



## Effect of calcite precipitation on stable strontium isotopic compositions: Insights from riverine and pool waters in a karst cave

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### ABSTRACT

Radiogenic and stable Sr isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{88/86}\text{Sr}$ ) serve as potential tracers for evaluation of weathering sources and associated physicochemical processes in terrestrial environments. Despite carbonate weathering sourcing two-thirds of the total continental Sr flux to the ocean, however, few attempts have been aimed at studying stable Sr isotope fractionation in carbonate-dominated aquifers. Here we present a monthly-resolved monitoring dataset of major ion concentrations and Sr isotope ratios for karst riverine and pool waters at the Luofang Cave in the Central China to understand the potential controls responsible for water  $\delta^{88/86}\text{Sr}$  compositions under various climatic conditions. With the exception of some pool waters in the dry period, significantly heavier  $\delta^{88/86}\text{Sr}$  were detected in the riverine and pool waters (0.20‰ to 0.42‰) compared to bedrock  $\delta^{88/86}\text{Sr}$  (0.24‰ to 0.28‰), which can't be interpreted solely by lithology. A sequential leaching experiment of the local soils suggests limited stable Sr isotope fractionation during incongruent silicate mineral dissolution. Local plant utilization and biological activity in the soil overlying the cave are possible processes for causing the observed heavier  $\delta^{88/86}\text{Sr}$  in cave water. However, air partial pressure of  $\text{CO}_2$  in cave, monitoring water pH, and Sr isotopic mass balance calculations suggest that plant utilization is unlikely to be the primary control on the heavier water  $\delta^{88/86}\text{Sr}$ . On the other hand, significant stable Sr isotope fractionation was found between the cave dripping waters and calcite precipitates, and the  $\Delta^{88/86}\text{Sr}_{\text{car-aq}}$  was estimated to be  $-0.15\% \pm 0.07\%$  (2SD). Precipitation of secondary calcites might be a potential process responsible for the heavier  $\delta^{88/86}\text{Sr}$  in the waters. The negative correlation between  $\delta^{88/86}\text{Sr}$  and Sr/Na ratios in the cave waters is consistent with a scenario of preferential incorporation of the light Sr isotope by solid phase. Furthermore, by combining the calcite saturation states and water pH, our results suggest that calcite precipitation is the most likely process controlling  $\delta^{88/86}\text{Sr}$  compositions in cave water. We demonstrate that secondary calcite precipitation in carbonate-dominated catchments could be important in controlling the riverine water  $\delta^{88/86}\text{Sr}$  compositions.

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### 1. Introduction

Strontium has four stable isotopes:  $^{84}\text{Sr}$ ,  $^{86}\text{Sr}$ ,  $^{87}\text{Sr}$ , and  $^{88}\text{Sr}$ . The  $^{87}\text{Sr}$  is the radiogenic product of  $^{87}\text{Rb}$ , by the beta-decay process and has a half-life of  $4.88 \times 10^{10}$  years (Banner, 2004). Although the minerals in igneous rocks have equivalent Sr isotopic compositions when they form, various Rb/Sr ratios result in different  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios over time. Hence, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the products of weathering, namely dissolved loads and suspended particles in rivers, are widely used to

discriminate between carbonate and silicate weathering sources (Bain and Bacon, 1994; Palmer and Edmond, 1992), relative mineral weathering rates (Bullen et al., 1997; Hodell et al., 1990), and the cycling of Sr in marine environments (Edmond, 1992; Mokadem et al., 2015).

The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope system has been widely applied for definitive quantification of the marine Sr isotopic budget, however, it is still restrictive and faces complexities such as the occurrence of radiogenic carbonates (Palmer and Edmond, 1992; Quade et al., 1997) and Sr released from rapidly weathering trace mineral phases (Oliva et al., 2004). These raise uncertainty and hamper discrimination of weathering sources between silicates and carbonates. Most importantly, the internally normalized  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio inherently eliminates any

