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Seasonal and annual changes in soil/cave air pCO_2 and the $\delta^{13}C_{DIC}$ of cave drip water in response to changes in temperature and rainfall

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ABSTRACT

This study analyzes cave pCO_2 and the $\delta^{13}C_{DIC}$ of drip water in response to surface environmental changes in the Furong Cave, Chongqing, southwestern China, between 2009 and 2016. Several indices were continuously monitored, including air temperature, rainfall, soil pCO_2 outside the Furong Cave, as well as cave air pCO_2 and $\delta^{13}C_{DIC}$ of drip water inside the Furong Cave. The results revealed that (1) the overlying soil pCO_2 at the Furong Cave is directly controlled by the surface temperature and rainfall. Soil pCO_2 is higher in summer and autumn and lower in winter and spring. On an interannual time scale, soil pCO_2 shows a trend similar to annual rainfall. (2) Cave pCO_2 and soil pCO_2 both show characteristics of significant seasonal variation, which is similar to the seasonal variation in rainfall in Chongqing. Rainfall significantly affects cave pCO_2. (3) The $\delta^{13}C_{DIC}$ values of the drip water at Furong Cave are generally lower in summer and autumn and higher in winter and spring. They are mainly affected by seasonal variation in rainfall and the consequent soil CO_2 yield, which is also related to the increase in CO_2 degassing of the drip water caused by cave pCO_2 decreases in winter and spring. (4) The annual rainfall decreased in 2010–2011, and the $\delta^{13}C_{DIC}$ of the drip water was generally high. The annual rainfall gradually increased from 2012 to 2016, and the $\delta^{13}C_{DIC}$ of the cave drip water showed a consistent reduction. The $\delta^{13}C_{DIC}$ of the drip water at the Furong Cave may be used as an index of changes in surface rainfall which can reflect drought and flood events.

1. Introduction

Carbon isotopes ($\delta^{13}C$) of cave calcites are an alternative index in paleoclimate and paleoenvironment reconstruction studies of stalagmites. These have drawn broad attention for many years (Hendy, 1971; Bar-Matthews et al., 1996, 1999; Baker et al., 1997; McDermott, 2004; Fohlmeister et al., 2011; Frisia et al., 2011) because of their important potential for interpreting ecosystem and climate changes (Huang et al., 2016).

Stalagmite $\delta^{13}C$ is affected by air, soil, vegetation, the epikarst zone, and the cave, all of which lead to complex carbon sources and numerous contributing factors for the change of stalagmite $\delta^{13}C$. The overlying vegetation type (C3/C4 vegetation) determines the $\delta^{13}C$ of soil CO_2 (Dorale et al., 1992, 1998; Denniston et al., 2000). Surface temperature and rainfall affect the CO_2 productivity of the overlying soil of caves (Hesterberg and Siegenthaler, 1991; Amundson et al., 1998; Genty et al., 2003; Moreno et al., 2010). The openness of the epikarst zone determines the proportion of carbon from different sources (such as the atmosphere, soil, air, and the bedrock) in drip water and cave deposits (Genty et al., 2001, 2003; Kong et al., 2005; Spötl et al., 2005; Cruz et al., 2006; Cosford et al., 2009; Moreno et al., 2010). Cave air pCO_2 affects the degassing rate of drip water and the growth rate of cave deposits (Spötl et al., 2005; Dreybrodt and Scholz, 2011; Deininger et al., 2012). Prior calcite precipitation (PCP), which is the result of CO_2 degassing from groundwater in the epikarst zone in dry climatic periods is also an important factor that can increase the $\delta^{13}C$ values of the dissolved inorganic carbon (DIC) in cave drip water ($\delta^{13}C_{DIC}$) (Baker et al., 1997; Verheyden et al., 2000; Fairchild and Treble, 2009). Given these factors, the difference in $\delta^{13}C$ values of different stalagmites in the same cave, during the same time period, can be 4–10‰ (Linge et al., 2001; Serefiddin et al., 2004), which makes it difficult to correctly interpret climate and environmental information from stalagmite $\delta^{13}C$.

