

## Speleothem Mg, Sr and Ba records during the MIS 5c-d, and implications for paleoclimate change in NE Sichuan, Central China

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Trace metals of Mg, Sr and Ba in a stalagmite (SZ2) collected from Suozi Cave in NE Sichuan, Central China, were analyzed with ICP-AES. The stalagmite was dated to have developed between 120 and 103 ka BP. Results indicate that the Mg/Ca, Sr/Ca and Ba/Ca ratios of SZ2 varied between  $(9500-14700) \times 10^{-6}$ ,  $(54-123) \times 10^{-6}$  and  $(31-82) \times 10^{-6}$ , respectively. The three records displayed significant millennial scale variations, which correlate with changes in past climate and environment. Lower values of Mg/Ca ratios and higher values of Sr/Ca and Ba/Ca ratios of SZ2 occurred during relatively cold-dry marine isotope stage (MIS) 5d, while the opposite trend was observed during relatively warm-humid MIS 5c. Trace metals in speleothems can be affected by distribution coefficients or trace metal concentrations in solutions from which speleothems precipitate. Temperature is suggested to be the dominant controller of Mg/Ca ratios in SZ2, whereas the Sr/Ca and Ba/Ca ratios may have been influenced by surface soil and atmospheric dust activities and prior calcite precipitation in Suozi Cave. Further investigations are warranted as to whether Sr/Ca and Ba/Ca ratios were affected by temperature and growth rate of the speleothem. The shifts of Mg/Ca, Sr/Ca and Ba/Ca records in SZ2 during the transition from MIS 5d to 5c apparently were earlier than the oxygen isotope record ( $\delta^{18}\text{O}$ ) of the same stalagmite. This possibly indicates (1) that atmospheric dust activity (the mechanism affecting SZ2 Sr/Ca and Ba/Ca ratios) is closely related to temperature, and (2) that temperature changes (dominated by solar insolation) precedes change in speleothem  $\delta^{18}\text{O}$  records which are controlled by both summer monsoons and winter temperatures.

### MIS 5c-d, speleothem, trace elements, Central China, paleoclimate and paleoenvironment

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Climate change is currently one of the most significant problems facing human society. One of the most important issues for understanding climate change is to investigate variations of past climate and environment on various time scales, and to investigate their controlling mechanisms. In the past several decades, speleothems have been increasingly used for reconstruction of past climate and environments, and for the investigation of characteristics and controlling mechanisms of paleoclimatic and paleoenvironmental change [1–5]. In the East Asian summer monsoon (EASM) regime, speleothem-based reconstructions of past climates and environments have led to significant advances.

However, most of these reconstructions have focused solely on speleothem oxygen isotope ( $\delta^{18}\text{O}$ ) records, and much less attention has been paid to other proxies, including geochemical ones [4–11]. In particular, trace metals, such as Mg, Sr and Ba, which are common in speleothems, are seldom explored [4,7,8,11]. In fact, various geochemical proxies other than  $\delta^{18}\text{O}$  (e.g. carbon isotopes [ $\delta^{13}\text{C}$ ], strontium and uranium isotope ratios [ $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{234}\text{U}/^{238}\text{U}$ ], and many trace elements [e.g. Mg, Sr, Ba, U, Si, Mn, P and rare earth elements]) have been shown to be closely associated with variations in past climates and environments [12,13]. For example, Ma et al. [4] reconstructed temperature changes during the last three thousand years (ka) using Mg/Sr ratios of a stalagmite ZFFS-1, which was collected in Jingdong

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Cave, Beijing. Zhou et al. [11] suggested that Sr content and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of speleothems from NE Sichuan, Central China, might be correlated with local wind-blown dust and, thus, could be used to investigate atmospheric dust activity and winter monsoons. These researchers indicated that geochemical proxies, other than  $\delta^{18}\text{O}$ , may provide information about past climates and environments, which cannot be derived from speleothem  $\delta^{18}\text{O}$  records. Thus, these types of studies are useful for a comprehensive understanding of past climate and environment information recovered from speleothems.

