



# Triple isotope ( $\delta\text{D}$ , $\delta^{17}\text{O}$ , $\delta^{18}\text{O}$ ) study on precipitation, drip water and speleothem fluid inclusions for a Western Central European cave (NW Switzerland)



Stéphane Affolter<sup>a, c, \*</sup>, Anamaria D. Häuselmann<sup>b, c</sup>, Dominik Fleitmann<sup>d, c</sup>, Philipp Häuselmann<sup>e</sup>, Markus Leuenberger<sup>a, c</sup>

<sup>a</sup> Climate and Environmental Physics, Physics Institute, University of Bern, 3012 Bern, Switzerland

<sup>b</sup> Institute of Geological Sciences, University of Bern, 3012 Bern, Switzerland

<sup>c</sup> Oeschger Centre for Climate Change Research, University of Bern, 3012 Bern, Switzerland

<sup>d</sup> Department of Archaeology, School of Archaeology, Geography and Environmental Sciences and Centre for Past Climate Change, University of Reading, Whiteknights, PO Box 227, Reading RG6 6AB, UK

<sup>e</sup> Swiss Institute for Speleology and Karst Studies, 2301 La Chaux-de-Fonds, Switzerland

## ARTICLE INFO

### Article history:

Received 3 March 2015

Received in revised form

28 August 2015

Accepted 30 August 2015

Available online 26 September 2015

### Keywords:

Speleothems

Water isotopes ( $\delta\text{D}$ ,  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ )

$^{17}\text{O}_{\text{excess}}$

Precipitation

Drip water

Fluid inclusions

Milandre cave

## ABSTRACT

Deuterium ( $\delta\text{D}$ ) and oxygen ( $\delta^{18}\text{O}$ ) isotopes are powerful tracers of the hydrological cycle and have been extensively used for paleoclimate reconstructions as they can provide information on past precipitation, temperature and atmospheric circulation. More recently, the use of  $^{17}\text{O}_{\text{excess}}$  derived from precise measurement of  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  gives new and additional insights in tracing the hydrological cycle whereas uncertainties surround this proxy. However,  $^{17}\text{O}_{\text{excess}}$  could provide additional information on the atmospheric conditions at the moisture source as well as about fractionations associated with transport and site processes. In this paper we trace water stable isotopes ( $\delta\text{D}$ ,  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ ) along their path from precipitation to cave drip water and finally to speleothem fluid inclusions for Milandre cave in northwestern Switzerland. A two year-long daily resolved precipitation isotope record close to the cave site is compared to collected cave drip water (3 months average resolution) and fluid inclusions of modern and Holocene stalagmites. Amount weighted mean  $\delta\text{D}$ ,  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  are  $-71.0\text{‰}$ ,  $-9.9\text{‰}$ ,  $-5.2\text{‰}$  for precipitation,  $-60.3\text{‰}$ ,  $-8.7\text{‰}$ ,  $-4.6\text{‰}$  for cave drip water and  $-61.3\text{‰}$ ,  $-8.3\text{‰}$ ,  $-4.7\text{‰}$  for recent fluid inclusions respectively. Second order parameters have also been derived in precipitation and drip water and present similar values with 18 per meg for  $^{17}\text{O}_{\text{excess}}$  whereas d-excess is 1.5‰ more negative in drip water. Furthermore, the atmospheric signal is shifted towards enriched values in the drip water and fluid inclusions ( $\Delta$  of  $\sim +10\text{‰}$  for  $\delta\text{D}$ ). The isotopic composition of cave drip water exhibits a weak seasonal signal which is shifted by around 8–10 months (groundwater residence time) when compared to the precipitation. Moreover, we carried out the first  $\delta^{17}\text{O}$  measurement in speleothem fluid inclusions, as well as the first comparison of the  $\delta^{17}\text{O}$  behaviour from the meteoric water to the fluid inclusions entrapment in speleothems. This study on precipitation, drip water and fluid inclusions will be used as a speleothem proxy calibration for Milandre cave in order to reconstruct paleotemperatures and moisture source variations for Western Central Europe.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Water isotopes in precipitation (hereafter discussed as  $\delta\text{D}_p$ ,  $\delta^{17}\text{O}_p$  and  $\delta^{18}\text{O}_p$ ) reflect the moist air masses history through moisture source, atmospheric circulation and evaporation/condensation processes. On a regional scale  $\delta^{18}\text{O}_p$  varies according to surface air temperature, amount of precipitation, moisture

\* Corresponding author. Climate and Environmental Physics, Physics Institute, University of Bern, 3012 Bern, Switzerland.

