



# Calcium isotopic fractionation during travertine deposition under different hydrodynamic conditions: Examples from Baishuitai (Yunnan, SW China)



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## ABSTRACT

Revealing the potential of Ca isotopes in the research of travertine formation processes is the principal goal of this study. To achieve this, the hydrochemistry, travertine precipitation rates, and variations in Ca isotopic compositions ( $\delta^{44/40}\text{Ca}$ ) of present-day endogenic (thermogenic) travertine in two different hydrodynamic systems (canal and pool) are studied at Baishuitai (Yunnan, SW China). In the canal, where the travertine precipitation is faster,  $\delta^{44/40}\text{Ca}$  values of both solution and travertine show a downstream increase, with Ca isotopic fractionation ( $\Delta^{44/40}\text{Ca}_{\text{CaCO}_3\text{-aq}}$ ) equal to  $\sim -1.6\%$ . Compared to the canal, Ca isotopic fractionation between travertine and aqueous  $\text{Ca}^{2+}$  is smaller ( $\Delta^{44/40}\text{Ca}_{\text{CaCO}_3\text{-aq}} \approx -1.2\%$ ) in the pools where travertine precipitation rates are lower. The spatial variations in  $\delta^{44/40}\text{Ca}$  values of solution and travertine are related to the amount of Ca removed from the solution when  $\delta^{44/40}\text{Ca}$  values of spring water remain stable. In addition, the results confirm the control of precipitation rates on Ca isotopic fractionation between calcite and parent aqueous  $\text{Ca}^{2+}$  using natural samples. The observed negative correlation between  $\Delta^{44/40}\text{Ca}_{\text{CaCO}_3\text{-aq}}$  and travertine precipitation rates can be explained by the steady-state kinetic surface reaction model proposed by DePaolo (2011), with equilibrium and kinetic fractionation factors of  $\alpha_{\text{eq}} = 1.0000 \pm 0.0001$  and  $\alpha_{\text{f}} = 0.9983 \pm 0.0002$ , respectively. An important consequence of this study is that Ca isotopes in travertine systems are good tools to have access to variations of  $\delta^{44/40}\text{Ca}_{\text{aq}}$ , which are directly linked to the amount of precipitated Ca. This could then be useful for reconstructing past hydrodynamic conditions when applied to travertine core data.

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## 1. Introduction

Speleothems, tufa and travertine are widespread terrestrial carbonates that form in caves, lakes, and rivers/streams, respectively, and are among the most important continental climate-related deposits (Ford and Pedley, 1996; Pentecost, 2005; Liu et al., 2006; Jones and Renaut, 2010). Their deposition is controlled by several factors, such as  $\text{CO}_2$  degassing due to inorganic or organic processes. Travertine and tufa consist of microgranular calcite, which result from two main formation processes: (1)  $\text{CaCO}_3$  encrusts filamentous microbionts, whose biannual laminations reflect seasonal changes in the water chemistry,

cyanobacterial growth and/or hydrology of the depositional environment (Chafetz et al., 1991; Matsuoka et al., 2001; Andrews and Brasier, 2005; Kano et al., 2007; Kawai et al., 2009), and (2)  $\text{CaCO}_3$  forms in an endogenic (thermogenic) way with multiple  $\text{CO}_2$  sources, including the hydrolysis and oxidation of reduced carbon, decarbonation of limestone, or direct contributions from the deep crust or upper mantle (Ford and Pedley, 1996; Minissale et al., 2002; Crossey et al., 2009). Due to high growth rates (mm to cm per year), travertine has unique advantages in providing high-resolution (up to seasonal, monthly or even daily) palaeoclimatic and palaeo-environmental information (Kano et al., 2003; Liu et al., 2010).