In this study, trace metals of Mg, Sr and Ba in stalagmite SZ2, which was collected from Suozi Cave in NE Sichuan, Central China, were measured with ICP-AES. The trace metal sources, variations, controlling mechanisms and implications for paleoclimate and paleoenvironment were explored. Results indicate that Mg, Sr and Ba in SZ2 may provide information on various aspects of past climates and environments, and thus, are important geological archives for speleothem-based climatic and environmental reconstruction.

## 1 Geological setting, sample description and analytical methods

The stalagmite SZ2 was collected from Suozi Cave (~680 m elevation), which is one of the many caves in Nuoshuihe, NE Sichuan, Central China (32°26'N, 107°10'E). Nuoshuihe is close to the boundary between Sichuan and Shanxi provinces, and is located in the south flank of the middle part of the Qinling Mountain Range. The study site is currently influenced by both intensive summer and winter monsoons. Summer monsoons are associated with seasonally higher temperatures and precipitation. Summer precipitation (JJA) accounts for ~45% of the annual rainfall amount for this area. The winter season is characterized by a cold and dry climate, and winter monsoons transport a large amount of aeolian sediments to the study site. The annual average temperature at the study site is ~15°C and the annual precipitation is 1000–1200 mm (Bazhong and Wanyuan, the two nearest weather stations, yield annual temperatures of 17.1°C and 14.7°C, respectively, and annual precipitation of 1030 mm and 1204 mm, respectively, for 1952–1990; data source: <http://www.ncdc.noaa.gov/oa/climate/ghcn-monthly/index.php>).

The host rock of Suozi Cave is Late Permian limestone [14]. The overlying soil layer on the cave is thin, usually less than 30 cm in thickness, or absent in places. The soil is derived mainly from wind-blown dust, which is evident from rare earth elements (unpublished data), and is in line with observations that aeolian sediments have accumulated on Qinling Mountain since the Middle Pleistocene [15,16]. Local vegetation consists mainly of trees, including pines, cypresses and some deciduous broadleaf species.

Suozi Cave has a very small entrance, which allows only

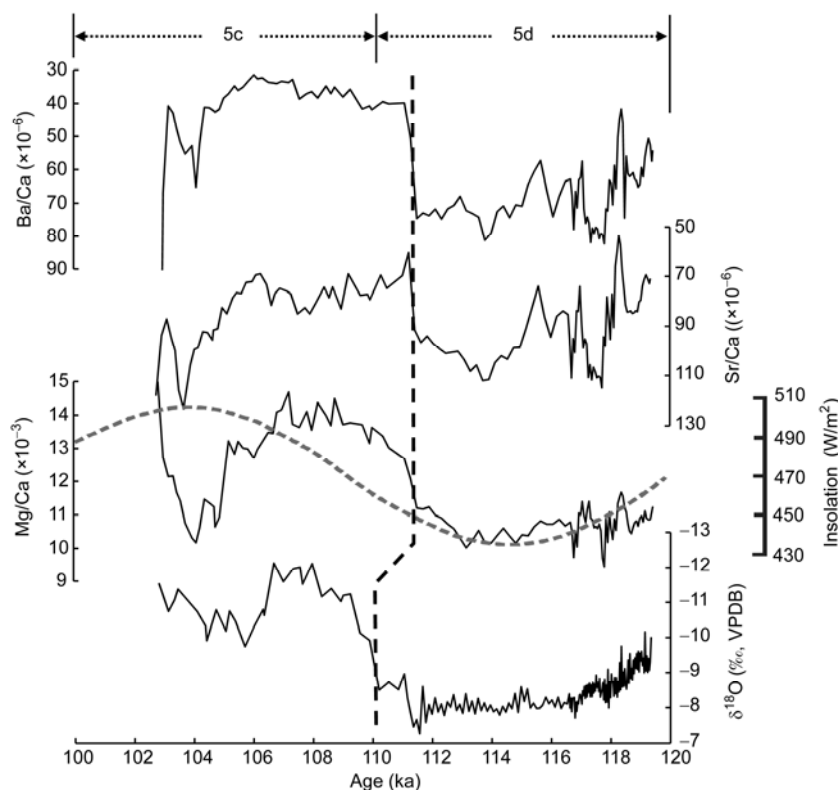
one person to climb into or out of the cave at a time. Stalagmite SZ2 was collected from a site deep (>100 m) inside the cave. TIMS U- $^{230}\text{Th}$  dating indicates that SZ2 developed from 120 to 103 ka, corresponding roughly to marine isotope stages (MIS) 5d and 5c, which constitute the period directly after the full last interglaciation of MIS 5e. The  $\delta^{18}\text{O}$  record for SZ2 was previously reported and discussed by Zhou et al. [14], and details of sample description and chronology of SZ2 can be obtained therein.