E-mail address: [affolter@climate.unibe.ch](mailto:affolter@climate.unibe.ch) (S. Affolter).

source origin and rainout effect (Rozanski et al., 1992; Araguas–Araguas et al., 2000). These changes are recorded in speleothems, which are therefore now widely used for continental paleoclimate reconstructions. However, in order to interpret  $\delta^{18}\text{O}_p$  in speleothems, an understanding of the key processes that govern the isotopic composition of precipitation, cave drip water, speleothem calcite and fluid inclusions must be well documented. Only with these prerequisites speleothem data can be interpreted in terms of climate and hydrology (Riechelmann et al., 2011). Cave monitoring studies constitute a new standard for the interpretation of speleothem proxies and characterising the relationship between water isotopes of precipitation and cave drip water is becoming routine in caves worldwide (Cruz et al., 2005; Moerman et al., 2010; Cuthbert et al., 2014; Genty et al., 2014).

Stalagmites in particular allow the reconstruction of climate for long time intervals throughout the Quaternary (Cheng et al., 2009; Fleitmann et al., 2009; Meckler et al., 2012). They can be precisely dated using laminae counting (Fleitmann et al., 2004; Shen et al., 2013; Duan et al., 2015) or more commonly by Uranium series dating (Cheng et al., 2013) and can provide information on past climate change at high resolution (Henderson, 2006).

The majority of speleothem-based paleoclimate reconstructions rely on calcite geochemistry (Shakun et al., 2007). Routinely measured are  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  for calcite ( $\delta^{18}\text{O}_c$  hereinafter), which are respectively proxies for moisture supply (Burns et al., 2001; Fleitmann et al., 2003; Kennett et al., 2012; Vaks et al., 2013; Luetscher et al., 2015) and vegetation dynamics (Genty et al., 2010; Rudzka et al., 2011; Blyth et al., 2013) above the cave. Although widely used,  $\delta^{18}\text{O}_c$  can be influenced by several processes above or within the cave such as temperature- and humidity-driven isotope fractionation of the atmospheric water cycle, fractionation associated with the biospheric exchanges, equilibrium and kinetic fractionation in the epikarst and within the cave during calcite precipitation. These effects can make the interpretation of  $\delta^{18}\text{O}_c$  difficult (Lachniet, 2009).

Fluid inclusions represent past drip water and are consequently relics of past precipitation above the cave at the time when fluid inclusions were sealed (Schwarcz et al., 1976). Hence, they can be used as a direct proxy for paleotemperature or moisture history (Fleitmann et al., 2003; van Breukelen et al., 2008; Griffiths et al., 2010). Based on the correlation between mean annual temperature and mean annual  $\delta^{18}\text{O}_p$  on a global scale (Dansgaard, 1964), past temperature can thus be reconstructed using for instance the relationship that exists for calcite precipitation at equilibrium (Kim and O'Neil, 1997). However, one has to consider that the seasonal distribution of precipitation is an additional factor that could easily yield misleading temperature estimates for the past. Moreover, most cave stalagmites are not deposited in oxygen equilibrium with their parent drip waters (McDermott et al., 2006). Thus, it was observed that temperatures calculated on modern speleothems using an empirical relationship (Craig, 1965) were closer to corresponding cave air temperatures. Recently, Tremaine et al. (2011) suggested a new empirical calibration based on several caves data already taking into account a mean disequilibrium that seems to provide more reliable speleothem-based temperature estimates. A comparison of multiple proxies (Meckler et al., 2015) shows the potential of speleothems for absolute paleotemperature reconstructions by comparing the results of four different paleothermometers that are (i) speleothem fluid inclusions (Dublyansky and Spötl, 2009; Affolter et al., 2014), (ii) liquid–vapour homogenization of fluid inclusions (Krüger et al., 2011), (iii) noble gases concentration in stalagmite water (Vogel et al., 2013), and (iv) clumped isotopes (Meckler et al., 2014). It is thus important to monitor the isotope proxies from the precipitation falling above the cave to evaluate whether the isotopic composition of cave drip and