Palaeoenvironmental changes can be recorded in travertine via variations in lamina thickness, textures, trace element concentrations and their stable isotope compositions (Ihlenfeld et al., 2003). Oxygen (O) and carbon (C) isotopic compositions ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , respectively) are by far the most commonly investigated paleo-proxies in travertine (Andrews, 2006; Kano et al., 2007). However, it is difficult to unambiguously relate directly the measured isotopic variations in travertine to

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specific environmental changes. For instance,  $\delta^{18}\text{O}$  values of travertine formed in different hydrodynamic environments may show similar seasonal trends, where one is due to the temperature variation and the other to the dilution by rainfall (Wang et al., 2014). A potential approach to solve this problem is to employ combined isotopic systems so that various environmental information can be separated from each other. Though calcium (Ca) is one of the main elements in travertine, little or no data have been reported so far on variation in its isotopic compositions.

Ca isotope fractionation during inorganic  $\text{CaCO}_3$  precipitation (calcite and aragonite) has been primarily studied for a decade via several laboratory experiments (Gussone et al., 2003; Lemarchand et al., 2004; Marriott et al., 2004; Gussone et al., 2005; Tang et al., 2008; Gussone et al., 2011; Reynard et al., 2011; Tang et al., 2012). In contrast, few studies dealt with continental carbonate field samples (Tipper et al., 2006; Nielsen and DePaolo, 2013). Tipper et al. (2006) reported results on travertine from the southern Tibetan Plateau and showed that those travertine were isotopically light compared to surrounding river water and limestone samples. More recently, Nielsen and DePaolo (2013) studied tufa that precipitated from supersaturated lake water in Mono Lake (California) and observed that the intensity of Ca isotopic fractionation depends on the solution chemistry, with variations that are consistent with the theoretical model proposed by the authors for the formation of those carbonates.

Here, we focus on the endogenic travertine-depositing canal and pools of Baishuitai (Yunnan, SW China), a natural laboratory to study isotopic fractionation associated with calcite precipitation. Some of previous studies at this site attempted to understand seasonal variations in the hydrochemistry,  $\text{CaCO}_3$  precipitation rates and formation of biannual laminae in the canal and to discuss their climatic implications (Liu et al., 2003, 2006, 2010). Other studies dealt with the C and O isotope ratios in modern travertine from the canal and the pools (Liu et al., 2006; Sun and Liu, 2010; Yan et al., 2012; Sun et al., 2014). In the present study, we aim 1) to determine the variations in  $\delta^{44}/^{40}\text{Ca}$  values of present-day travertine and their controlling factors, 2) to test if the precipitation rate dependence of Ca isotope fractionation between calcite and solution found in the laboratory could also be observed in naturally travertine-depositing systems, and 3) to discuss the potential of Ca isotopes applied to travertine.

## 2. General Settings of the study

The Baishuitai travertine site (N27°300', E100°02') is located ~100 km south of Shangri-La Town, Yunnan Province, China. The elevation ranges from 2380 to 3800 m asl. The area is characterised by a subtropical monsoon climate, with >75% of the annual precipitation (~750 mm) occurring during the rainy season from May to October. The annual mean air temperature is 8 °C (Liu et al., 2003).

Baishuitai has a typical karst landscape and features one of the largest travertine deposits in China, which formed due to calcite-supersaturated aqueous solutions. Baishuitai spring water originates from the mixing of infiltrated rainfall and groundwater flow. An endogenic  $\text{CO}_2$  source dissolves limestone from the Triassic Beiya Formation. When the spring emerges, a huge quantity of  $\text{CO}_2$  at a high internal partial pressure is released to the atmosphere. This process creates an increase in the calcite saturation index of the water, thereby leading to  $\text{CaCO}_3$  precipitation (Liu et al., 2003).

