



Factors controlling the growth rate, carbon and oxygen isotope variation in modern calcite precipitation in a subtropical cave, Southwest China



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ABSTRACT

A prerequisite for using cave speleothems to reconstruct palaeoenvironmental conditions is an accurate understanding of specific factors controlling calcite growth, in particular the isotopic partitioning of oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) which are the most commonly used proxies. An *in situ* monitoring study from April 2008 to September 2009 at Xueyu Cave, Chongqing, SW China, provides insight into the controls on calcite growth rates, drip water composition, cave air parameters and $\delta^{18}O$ and $\delta^{13}C$ isotopic values of modern calcite precipitation. Both cave air PCO_2 and drip water hydrochemical characteristics show obvious seasonality driven by seasonal changes in the external environment. Calcite growth rates also display clear intra-annual variation, with the lowest values occurring during wet season and peak values during the dry season. Seasonal variations of calcite growth rate are primarily controlled by variations of cave air PCO_2 and drip water rate. Seasonal $\delta^{18}O_{-VPDB}$ and $\delta^{13}C_{-VPDB}$ in modern calcite precipitates vary, with more negative values in the wet season than in the dry season. Strong positive correlation of $\delta^{18}O_{-VPDB}$ vs. $\delta^{13}C_{-VPDB}$ is due to simultaneous enrichment of both isotopes in the calcite. This correlation indicates that kinetic fractionation occurs between parent drip water and depositing calcite, likely caused by the variations of cave air PCO_2 and drip rate influenced by seasonal cave ventilation. Kinetic fractionation amplifies the equilibrium fractionation value of calcite $\delta^{18}O$ (by $\sim 1.5\%$) and $\delta^{13}C$ (by $\sim 1.7\%$), which quantitatively reflects surface conditions during the cave ventilation season. These results indicate that the cave monitoring of growth rate and $\delta^{18}O$ and $\delta^{13}C$ of modern calcite precipitation are necessary in order to use a speleothem to reconstruct palaeoenvironment.

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1. Introduction

Calcite speleothems (stalagmites, stalactites and flowstones in caves) offer multiple geochemical proxy measures such as growth rate, $\delta^{18}O$, $\delta^{13}C$, trace elements, fluorescent laminae, and fluid inclusions to record the prevailing environmental conditions when combined with high-precision dating methods (McDermott, 2004; Fairchild et al., 2006). Generally, changes in rainfall, mean annual temperature, moisture sources and vegetation composition (C3 vs. C4) are interpreted from the parameters mentioned above (McDermott, 2004; Lauritzen, 2005; Fairchild et al., 2006; Lambert and Aharon, 2011). Thus, the laminae, oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotopic values of calcite in speleothems are widely used in palaeoclimate researches/reconstructions (Baker et al.,

1997; Genty et al., 2003; Yuan et al., 2004; Tan et al., 2006; Scholz et al., 2012; van Rampelbergh et al., 2014).

The calcite growth rate is a key factor in formation of distinct laminae in a speleothem that may offer a high-resolution record of palaeoenvironment variations outside the cave (Tan et al., 2006; Cai et al., 2011). Generally, the calcite growth rate is controlled by parent drip water and cave parameters including drip water composition, water film thickness and cave air PCO_2 (Dreybrodt, 1988; Fairchild et al., 2006; Banner et al., 2007). Thus, it can capture signals of environmental change and may exhibit obvious seasonal variation reflecting these controlling factors. Further, calcite growth rates may also show different seasonal patterns. For instance, in some caves in the Asian monsoon area, the calcite growth rate is faster during the wet season (Zhang et al., 2009; Ruan and Hu, 2010), while in others, it is faster during the dry season (Duan et al., 2012; Cai et al., 2011). This different behavior indicates that the controlling factors of calcite growth rate can vary even within caves located in the same climate zone. Thus,

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analysis of a given sample needs correlation with different features of a cave before the calcite is used to reconstruct palaeoenvironment. Calcite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values in speleothems are the end product of complex interactions between environmental processes in the surface environment, soil, overlying karst aquifer, and the cave system (Lambert and Aharon, 2011; Feng et al., 2012). Valid interpretation of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ environmental signals depends on detailed knowledge of the isotope fractionation processes occurring in the karst system and the cave (McDermott, 2005). Recently, many papers have interpreted the impacts of temperature, drip rate, amount of CO_2 degassing or exposure time of a water film on the variations found in the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signals and isotopic fractionation between parent drip water and depositing calcite (Hendy, 1971; Mühlinghaus et al., 2007, 2009; Wiedner et al., 2008; Dreybrodt and Scholz, 2011; Deininger et al., 2012; Feng et al., 2012, 2014; Meyer et al., 2014). These studies have provided valuable knowledge about the evolution of isotopic and geochemical systems in caves. However, the complexity of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ fractionation mechanisms and conditions in the cave frequently lead to ambiguity in the environmental interpretation. Therefore, some studies have attempted to interpret the isotope fractionation effects and controlling processes occurring between parent drip water and depositing calcite by investigating modern calcite precipitation on to artificial substrates (convex glass, plexiglass or plastic plate) in cave monitoring (Frisia et al., 2000; Mickler et al., 2006; Surić et al., 2010; Tremaine et al., 2011; Li et al., 2011; Feng et al., 2012, 2014; Meyer et al., 2014).