The factors mentioned above are related to climate change and are affected by differences in epikarst zones and caves. In addition, most soil CO_2 comes from the respiration of plant roots or is released by microorganisms during the decomposition of organic debris (Dreybrodt, 1988; Hess and White, 1993; Gillieson, 1996; Murthy et al.,

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2003; Baldini et al., 2008; Bond-Lamberty and Thomson, 2010). Ecosystem and climate warming experiments (Luo et al., 2001; Bronson et al., 2008), model analysis (McGuire et al., 1995; Raich et al., 2002), and biodynamics studies have shown that plant root respiration and the activity of microorganisms in soil are mainly affected by climate change (Davidson and Janssens, 2006).

Cave simulation and monitoring plays an important role in understanding the factors that control stalagmites, and in further analyzing the transmission process and mechanism of the $\delta^{13}C$ signal in karst cave systems (Genty and Massault, 1999; Mickler et al., 2004, 2006; Spötl et al., 2005; Fairchild et al., 2006; Genty and Dominique, 2008; Mattey et al., 2008; Deininger et al., 2012; Luo et al., 2013; Dreybrodt and Deininger, 2014). Through simulating cave temperature, the water drip rate, CO_2 degassing in drip water, and the residence time of drip water on top of a stalagmite, researchers can study the effects of these factors on the $\delta^{13}C$ of cave deposits (Baldini et al., 2006; Mühlinghaus et al., 2007, 2009; Whitaker et al., 2009; Dreybrodt and Scholz, 2011; Deininger et al., 2012). Cave monitoring can lead to the understanding of the isotope fractionation process between drip water and active carbonate deposits (Verheyden et al., 2008; Li et al., 2011b; Tremaine et al., 2011; Riechelmann et al., 2013). The systematic investigation of factors such as surface temperature, rainfall, vegetation type and distribution, and soil and cave air pCO_2 can help in the interpretation of the effects of processes in the epikarst zone on the $\delta^{13}C$ values of cave drip water and active deposits (Whitaker et al., 2009; Li et al., 2012; Luo et al., 2013; Feng et al., 2014; Meyer et al., 2014).

In order to gain a better understanding of the sources of cave CO_2 and the transmission mechanism of CO_2 from the epikarst zone to the cave, as well as the relationship between $\delta^{13}C$ of drip water and cave pCO_2, a multi-parameters monitoring program has been underway at Furong Cave, Chongqing, southwest China, since 2005. Li et al. (2012) analyzed the differences in seasonal DIC $\delta^{13}C$ in drip water and pool water. Differences were attributed to variable degrees of CO_2 degassing in winter and summer. However, the main factors affecting seasonal variation in cave pCO_2 and the sources of cave CO_2 were not discussed in this earlier paper. This study also had a short monitoring time (from March 2009 to June 2010). In the current study, based on the monitoring data of surface temperature, rainfall, soil/cave air pCO_2, and $\delta^{13}C_{DIC}$ values of drip water measured at Furong Cave from 2009 to 2016, we discuss the relationships between both cave air pCO_2 and drip water $\delta^{13}C_{DIC}$ and surface hydrological and thermal conditions on the annual time scale, and analyze the effect of regional drought events on the $\delta^{13}C_{DIC}$ of cave drip water. The data presented here provides an opportunity to explore the link between rainfall and both soil pCO_2 and cave pCO_2.

2. Study area

Furong Cave (29°13′ N, 107°54′ E) is located near the Furong River at Jiangkou Town, Wulong County, Chongqing, southwest China. It is approximately 5 km away from the confluence of the Furong and Wujiang Rivers (Fig. 1A). The region has a typical subtropical humid monsoon climate, affected by both the Asian southeast summer monsoon and the Asian southwest summer monsoon. The annual mean temperature and precipitation was 17.9 °C and 1080 mm, respectively, during 2005–2016, as recorded at the Wulong weather station. The precipitation from May to October accounts for 70–80% of the precipitation for the entire year (Li et al., 2011b). The overlying strata are Mid-Cambrian limestone and dolomite. The surface vegetation cover is 95%, and mostly consists of trees and shrubs. The soil is affected by slope gradient, slope direction, and surface vegetation cover, and its thickness is 20–100 cm (Li et al., 2012).