speleothem fluid inclusion water is comparable. So far, most investigations study the relationship between precipitations and drip water, while in this study we additionally investigate the climate signal transmission to speleothem fluid inclusions. Recent developments in speleothem fluid inclusion measurement techniques allow determining both  $\delta D_{fi}$  and  $\delta^{18}\text{O}_{fi}$  on a single sample (Arienzo et al., 2013; Affolter et al., 2014). Here we provide a further development of the method by measuring  $\delta^{17}\text{O}$  in fluid inclusion water ( $\delta^{17}\text{O}_{fi}$ ) offering new horizons for paleoclimate research based on speleothems.  $\delta^{17}\text{O}$  measurements on water samples were so far achieved using  $\text{CoF}_3$  fluorination of water (Landais et al., 2012a), but a more recent laser absorption spectroscopy based technique allows now fast and simple triple isotope measurements on water samples (Steig et al., 2014).

The d-excess and  $^{17}\text{O}_{\text{excess}}$  can be calculated from the triple isotope measurements on water aliquots. Deuterium excess is obtained from hydrogen ( $\delta D$ ) and oxygen ( $\delta^{18}\text{O}$ ) isotopes values and is defined as  $d = \delta D - 8 \times \delta^{18}\text{O}$  (Dansgaard, 1964). It carries information about the ocean surface conditions and is used to characterise the disequilibrium conditions at the moisture source. The d-excess is mainly dependent on sea surface temperature, normalised relative humidity and wind speed at the moisture source (Jouzel and Merlivat, 1984; Uemura et al., 2008; Pfahl and Sodemann, 2014) but is also dependent on local conditions such as recycling of local moisture. Similarly to d-excess,  $^{17}\text{O}_{\text{excess}}$  is calculated (see section 3.2.2) from small variations in oxygen isotopes ( $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ ) and corresponds to the deviation from the line of 0.528 corresponding to meteoric waters (Luz and Barkan, 2010). It constitutes a promising, but debated parameter to provide additional information on the water cycle (Winkler et al., 2012; Schoenemann et al., 2014; Li et al., 2015). The  $^{17}\text{O}_{\text{excess}}$  can be used as an indicator of evaporation conditions at the moisture source (Angert et al., 2004; Barkan and Luz, 2007) and has been so far mostly studied in the Polar Regions (Landais et al., 2008, 2012b; Schoenemann et al., 2014) and poorly in the lower latitudes (Landais et al., 2010; Luz and Barkan, 2010; Li et al., 2015). Over the ocean,  $^{17}\text{O}_{\text{excess}}$  is negatively correlated with the normalised relative humidity (Uemura et al., 2010). A direct link with relative humidity was observed in the coastal area of Antarctica (Winkler et al., 2012) but Schoenemann et al. (2014) showed that in Antarctica,  $^{17}\text{O}_{\text{excess}}$  has a strong dependence on the atmospheric temperature during transport due to the temperature dependence of supersaturation that override any information about the relative humidity. Furthermore,  $^{17}\text{O}_{\text{excess}}$  can also be influenced by processes of the terrestrial biosphere (Landais et al., 2007) and local conditions (Winkler et al., 2012; Steen-Larsen et al., 2014; Li et al., 2015).

In Switzerland, isotopes in precipitation have been surveyed for decades within the isotope network ISOT by the Climate and Environmental Physics at the University of Bern (CEP), financially supported by the Swiss Federal Office for the Environment (FOEN). The results of this survey are summarised for a west/east transect across Switzerland for three distinct areas representing the Jura Mountains (La Brévine station), the Swiss Plateau (Bern station) and the Southern Alps (Locarno station) (Schürch et al., 2003). The study performed at the Mormont station (Fig. 1) constitutes a prolongation of this transect up to the Tabular Jura that constitutes a flat Plateau to the NW of the last elevation of the Jura Mountains and provides additional information on  $\delta^{18}\text{O}_p$  and  $\delta D_p$  behaviour preventing the rainout effect that may occur when moisture encounters the first escarpment of the Jura Mountains. The link between  $\delta^{18}\text{O}$  in precipitation and cave waters has been previously studied in Milandre cave by Perrin et al. (2003a).

In this paper, we present a comprehensive overview of the hydrogen ( $\delta D$ ) and oxygen ( $\delta^{18}\text{O}$  and for the first time  $\delta^{17}\text{O}$  in drip water and speleothem fluid inclusions) isotope signal in

Download English Version:

<https://daneshyari.com/en/article/6445793>

Download Persian Version:

<https://daneshyari.com/article/6445793>

[Daneshyari.com](https://daneshyari.com)