This study reports the results of modern calcite precipitation and parent drip water monitoring in Xueyu Cave, a limestone cave located in Chongqing Municipality, SW China. Previous studies in this cave have revealed that the drip water hydrochemistry responds seasonally to external environmental factors and that it is further changed by cave ventilation and prior calcite precipitation processes (Pu et al., 2015). This study aims to elucidate the factors affecting the growth rate and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of modern calcite precipitation in Xueyu Cave by monitoring drip water hydrochemistry, cave environmental parameters and the calcite isotopes.

2. Study area and sampling sites

Xueyu Cave (29°47'00"N; 107°47'13"E; alt. 233 m) is a typical karst vadose zone cave developed in Lower Triassic limestone (T_{1j}). It is located on the lower reach of Long River, a tributary of Yangtze River about 12 km southeast of Fengdu County, Chongqing Municipality, SW China (Fig. 1). The cave has been developed by perennial cave stream flow through the limestone (Fig. 2). The outlet of the water is also the only known cave entrance. There are no known allogenic streams sinking underground at the head of the cave. Precipitation is the only recharge source. The regional climate is dominated by the Asian Monsoon, characterized by a cold-dry winter from November to April and hot-rainy summer from May to October. On average, the local annual precipitation is 1072 mm, with 70% of the rainfall in the wet season from May to October. The local annual average air temperature is 17.5 °C. As a typical monsoon region, air temperature and precipitation in the Xueyu cave catchment vary in a complementary manner, both being high in the wet season and low in the dry season. The inner parts of Xueyu Cave, beginning ~300 m from the entrance, are moderated with air temperature ranging from 16.8 °C to 19.1 °C and the relative humidity ranging from 76.7% to 100%.

The cave stream catchment is about 8–9 km². The surveyed portion of the cave extends 1644 m. Most parts of the cave are narrow, deep passages (canyon passages). It can be divided into three broad levels at 233–236 m (Level I), 249–262 m (Level II) and 281–283 m

(Level III) above sea level (Fig. 2). The modern stream flows only in the bottom level. The overburden consists of 150–250 m of limestone with well vegetated evergreen broadleaf woods above it. The soil thickness is heterogeneous outside the cave. Generally, it is typically thin (<20 cm depth) along slopes above the cave, but it is thicker (>80 cm depth) in the mountain top area.

A perennial drip (D1) was chosen for monitoring. It comes from an active soda-straw tip and feeds a stalagmite. The D1 site is in Level II, about 250 m below the surface and 250 m from the cave entrance (Fig. 2). There is a narrow passage from the D1 site to Level I in the cave.

3. Methods

The D1 drip site was sampled and monitored every 1–2 months from April 2008 to September 2009. Sampling regularly included collection of drip water for geochemical analysis and collection of modern calcite deposits on a convex glass plate under D1 (Fig. 2). Both cave air parameters (air temperature, cave air CO_2 concentration) and selected geochemical parameters of D1 drip water (pH, specific conductivity, water temperature and bicarbonate) were tested regularly *in situ* using the procedures described below. Cave bedrock samples and calcites on the tops of some active stalagmites were also collected at December, 2008.

Partial pressure of carbon dioxide (cave air PCO_2) was determined with a calibrated CDU 440 CO_2 meter (measuring range 0×10^4 – 6×10^4 ppm, resolution 10 ppm; Industrial Scientific, Pittsburgh, PA, USA). A calibrated thermometer with a resolution of 0.1 °C (TES-1360 model, TES Electrical Electronic Corp., Taipei, Taiwan) was employed for the cave air temperature. Drip water samples were collected in acid-washed 10 ml and 100 ml high-density polyethylene bottles (HDPE) at the drip tip. Drip rate was manually calculated at the time of collection using 10 ml sample bottles (measured in triplicate) from April 2008 to May 2009 only. The pH of the 10 ml sub-sample was measured *in situ* immediately, using a HACH HQ340d multi-parameter meter (± 0.01 pH units). The glass tip of the pH probe is very small (micro pH meter) and sensitive to pH changes; when immersed in about 3–5 drips it can measure the pH value and record it. Although there can be some deviation due to rapid degassing once drips emerge from the central canal of a soda-straw, this study reduced it by immediately testing after collecting a few drips. HCO_3^- was titrated immediately in the field using a portable testing kit by Merck KGaA CO., Darmstadt, Germany, with an accuracy of 0.05 mmol/l. The 100 ml sample was immediately divided into two sub-samples of 50 ml. To determine the major cation contents (K^+ , Na^+ , Ca^{2+} , Mg^{2+} and Sr^{2+}), one sub-sample was filtered through 0.45 μm cellulose acetate membrane filters and acidified to a pH of 2.0 using distilled 7 M HNO_3 . The other sub-sample was used to test major anions (Cl^- , SO_4^{2-}). Both sub-samples were stored in a refrigerator at 4 °C prior to analysis. Major anions (Cl^- , SO_4^{2-}) were measured by ion chromatography in the Water Environmental Laboratory, School of Geographical Sciences, Southwest University, China, following US Environment Protection Agency (EPA) standard methods. Major cations were analyzed by ICP-OES (Optima. 2100DV, Perkin-Elmer CO., Wellesley, MA, USA) in the Geochemistry and Isotope laboratory of Southwest University of China. Estimated analytical errors were within $\pm 5\%$. The hydrochemical data sets, including pH, water temperature and concentrations of K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and HCO_3^- were processed with the program WATSPEC (Wigley, 1977), which calculates drip water CO_2 partial pressure (drip water PCO_2) and the saturation index of calcite (SIc). Some drip water samples were also collected for oxygen isotope analysis and stored in an acid-washed 10 ml high-density polyethylene bottles that were filled and sealed completely to prevent evaporation.

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