Earth and Planetary Science Letters 482 (2018) 367–376

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Ion microprobe $\delta^{18}O$ analyses to calibrate slow growth rate speleothem records with regional $\delta^{18}O$ records of precipitation

David Domínguez-Villar[a,*], Sonja Lojen[b,c], Kristina Krklec[d], Reinhard Kozdon[e,f], R. Lawrence Edwards[g], Hai Cheng[g,h]

[a] School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, B15 2TT Birmingham, United Kingdom
[b] Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, SI-1000, Ljubljana, Slovenia
[c] Faculty of Environmental Sciences, University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia
[d] Department of Soil Science, Faculty of Agriculture, University of Zagreb, Svetošimunska 25, 10000 Zagreb, Croatia
[e] Lamont-Doherty Earth Observatory of Columbia University, 10964 Palisades (NY), USA
[f] Department of Geoscience, University of Wisconsin-Madison, 1215 West Dayton St., Madison 53706 (WI), USA
[g] Department of Earth Sciences, University of Minnesota, 55455 Minneapolis (MN), USA
[h] Institute of Global Environmental Changes, Xian Jiaotong University, 710049 Xian, China

ARTICLE INFO

Article history:
Received 19 July 2017
Received in revised form 14 October 2017
Accepted 4 November 2017
Available online xxxx
Editor: M. Frank

Keywords:
speleothem
paleoclimate
calibration
$\delta^{18}O$
ion microprobe
Postojna

ABSTRACT

Paleoclimate reconstructions based on speleothems require a robust interpretation of their proxies. Detailed transfer functions of external signals to the speleothem can be obtained using models supported by monitoring data. However, the transferred signal may not be stationary due to complexity of karst processes. Therefore, robust interpretations require the calibration of speleothem records with instrumental time series lasting no less than a decade. We present the calibration of a speleothem $\delta^{18}O$ record from Postojna Cave (Slovenia) with the regional record of $\delta^{18}O$ composition of precipitation during the last decades. Using local meteorological data and a regional $\delta^{18}O$ record of precipitation, we developed a model that reproduces the cave drip water $\delta^{18}O$ signal measured during a two-year period. The model suggests that the average water mixing and transit time in the studied aquifer is 11 months. Additionally, we used an ion microprobe to study the $\delta^{18}O$ record of the top 500 μm of a speleothem from the studied cave gallery. According to U–Th dates and ^{14}C analyses, the uppermost section of the speleothem was formed during the last decades. The $\delta^{18}O$ record of the top 500 μm of the speleothem has a significant correlation ($r^2 = 0.64$; p-value <0.001) with the modelled $\delta^{18}O$ record of cave drip water. Therefore, we confirm that the top 500 μm of the speleothem grew between the years 1984 and 2003 and that the speleothem accurately recorded the variability of the $\delta^{18}O$ values of regional precipitation filtered by the aquifer. We show that the recorded speleothem $\delta^{18}O$ signal is not seasonally biased and that the hydrological dynamics described during monitoring period were stationary during recent decades. This research demonstrates that speleothems with growth rates <50 μm/yr can also be used for calibration studies. Additionally, we show that the fit of measured and modelled proxy data can be used to achieve annually resolved chronologies in speleothems that were not actively growing at the time of collection and/or that do not record annual laminae.

1. Introduction

Speleothems can be excellent archives of paleoenvironment and/or paleoclimate (Fairchild and Baker, 2012), and the oxygen isotope composition of speleothems is the most commonly used proxy in speleothem records (e.g., Lauritzen and Lundberg, 1999; Wang et al., 2001; Domínguez-Villar et al., 2017). Most researchers interpret the variability of speleothem $\delta^{18}O$ records in relation to the variability of the inter-annual/long-term oxygen isotope composition of precipitation over the region. However, multiple controls affect the initial $\delta^{18}O$ value of precipitation once the water enters the karst system and before the isotopic composition of drip water is transferred to the speleothems (Baker et al., 2012). Detailed studies have proven that the $\delta^{18}O$ values of speleothems may be dominated by variability of the fractionation factor between the solution and the forming carbonate (Feng et al., 2014). The epikarst hydrology has a significant control on