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mass-dependent isotope fractionation that might occur in nature. Thus, the equivalent  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between the seawater and marine carbonates limit the Sr output flux estimation. Accordingly, it is rather difficult to constrain all Sr sources and sinks comprehensively. This difficulty has recently been improved by the application of  $\delta^{88/86}\text{Sr}$  owing to its sensitivity to fractionation during marine carbonate precipitation (e.g., Krabbenhöft et al., 2010). Field and laboratory studies demonstrated that carbonate precipitates have significantly lowering  $\delta^{88/86}\text{Sr}$  relative to the fluid in which they formed. The  $\Delta^{88/86}\text{Sr}_{\text{carbonate-fluid}}$  offsets were estimated to be between  $-0.02$  and  $-0.37\%$  (Fietzke and Eisenhauer, 2006; Halicz et al., 2008; Rüggeberg et al., 2008; Böhm et al., 2012; Raddatz et al., 2013; Stevenson et al., 2014; Vollstaedt et al., 2014; Fruchter et al., 2016). The isotopic composition of the marine carbonates coupled with other carbonate system parameters therefore has a great potential for reconstructing past changes in seawater  $\delta^{88/86}\text{Sr}$  (Vollstaedt et al., 2014). In order to have confidence in the interpretation of the  $\delta^{88/86}\text{Sr}$ -based proxy, it is necessary to understand the relevant controls on the Sr input and output fluxes to the ocean through time. However, in comparison with the stable Sr isotope fractionation in marine carbonates, there are only a few studies available for discussing the factors that control the  $\delta^{88/86}\text{Sr}$  in riverine systems (Krabbenhöft et al., 2010; Pearce et al., 2015a).

Although lithology is the principle control on the riverine  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{88/86}\text{Sr}$  compositions may depend on a variety of fractionation mechanisms. For instance, plants preferentially incorporate  $^{86}\text{Sr}$  and can fractionate soil waters to higher  $\delta^{88/86}\text{Sr}$  values in vegetation abundant environments (De Souza et al., 2010). This plant fractionation effect has been confirmed in a catchment study of the Milford Sound region of Fiordland, New Zealand, where the soil water is the isotopically heavy reservoir for contributing to riverine Sr (Andrews et al., 2016). On the other hand, laboratory-based leaching experiments on riverine suspended particles suggest the preferential release of  $^{88}\text{Sr}$  to river waters during incipient silicate mineral dissolution (Chao et al., 2015). Consequently, incongruent silicate weathering in the Hou-ku River, Taiwan, results in a heavier riverine  $\delta^{88/86}\text{Sr}$  ratio compared with its corresponding bulk bedrock. Time-series monitoring of stream waters in a carbonate-dominated catchment of the Xijiang River, China, indicates a significant seasonal variability in the water  $\delta^{88/86}\text{Sr}$  compositions (0.147 to 0.661‰, Wei et al., 2013). A positive correlation between the water  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{88/86}\text{Sr}$  could be a result of preferential release of heavy Sr to the dissolved phase during silicate weathering. In fact, secondary calcite precipitation occurring frequently during water transport processes, especially in the carbonate-hosted aquifer, where dissolved carbonate species supersaturates with calcium (Ca). Studies in some limestone and dolostone aquifers reported that initial dissolved Ca was removed by calcite precipitation (Jacobson et al., 2002) and caused significantly fractionation of Ca isotopes in water (Jacobson and Holmden, 2008; Tipper et al., 2006, 2008). Thus, fractionation of stable Sr isotopes by secondary phase precipitation could be of significance in waters draining through carbonate-dominated aquifers. However, stable Sr isotope fractionation during calcite precipitation in freshwater systems and its potential implications in riverine waters have not yet been reported.

To improve our knowledge regarding potential effect of secondary calcite precipitation on river water  $\delta^{88/86}\text{Sr}$  in carbonate-dominated aquifers, we present monthly time-series water chemistry and Sr isotope data from a karst cave river system. This system offers simplified mono-lithology characteristics in limestone cave compared with any ground surface water system. The only silicate-driven flux can come from a thin soil layer overlying the caps limestone. To evaluate stable Sr isotope fractionation during calcite precipitation in freshwater, drip waters and modern precipitated calcites were sampled from caves in southern to central China. The time-series hydrological data provide a perspective in the context of: (1) lithology and fractionation controls on the variability of water  $\delta^{88/86}\text{Sr}$  in carbonate-dominated settings, and (2) the sensitivity of water  $\delta^{88/86}\text{Sr}$  composition to climatic and environmental changes.