The cave entrance of the Furong Cave is at an elevation of 480 m. The total cave length is approximately 2800 m. The width and height are 30–50 m, each. The current developed area is approximately 1800 m long. There is only one entrance and the exit is an artificial tunnel excavated in 1996, with a length of 180 m and a height of 3 m. The cave air temperature is 16.0–16.3 °C and the humidity in the Great Hall, which is located about 1500 m from the cave entrance, is 95–100% year round (Li et al., 2011b) (Fig. 2).

3. Sample collection and experimental analysis

A HOBO miniature meteorological monitor, manufactured by ONSET (USA), was installed outside the Furong Cave, about 50 m from the entrance, to monitor the air temperature (range 40–75 °C, precision ± 0.2 °C), humidity (range 0–100%, precision ± 2.5%), and precipitation (resolution 0.2 mm, precision ± 1.0%). We selected five soil profiles along the two sides of the valley above the Furong Cave where CO_2-monitoring apparatuses were installed (Fig. 1B). Their labels (depths) were SA (50 cm), SB (20 cm), SC (50 cm), SD (50 cm), and SE (50 cm), respectively. They were all located at the interface between the bedrock and the soil. We used an AP-20 CO_2 sampler manufactured by Komyo Rikagaku Kogyo K.K. and a 126SA testing tube to measure the soil CO_2 concentration monthly. The measurement range was a 0.1–2.6% volume concentration.

An automatic thermometer was placed in the Great Hall (StowAway TidbiT Temp Logger, Onset Computer Corporation model TBI32-20 + 50, temperature range −20–70 °C, precision ± 0.2 °C) to record the cave temperature every 2 h, from November 2006 to October 2007 (Li et al., 2011b). Six sites (#2, #4, MP1-MP4) inside the cave were chosen to measure cave air pCO_2 once a month. Five sites (#2, #4, MP1-MP3) were located in the Great Hall, and MP4 was in the corridor, approximately 600 m from the entrance (Fig. 2). We used a Testo535 infrared CO_2 meter manufactured by Testo, Germany, to measure the air CO_2 concentration inside and outside of the cave (#5) (range of 0–9999 ppmv; measurement precision greater than 2%). We used a Testo635 temperature and moisture meter to measure the air temperature and humidity at every monitoring site inside and outside the cave (temperature range −40–150 °C, precision ± 0.2 °C; relative humidity range 0–100%, precision ± 0.1%).

We selected five drip water monitor sites (MP1 ~ MP5) inside the Furong Cave (Fig. 2) and drip water was collected monthly from 2009 to 2016. For collection of drip water samples, we used clean PE sample bottles that had been rinsed in 1:1 HCl and washed with deionized water. To avoid isotope fractionation caused by microorganisms, 0.2 mL saturated $HgCl_2$ solution was added into the samples used for $\delta^{13}C_{DIC}$ measurements (20 mL). The samples were sealed, brought back to our laboratory, and stored at 5 °C for analysis. The $\delta^{13}C_{DIC}$ of drip water analyses were completed at the Geochemistry and Isotope Laboratory of the Southwest University. Analyses were performed using a Delta-V-Plus Mass Spectrometer connected to a Gas Bench pretreatment apparatus. The analysis precision was greater than 0.2% (1σ). The $\delta^{13}C$ results are reported using V-PDB as the reference.

4. Results

4.1. Regional temperature, precipitation, and air pCO_2

For this study, the monitoring period was from January 2009 to December 2016. Monthly mean temperature and precipitation are shown for each year (Fig. 3E and F). Monthly temperature data reveal low values in December and January (mean T = 7.8 ± 1.3 °C), and high values in July and August (mean T = 28.0 ± 0.9 °C). The lowest monthly mean temperature (4.3 °C) was observed in January 2011 (Fig. 3E).

The lowest annual precipitation sum (751 mm) was recorded in 2009, while the highest value occurred in 2016 (1498 mm). The lowest monthly rainfall (4–19 mm) was primarily in January and February, except in 2016 (December). However, the highest monthly precipitation (154–423 mm) was in a different month every year; highest monthly precipitations were observed from April to July and September