Subsamples from SZ2 were used for Mg, Sr and Ba analyses, and were collected as follows. First, a thin slab (about 8 mm wide and 6 mm thick) was taken from the central growth axis of SZ2. Then, the slab was ultrasonically cleaned in deionized water. Subsamples were then manually scraped with a scalpel, with about eight subsamples obtained every millimeter. A total of 122 subsamples were selected for analyses of Mg, Sr and Ba trace metals. Changes in the growth rate of SZ2 [17] were considered in the selection of the subsamples aimed at a roughly constant temporal resolution. Cross-contamination also was taken into account in the selection process.

Determination of Mg, Sr and Ba contents was conducted at the Key Laboratory of Geochemistry and Geochronology, Guangzhou Institute of Geochemistry, CAS, using ICP-AES (Varian Vista-PRO). Carbonate powder of each subsample was first dissolved with 3%  $\text{HNO}_3$ . Since no residue was found for each subsample after dissolution, solutions of each subsample were diluted with 3%  $\text{HNO}_3$ , using a dilution factor of ~10000 before measurements were taken. Four elements (Ca, Mg, Sr and Ba) were measured with detection limits of: <250 ppb for Ca, <10 ppb for Mg, <0.1 ppb for Sr and <0.3 ppb for Ba. Analytical uncertainties were better than 1% for Ca and better than 5% for Mg, Sr and Ba. In the results, trace metals are reported as their ratios to Ca (i.e. Mg/Ca, Sr/Ca and Ba/Ca).

## 2 Results and discussion

The Mg/Ca, Sr/Ca and Ba/Ca records for SZ2 are shown in Figure 1. The Mg/Ca ratios of SZ2 varied between  $(9.5\text{--}14.7)\times 10^{-3}$ , the Sr/Ca ratios varied between  $(54\text{--}123)\times 10^{-6}$ , and the Ba/Ca ratios between  $(9.4\text{--}11.6)\times 10^{-6}$ . These ratios had significant millennial scale variations. For example, the Mg/Ca ratio varied between  $(9.4\text{--}11.6)\times 10^{-3}$  during 120–111.5 ka, but it increased abruptly at 111.5 ka, and reached a maximum during 109–107 ka. Thereafter, the Mg/Ca ratio decreased with large amplitude and finally rebounded, forming a minimum centered at ~104 ka. The long-term trends for the Sr/Ca and Ba/Ca ratios were opposite to those of the Mg/Ca ratio. The averages of the two records before 111.5 ka were markedly higher than after 111.5 ka. However, the two records still had significant variations before 111.5 ka, and minima are notably observed between 115.6–117 ka. Variations of the Mg/Ca, Sr/Ca and Ba/Ca records



**Figure 1** Mg/Ca, Sr/Ca and Ba/Ca ratios of SZ2, and comparisons with  $\delta^{18}\text{O}$  record of the same stalagmite [17]. Overlapped on the Mg/Ca record is the summer insolation (JJA) at  $25^\circ\text{N}$ . The vertical dashed line indicates the boundary between MIS 5d and 5c and is based mainly on speleothem  $\delta^{18}\text{O}$  records in the East Asian summer monsoon regime.

for SZ2 appear to be closely associated with changes in past climate and environment, which is indicated by the  $\delta^{18}\text{O}$  record of the same stalagmite [17] (Figure 1). Lower Mg/Ca ratios and higher Sr/Ca and Ba/Ca ratios occurred during MIS 5d when the  $\delta^{18}\text{O}$  values were higher, whereas higher Mg/Ca ratios and lower Sr/Ca and Ba/Ca ratios occurred during MIS 5c when the  $\delta^{18}\text{O}$  values were lower.