There are two travertine-depositing systems at Baishuitai: a fast-flowing canal system and a slow-flowing pool system (Fig. 1). In the canal system, a spring water rich in  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  (S1-3) emerges from a middle Triassic limestone aquifer and mixes with a small amount of surface water from the Baishui River, which contains lower concentrations of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  (Liu et al., 2010; Yan et al., 2012) (Fig. 1c). Then, the mixed water flows along an ~2.5-km-long artificial canal that descends from 2900 to 2600 m asl and is accompanied by intense travertine deposition. The width of the canal ranges from 30 to 70 cm

and its depth varies from 10 to 20 cm. The flow rate in the canal varies between 50 and 100 L/s.

The pools system is part of a set of large travertine terraces, which are chiefly supplied by two springs (S1-1 and S1-2, Fig. 1b). In this study, only S1-1 is studied because the hydrochemistry of the two springs is almost identical and is stable throughout the year (Sun et al., 2014). The pools are 50 to 250 cm wide, 100 to 400 cm long, and 10 to 40 cm deep. Most of the pools are located approximately 300 m (along the flow path) from the springs (S1-1 and S1-2) and have an elevation of approximately 2555 m (Fig. 1b) (for more details, see Yan et al., 2012).

## 3. Sampling and analytical techniques

### 3.1. Sampling and sample description

Two field sampling campaigns, summer 2010 and winter 2011/2012, were conducted to evaluate seasonal variations in Ca isotopic compositions. Plexiglass substrates with the dimensions 5 cm × 5 cm × 0.5 cm were placed in the flowing water (at 2–5 cm depth, in the middle of the canal or pools where water flows fast to hamper accumulation of upper calcite particles on the downward substrates) at eight different sites: Five sites (W1–W5) were selected at approximately equal intervals along the sample canal, and three sites (P4, P4.5 and P5) were chosen in three different pools (Fig. 1). The substrates were replaced every 10 days at the same locations. The travertine samples were collected from the substrates to measure the precipitation rates and stable isotopic compositions of Ca.

During each travertine sample collection, related water samples were also sampled and stored after filtration in acid-cleaned polyethylene bottles. Additionally, S1-1 and S1-3 spring waters were collected in summer 2010 and winter 2011/2012. The spring water of S1-3 corresponds to a mixture of spring and Baishui River water because it was not possible to collect pure spring water. A winter rainwater sample ~200 m away from the travertine terraces and a summer sample from the Baishui River near the S1-3 sampling location were analysed. In summer, an overland flow that contributes to the canal was also collected. A limestone sample from the middle Triassic aquifer was used to constrain the Ca isotopic composition of the bedrock.

### 3.2. Methods

#### 3.2.1. Hydrochemical measurements

For each water sample (including rainwater and the S1-1 and S1-3 spring waters), the pH, water temperature, dissolved oxygen concentration (DO) and electrical conductivity (SpC) were measured in situ with a hand-held water quality meter (WTW 350i) with accuracies of  $\pm 0.05$  pH units,  $\pm 0.1$  °C,  $\pm 0.05$  mg/L and  $\pm 0.5\%$ , respectively. The instrument was calibrated prior to use with pH 7 and pH 10 buffers. The concentrations of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  were titrated on site via an Aquamerck® Alkalinity Test and Hardness Test with analytical resolutions of approximately  $\pm 6$  and  $\pm 1$  mg/L, respectively.

To measure the chemistry more accurately and perform Ca isotope analysis, water samples at the sampling sites were collected in acid-cleaned polyethylene bottles and filtered through 0.45  $\mu\text{m}$  Minisart® filters. A non-acidified water aliquot was used for major element concentration measurements and analysed at the State Key Laboratory of Environmental Geochemistry of the Institute of Geochemistry, Chinese Academy of Sciences. The concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$  were determined via an inductively coupled plasma optical emission spectrometer (ICP-OES) with an RSD of less than 5%, and the concentrations of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  were determined by ion chromatography (Dionex® ICS-90) with RSDs of less than 2% and 4%, respectively. Another aliquot of the waters was acidified to pH < 1 via ultrapure  $\text{HNO}_3$  for Ca isotope analyses and refrigerated.

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