## 2. Study area and materials

### 2.1. Time-series monitoring of cave waters in the Loufang Cave

The Loufang Cave ( $32^{\circ}25'46''\text{N}$ ,  $107^{\circ}10'48''\text{E}$ ) is located in northeastern Sichuan Province, central China, near the south flank of the Qinling Mountains and the southern boundary of the Chinese Loess Plateau (CLP) (Fig. 1A). This region has a typical monsoon-influenced subtropical climate with warm/humid summers and cold/dry winters. Annual temperatures fluctuate between  $5^{\circ}\text{C}$  and  $35^{\circ}\text{C}$  with a mean of approximately  $15^{\circ}\text{C}$ . Rainfall is concentrated between May and October with annual precipitation ranging from 1000 to 1200 mm. Atmospheric dust activity is strong during the dry season owing to the intensified northwesterly wind associated with a cold air emanating from the Mongolian anticyclone. Eolian dust are widely distributed in this area and are the dominant source for local soils. Local vegetation consists mainly of broadleaf deciduous species with some pine and cypress.

The Loufang cave (Fig. 1B) is capped by limestone approximately 40 to 100 m thick and is hosted within late Permian limestone (Bureau of Geology and Mineral Resource of Sichuan). The overlying soil layer is typically <30 cm thick or absent in places. This cave is approximately 2000 m long with an entrance on the east side of the Nuoshui River, a secondary tributary of the Yangtze River. One water pool located approximately 50 m east of the cave entrance is charged by dripping water. Thus, rainfall actively controls the water supply flux. A perennially running river develops and eventually outflows westward to the Nuoshui River. The river is supplied by a waterfall located roughly 500 m into the cave although the water source and river flow channel are not fully exposed. Two monitoring sites, at the pool and at the river (near the waterfall), were sampled monthly from July 2011 to August 2012 to evaluate the seasonal variations in water chemistry and Sr isotopic compositions. Waters were firstly sampled using a 1 L container. After ~4 h of settlement, 500 mL of water was carefully transferred into an acid cleaned polypropylene bottle. The long-time water settlement was performed to reduce the possibility of very fine grain carbonate particles suspended in the collected water samples. Paired samples of the un-filtered and filtered waters had been tested in the early publication and suggested identical Ca, Mg, Sr and Ba concentrations (Zhou et al., 2008). Samples were acidified to  $\text{pH} < 2$  using doubly distilled  $\text{HNO}_3$ , then preserved at  $4^{\circ}\text{C}$ . The surface soil above the cave was collected. The host rock (the host limestone) was sampled from the cave floor using a hammer. Atmospheric wet and dry depositions were collected during the water-monitoring period to evaluate the possible impact of dust activities on cave water chemistry. The sampling container was put on a platform 8 m above the ground surface near the cave. There are no buildings or factories nearby the cave, thus effects of human activity or any artificial contamination on the samples were rather negligible. The collected samples typically contained water and fine-grained particles. Samples were collected monthly, and then leached using double-distilled  $\text{HNO}_3$  ( $\text{pH} \sim 2$ ). Subsequently, the acid-dissolved phase was filtered using  $0.45\ \mu\text{m}$  nylon membranes for further chemical and isotopic analyses.

### 2.2. Sequential extraction and bulk digestion of the soils and host rocks

Soil and host rock (limestone) samples were crushed and gently ground. Approximately 2 g of sample powder was weighed and placed in a 15 mL centrifuge tube for sequential extraction experiments. The sample size and reagent volume used for the extraction were based on the protocol described by Zhou et al. (2009). First each sample was ultra-sonicated in 10 mL Milli-Q water for 15 min and then the leachate was separated by centrifugation at 7000 rpm for 10 min. The exchangeable fraction was extracted by adding 10 mL acetic acid ( $0.05$  to  $2\ \text{mol L}^{-1}$ ). After mixture separation the residual fraction (mainly silicates) was further immersed in 10 mL  $0.3\ \text{mol L}^{-1}\ \text{HNO}_3$  for one week to partially dissolve the silicate materials. All the extraction procedures

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