Trace elements in inorganic carbonate may be influenced by different variables. If carbonates are precipitated under equilibrium conditions, two factors may affect trace elements in carbonates. One is the content of trace elements in solution from which carbonates precipitate and the other is the distribution coefficient of an element between its solution and solid carbonate states. However, the distribution coefficient and content of an element in solution may be affected by multiple mechanisms, and inconsistent results may be derived from various experiments. For example, in their co-precipitation experiment using seawater in an open system, Kinsman and Holland [18] found that the distribution coefficient of Sr between solution and precipitated aragonite decreased linearly with increasing temperature, from  $1.17 \pm 0.04$  at  $16^\circ\text{C}$  to  $0.88 \pm 0.03$  at  $80^\circ\text{C}$ . However, Katz et al. [19] found that Sr incorporation into calcite was only slightly affected by temperature changes in a closed system replacing aragonite by calcite. In an experiment by Lorens [20], a constant pH value was used to maintain a

constant degree of saturation and precipitation rate of calcite. Lorens [20] found that the distribution coefficient of  $\text{Sr}^{2+}$  ( $\lambda$ ) increased with precipitation rate of calcite ( $R$ ), according to the following equation:

$$\log \lambda_{\text{Sr}} = 0.249 \times \log R - 1.57R. \quad (1)$$

However, contrary to the observation by Lorens [20], Mucci and Morse [21] suggested that the precipitation rate of calcite might not be a significant mechanism affecting Sr incorporation into calcite. The above-mentioned observations suggest that the mechanisms influencing Sr incorporation into carbonates are currently poorly understood. Unlike Sr, Mg appears to provide more consistent results from experiments. For example, the experiments carried out by both Katz [22] and Mucci [23] indicate that the distribution coefficient of Mg increased linearly with increasing temperature despite the fact that the slopes of the distribution coefficient-temperature correlation were different, which might arise from the different experimental protocols they used. In addition, it was found that when relatively constant temperature was maintained, precipitation rates of calcite did not exert a significant influence on the distribution coefficient of Mg [21,23]. Other than temperature and precipitation rates of calcite, partial pressure of  $\text{CO}_2$  ( $P_{\text{CO}_2}$ ) in solution from which carbonates precipitate also has been found to exert significant effects on both the distribution coefficient

of Mg and Mg content [24]. Thus, increases in  $P_{\text{CO}_2}$  would lead to a reduction in the distribution coefficient of Mg and Mg content. Since the distribution coefficients of Mg and Sr for calcite are remarkably differently from those for aragonite [25], carbonate mineralogy also is a key mechanism affecting these trace elements in carbonates.

### 2.1 Influences via distribution coefficients

Since SZ2 consisted only of calcite, the influences on Mg, Sr and Ba trace metals in SZ2 through changes in mineralogy could be excluded. Although the growth rate of SZ2 changed remarkably over time [17], this should not be a significant mechanism affecting Mg in SZ2 [21,23]. Thus, the most probable mechanism affecting Mg in SZ2 via distribution coefficients may be temperature. This is in accordance with the observation that the Mg/Ca ratios of SZ2 displayed lower values during relatively cold and dry MIS 5d, and higher values were observed during relatively warm and humid MIS 5c (Figure 1). Although the  $P_{\text{CO}_2}$  of the atmosphere differs under variable climatic phases [26], and alternations of cold-dry and warm-humid climates can lead to changes in  $P_{\text{CO}_2}$  of cave air and karst groundwater, the  $P_{\text{CO}_2}$  of the atmosphere, karst groundwater and cave air would increase under warm and humid climatic phases, prohibiting incorporation of Mg into calcite [24]. This notion is opposite to what was observed in this study and as shown in Figure 1. With respect to Sr, the experiments by Kinsman and Holland [18] and Lorens [20] indicate that temperature and growth rates of calcite may affect Sr in SZ2 via distribution coefficients, and the Sr content of SZ2 seems to agree with the growth rate of SZ2 [17]. However, as mentioned above, no consistent results have been derived from these experiments. Few studies have explored whether temperature and growth rates of calcite can affect distribution coefficients of Ba between the calcite and solutions from which it precipitate. Thus, it is currently not clear whether Sr and Ba in SZ2 were affected by temperature and growth rates of calcite via distribution coefficients, and thus further investigation is warranted.

