown in Table S1.

host rock dissolution, CO_2 degassing and prior calcite precipitation. In addition, to my knowledge no forward model has been developed that considers all of these processes and their interaction with each other. I argue here that we can 'see through' much of this complexity by averaging across a large number of speleothem records from regions with contrasting late Quaternary climate variations.

2. Methods

I averaged Quaternary speleothem $\delta^{13}C$ shifts from records spanning the globe (Fig. 1, Table 1, records from NOAA speleothem database, see methods for further details). Most of the speleothem $\delta^{13}C$ records compiled here were downloaded from the NOAA speleothem database (http://www.ncdc.noaa.gov/data-access/paleoclimatology-data/datasets/speleothem) which was accessed between October and December 2015. Four records (Cave Without a Name, McLean's Cave, Devils Hole, Pindal Cave) were personally communicated (Feng personal communication, October 2014; Oster personal communication, December 2015; Moseley personal communication, January 2016, Moreno, personal communication June 2016). The values for two records (Villars Cave and La Mine Cave) were determined from plots in original papers (Table S1) using GraphClick (http://www.arizona-software.ch/graphclick/). The speleothem $\delta^{13}C$ records span all continents except Antarctica (Fig. 1), latitudes from 42°S to 45°N and ages from 0 to 568 kyr BP. The dataset consists of 21,028 $\delta^{13}C$ values from 69 speleothems published in 29 papers (Table S1).

To construct a speleothem $\delta^{13}C$ mean anomaly ($\Delta^{13}C_{speleothem}$) curve, each $\delta^{13}C$ record was normalized by calculating anomalies with respect it's mean $\delta^{13}C$ value during glacial maxima (defined here as time periods when atmospheric $pCO_2 < 200$ ppmV). Records from multiple speleothems from the same cave or from the same region that were published together in the same paper were all normalized if any of the records overlapped a glacial maxima, even if an individual record did not. Individual speleothems from the same region and even from the same cave can have different coeval $\delta^{13}C$ values, most likely due to different flow path hydrologies of the percolating waters that feed each speleothem. If coeval $\delta^{13}C$ values are distinct or if records are non-overlapping, then such normalization could be inaccurate. For the most part, however, the individual speleothem records that were considered together here overlap in time and have similar coeval $\delta^{13}C$ values, although there are some composite records that contain non-overlapping individual records and there is one composite record that contains coeval records with distinct $\delta^{13}C$ values (Fig. S1). The mean $\delta^{13}C$ anomalies of each record within 1 kyr age bins were then calculated. Finally, these record means were averaged together to obtain grand means (among-record means) within each 1 kyr age bin. This averaging approach equally weights each speleothem $\delta^{13}C$ record. A locally weighted regression (LOESS, which assigns a higher weight to higher resolution records) has similar trends, especially where data density is high (averaging of >10 records).

To help quantify the sensitivity to pCO_2, values of $\Delta^{13}C_{speleothem}$ from the Last Glacial Maximum (LGM) to Holocene were considered. The effects of three variables were quantified and subtracted from the observed $\Delta^{13}C_{speleothem}$ values. These variables include changes from the LGM to the Holocene in $\delta^{13}C_a$, MAP and MAT. The first two predictably affect the $\delta^{13}C$ values of C_3 plants and the third affects the $\delta^{13}C$ value of speleothem calcite through the temperature sensitive calcite-CO_2 carbon isotope fractionation factor. The magnitudes of MAT and MAP change at the location of each record were estimated using simulated LGM–Preindustrial