* Corresponding author.
E-mail address: ddvillar@hotmail.com (D. Domínguez-Villar).

https://doi.org/10.1016/j.epsl.2017.11.012

the $\delta^{18}O$ values due to the mixing of groundwater reservoirs with different residence times (Bradley et al., 2010). Also, the interactive dynamics between the soil and the atmosphere can affect the isotope composition via groundwater evaporation (Ayalon et al., 1998; Markowska et al., 2016) or the thermal decoupling between ground and atmosphere temperature (Domínguez-Villar et al., 2013). Therefore, before conducting detailed paleoenvironmental and/or paleoclimate interpretations from speleothem records, it is desirable to evaluate whether such records can be calibrated with available geochemical, environmental or climatological time series that control the $\delta^{18}O$ values in the system. Previous studies have shown a lack of correlation or a non-stationary relationship between Holocene speleothem $\delta^{18}O$ records and climate variables due to the complexity on the controls affecting the $\delta^{18}O$ values in karst systems (Treble et al., 2005; Fischer and Treble, 2008; Baker et al., 2011). Therefore, it is a good practice to perform calibration tests covering a period lasting no less than a decade in order to conduct robust paleoclimate or paleoenvironmental reconstructions (Burns et al., 2002; Yudava et al., 2004; Jex et al., 2010; Riechelmann et al., 2017).

In order to perform accurate calibration tests, annually resolved chronologies and annual or sub-annual sampling resolutions of the studied proxy are required (e.g., Mattey et al., 2008). Since growth rate is a limiting factor for these studies, speleothems used to calibrate $\delta^{18}O$ records typically have growth rates in the order of several hundred of microns per year. The amount of sample required to perform $\delta^{18}O$ analyses by Gas Source Isotope Ratio Mass Spectrometry (GS-IRMS) limits the spatial sampling resolution along the growth rate of speleothems to a range between 50 and 100 μm in best scenarios (Spötl and Mattey, 2006; Pacton et al., 2013). However, $\delta^{18}O$ analyses can also be carried out using an ion microprobe, which smaller requirements for sample size allows a typical spatial resolution between 10 and 30 μm (Treble et al., 2007; Orland et al., 2009). The use of ion microprobes to study speleothems is not novel, although is still uncommon. This technology has been applied to speleothems to obtain high resolution $\delta^{18}O$ records (Kolodny et al., 2003; Treble et al., 2007), to unravel seasonal cycles (Liu et al., 2015), to study the paleo-seasonality (Orland et al., 2009, 2012, 2015) or to perform calibration of recent samples (Treble et al., 2005; Orland et al., 2014). These studies showed that the spatial resolution of the ion microprobe analyses represents an advantage compared to the combination of micromill sampling and GS-IRMS analyses.

During two years we monitored the water $\delta^{18}O$ values of several drip sites in a hall of Postojna Cave (Slovenia) and selected a laminated speleothem that grew under one of the studied drip sites. Due to the slow growth rate of the top 30 mm of the speleothem (<40 μm/yr), we used ion microprobe analyses to obtain a speleothem $\delta^{18}O$ record of the top 500 μm of the sample that was expected to precipitate over the last decades. The aim of the study is to compare the recent speleothem $\delta^{18}O$ record with the regional record of $\delta^{18}O$ values of precipitation to test whether this speleothem record will provide a robust proxy for the long-term evolution of the $\delta^{18}O$ values of precipitation in the region.