### 2.2 Effect of trace metal concentrations in solutions

The content of trace metals in solution may be influenced by sources, interaction of karst groundwater with limestone host rocks, as well as prior calcite precipitation (PCP) [7, 11–13]. Based on monitoring of Clamouse Cave in southern France and the Ernesto Cave in northeast Italy, Fairchild et al. [27] concluded that there were four mechanisms affecting trace elements in speleothems: (1) differential dissolution of calcite and dolomite in the host rocks; (2) PCP along flow paths; (3) incongruent dolomite dissolution; and (4) selective leaching of Mg and Sr with respect to Ca. The influence of flow route of karst groundwater and residence time on speleothem trace elements, or in other words, the

influence of the interaction between karst groundwater and host rocks [28–31], is essentially consistent with mechanisms (1), (3) and (4) of Fairchild et al. [27]. These mechanisms all concern the effects of trace metal contributions from one of the sources, the host rock. In addition to host rocks, surface soil and atmospheric dust activity also play a key role in affecting trace metal contributions to speleothems from different sources. In particular, some wind-blown sediments are rich in carbonates, and may exert significant influences on some trace elements and isotopes [11,32].

Among the four mechanisms suggested by Fairchild et al. [27], except for the differential dissolution of calcite and dolomite, the other three mechanisms would not lead to the opposite trend of the Mg/Ca record with respect to the Sr/Ca and Ba/Ca records (Figure 1). However, there is no dolomite in the host rocks of Suozi Cave. Relatively cold and dry climates during MIS 5d could have resulted in reduced precipitation, and in turn increased residence time of karst groundwater in host rocks. In this manner, more Mg and Sr would have been preferably leached out relative to Ca [28]. They would also lead to enhanced PCP and increased Mg/Ca, Sr/Ca and Ba/Ca ratios in speleothems. Although this scenario agrees with the long-term trend of Sr/Ca and Ba/Ca ratios (Figure 1), it is contrary to the long-term trend of the Mg/Ca record (Figure 1) and observations by Zhou et al. [11], which state that Sr contributions to speleothems from host rocks decreased during relatively cold and dry climates. Thus, residence time of karst groundwater should have exerted limited effects on the Mg/Ca, Sr/Ca and Ba/Ca ratios of SZ2. Although PCP may have affected Sr/Ca and Ba/Ca ratios of SZ2, it would not have been a key mechanism affecting the Mg/Ca ratios of SZ2. This is because the Mg/Ca ratios of SZ2 should increase, not decrease during MIS 5d, as is shown in Figure 1. Wind-blown sediments on the Asian continent are rich in carbonates, and have high Sr concentrations [33]. Relatively cold and dry climates would promote atmospheric dust activity, and in turn, result in higher Sr concentrations in speleothems. This is supported by analysis of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of another stalagmite (SJ3) collected from the same study site [33], and is also consistent with the observation that atmospheric dust activity was intensive in the Qinling Mountain Range as early as in the Middle Pleistocene [15,16].

It usually has been found that Ba/Ca ratios displayed a high similarity to Sr/Ca ratios in speleothems [13]. This implies that Sr/Ca and Ba/Ca ratios may be controlled by a common mechanism in speleothems. Thus, like the Sr/Ca ratios of SZ2, Ba/Ca ratios may be affected mainly by changes in PCP and sources (i.e. atmospheric dust activity). This is in line with the fact that at the study site, Ba in speleothems was sourced mostly from the surface soil [11].

Although it has been found that surface soil has been the most important source of Mg in speleothems at the study site and some other caves [11,34], the influence of wind-

blown sediments, like those of PCP, was not observed in the SZ2 Mg/Ca record (Figure 1). A plausible explanation for this incongruity is that temperature may have dominated the incorporation of Mg into SZ2 via distribution coefficients and suppressed the signals of PCP and wind-blown sediments.

### 2.3 Asynchronicity between trace metals and oxygen isotopes

As shown in Figure 1, all three trace metal records of SZ2 displayed an abrupt shift at ~111 ka during the transition from MIS 5d to 5c. However, the  $\delta^{18}\text{O}$  record for SZ2 showed only a slight decrease at the same time, but a large negative shift at ~110 ka, about 1 ka later than the abrupt shift of the three trace metal records. In fact, the trace metal records displayed a slight increase (for Mg/Ca ratios) or decrease (for Sr/Ca and Ba/Ca ratios) early, at 113–114 ka, before they showed the abrupt shift at ~111 ka. Shift of the three trace metal records during the transition from MIS 5d to 5c appear to be consistent with changes in summer (JJA) insolation of the northern hemisphere, whereas the SZ2  $\delta^{18}\text{O}$  record displayed a lag (Figure 1). Although  $^{230}\text{Th}$  dates of SZ2 were relatively less and they had relatively large errors [17], this does not affect the lag of the  $\delta^{18}\text{O}$  record behind the three metal records because all the four proxies arise from the same stalagmite.

In a recent alternative explanation of speleothem  $\delta^{18}\text{O}$  records from the EASM regime, Clemens et al. [35] indicated that these speleothem  $\delta^{18}\text{O}$  records lagged in phase behind the summer insolation of the northern hemisphere by  $2.9\pm 0.3$  ka, and suggested that these speleothem  $\delta^{18}\text{O}$  records might be controlled by both the summer monsoon and winter temperatures. Thus, the lag of the SZ2  $\delta^{18}\text{O}$  record behind the three metal records of SZ2, as shown in Figure 1, may reveal that it is appropriate to interpret the SZ2 Mg/Ca record with temperature, and that PCP in Suozi Cave and atmospheric dust activity (the two mechanisms probably affecting the Sr/Ca and Ba/Ca ratios of SZ2) are related to temperature. A combined effect of both the summer monsoon and winter temperatures, which control speleothem  $\delta^{18}\text{O}$  records in the EASM regime, created lags behind summer insolation and resulted in asynchronicity of the four proxies recovered from SZ2 (Figure 1). However, it should be kept in mind that the explanation by Clemens et al. [35] needs to be supported with more evidence from cave monitoring and fossil speleothem investigations.

## 3 Conclusions

Trace metals of Mg, Sr and Ba of stalagmite SZ2, which was collected from Suozi Cave in NE Sichuan, Central China, were analyzed with ICP-AES. Results indicate that the Mg/Ca, Sr/Ca and Ba/Ca ratios of SZ2 displayed signif-

icant millennial scale variations during 120–103 ka, which could be associated with changes in past climates and environments. Lower values of Mg/Ca ratios and higher values of Sr/Ca and Ba/Ca ratios occurred during the relatively cold and dry MIS 5d; whereas, during the relatively warm and humid MIS 5c, Mg/Ca, Sr/Ca and Ba/Ca variations had an opposite trend. The mechanisms affecting trace elements in SZ2 were explored via distribution coefficients and trace metal concentrations in karst groundwater. It has been suggested that temperature was the dominant controller of the Mg/Ca ratios of SZ2, whereas the Sr/Ca and Ba/Ca ratios of SZ2 may have been affected by surface soil and local atmospheric dust activity, as well as prior calcite precipitation in Suozi Cave. Whether the Sr/Ca and Ba/Ca ratios were affected by temperature and growth rates of speleothems is currently unclear and warrants further investigation. During the transition from MIS 5d to 5c, a shift of the Mg/Ca, Sr/Ca and Ba/Ca records of SZ2 preceded the SZ2  $\delta^{18}\text{O}$  record by ~1 ka (Figure 1). This observation may reflect (1) that the mechanisms affecting the Sr/Ca and Ba/Ca ratios of SZ2 (e.g. atmospheric dust activity) were related to temperature, and (2) that the speleothem  $\delta^{18}\text{O}$  records from the EASM regime are controlled by both the summer monsoons and winter temperatures and lag behind temperature changes in the northern hemisphere which are dominated by solar insolation, as suggested by Clemens et al. [35]. However, the proposals of Clemens et al. [35] need corroboration from other investigations.

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