2. Material and methods

2.1. Postojna Cave and water analyses

Postojna Cave is a 20 km long tourist cave in Slovenia (45.78°N; 14.20°E) (Fig. 1A). Within this cave, Pisani Rov is a ∼0.6 km long corridor aside from the major tourist route. We focus our study on Bela in Rdeča hall (hereafter referred to as BiR hall), which is the last chamber at the far end of Pisani Rov (Fig. 1B). BiR hall is 70 m long, 12 m wide and has an average height of 4.5 m. This hall has nearly 40 m of bedrock cover. The room is decorated with a multitude of speleothems, it has no appreciable air flow, and its average temperature is 8.4 °C (Domínguez-Villar et al., 2015). The surface over the cave has a patchy distribution of rendzina soils in between the dominant bedrock exposures that stands <0.5 m from the ground. According to artificial pits, the soil can locally reach depths >0.5 m (Krajnc et al., 2017). The vegetation consists of a dense mixed forest (i.e., spruce, fir and beech trees). In the studied site the climate is continental, and based on data from the Postojna meteorological station, located at 533 m asl (above sea level), the mean annual temperature was 8.7 °C during the period 1971–2000, with a mean temperature of 18.1 °C during the warmest month (July) and 0.1 °C during the coldest month (January). Over the same period, the average amount of annual precipitation (±1 SD; standard deviation) was 1590 ± 209 mm. There is no clear seasonality in the amount of precipitation. Snow is common during the winter and the snow cover over the ground can last for weeks during these months.

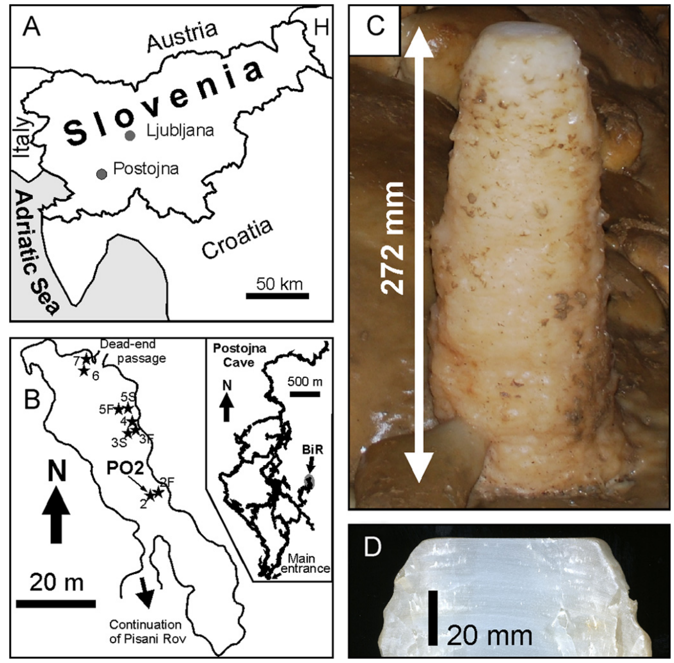

Fig. 1. Location map, cave sketch and speleothem images. A: Location map of Slovenia. Records of $\delta^{18}O$ values of precipitation are from Ljubljana and Postojna. The studied cave is in Postojna. B: Sketch of BiR hall (plan view) showing the location of drip sites (stars). Studied speleothem (PO2) was collected from drip site 2. Inset graph shows the location of BiR hall within Postojna Cave (grey shaded area pointed with an arrow). C: Image of stalagmite PO2 before collection. D: Detailed image of the top 30 mm of PO2 speleothem showing the flat surface of the centre of the speleothem.

During a two-year period (2009–2010), we studied the isotope composition of 9 drip sites in BiR hall, all of them located within 40 m (Fig. 1B). Drip water samples were collected twice per month for analyses of $\delta^{18}O$ values. These samples consisted of water accumulated in beakers left under the drip sites since the previous visit, except for one site (site 7; Fig. 1B) that had enough discharge to collect the water during every cave visit. Additionally, a total of 15 beakers containing 50 ml of water with a known initial $\delta^{18}O$ value (+19.16‰ VSMOW) were left to equilibrate with the moisture of the cave atmosphere in BiR gallery to evaluate potential evaporation processes. These samples were all set at once and collected one by one in different visits to the cave. The samples were set under an umbrella to prevent interferences caused by splashing water from nearby drip sites. Water samples of monthly precipitation were collected at the meteorological station of Postojna. All precipitation, rainfall, snow or hail, was collected daily and trans-