Characteristics of strontium isotopes and their implications in the Qixing Cave of Guizhou, China

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The strontium isotopic compositions (^{87}Sr/^{86}Sr) of samples including soils, bedrock, soil waters, drip waters and their corresponding speleothems in the Qixing Cave (QXC), Guizhou Province, China, were systemically measured and analyzed. The results indicate that there are significant Sr isotopic differences among samples. The mean ^{87}Sr/^{86}Sr ratios in drip water for the samples 1$^{\#}$, 4$^{\#}$ and 9$^{\#}$ were 0.709568, 0.709139 and 0.708761, respectively, which possibly result from different flow paths, residence times, and other hydrogeological processes in the unsaturated zone overlying QXC. Meanwhile, levels of 40.8%, 57.6% and 72.4% of Sr in drip waters for 1$^{\#}$, 4$^{\#}$ and 9$^{\#}$, respectively, were derived from bedrock dissolution, which was calculated by the mixture model of the two end-members (soil and bedrock). There is, however, no positive correlation between the relative proportion from bedrock dissolution (δ^{13}C value is 1.8‰) and drip water δ^{13}C$_{DIC}$ values. The mean drip water δ^{13}C$_{DIC}$ value in 1$^{\#}$ is the heaviest (–4.5‰) with the lowest contribution rate of bedrock dissolution, whereas the value in 9$^{\#}$ is the lightest (–9.3‰) with the highest contribution rate of bedrock dissolution. The proportion from host rock dissolution in 4$^{\#}$ is higher than that in 1$^{\#}$ and lower than that in 9$^{\#}$, while its mean drip water δ^{13}C$_{DIC}$ value (–8.6‰) is higher than that of 9$^{\#}$ and lower than that for 1$^{\#}$. This suggests that the prior calcite precipitation (PCP) processes in the unsaturated zone overlying the cave are responsible for the δ^{13}C$_{DIC}$ value differences between different drip waters, and not bedrock dissolution. Furthermore, this study also demonstrates that the ^{87}Sr/^{86}Sr ratios of speleothems in the 1$^{\#}$ and 4$^{\#}$ mainly reflect the variation in the relative proportions from the soil system (soil water) and bedrock dissolution overlying the cave. It is, therefore, feasible to use the strontium isotopic signals of speleothems as an indicator for soil chemical weathering intensity, and consequently as a monsoon proxy in the study area.

strontium isotope, cave drip water, source, prior calcite precipitation (PCP), Qixing Cave of Guizhou

In 1990, Avigour et al. [1] first studied the ^{87}Sr/^{86}Sr ratio of veins and secondary cave calcites in the south of Israel. Because there is no Sr isotopic fractionation in the processes of carbonate dissolution, transportation and calcite precipitation, the ^{87}Sr/^{86}Sr signal in speleothem (as stalagmite) has recently become an important indicator for tracing the source and studying changes in paleoclimate and paleoenvironment. For instance, Verheyden et al. [2] attributed the ^{87}Sr/^{86}Sr variations in a Belgian Holocene speleothem to changes in water residence time and weathering processes.

They analyzed the climatic and environmental change tendencies during 13–2 ka BP in that area. Li et al. [3] studied the ^{87}Sr/^{86}Sr ratios in a stalagmite from Heshang Cave in southern Shanxi Province by the mass-balance model, and successfully reconstructed the degree and variation in chemical weathering intensity for the soil overlying the cave. Moreover, Zhou et al. [4] found that the ^{87}Sr/^{86}Sr ratios of a stalagmite could be used to investigate the atmospheric dust activity and the Asian winter monsoon at the Songjia Cave in northeastern Sichuan Province, China. These results imply that the fluctuation of ^{87}Sr/^{86}Sr ratios in speleothems could be closely related with changes in

climate and environment. Although many significant achievements have been made on $^{87}Sr/^{86}Sr$ ratio in speleothems, there are few studies about the Sr isotopic compositions of different components in cave system. It is difficult to distinguish the relative proportions of Sr from various Sr sources composed of different Sr isotopes, and consequently, results can lead to various interpretations as a climate and environment proxy [2,5,6]. To understand climate and environment signals from $^{87}Sr/^{86}Sr$ ratios in speleothems, it is, therefore, important to monitor and analyze various types of potential Sr sources and changes. Our previous work has shown that it is difficult to distinguish the relative effects of host rock dissolution and prior calcite precipitation (PCP) processes based on C isotopic variabilities in drip water in the QXC [7] because both of them could result in the drip water $\delta^{13}C_{DIC}$ signal becoming heavier. Here, we attempt to use Sr isotopes as a tool to distinguish these processes because the PCP process will not interfere with the Sr isotopic compositions.

In this study, we chose QXC as study site where the stable isotopes, hydrology and hydrochemistry are already known to a certain degree [7–11]. We aim to use the Sr isotopic tool, coupled with other geochemical characteristics of drip water, to trace the sources of cave drip waters/ speleothems. This allowed us to further investigate the effects of hydrogeochemical processes on the C isotopic signals in drip water, which would provide a fundamental theoretical support for reconstructing paleoclimate from speleothem Sr isotopes.

1 Study area, sampling and methods

1.1 Study area

Qixing Cave (25°59'N, 107°16'E) is located ~1.5 km of northeast Kaiyou Village, Kaikou Town, Duyun in Guizhou Province, China (Figure 1(a)). The cave's bedrock comprises carboniferous limestone (C_{1b}–C_{2hn}) and dolomitic limestone, the thickness of roof overlying the cave is ~50–90 m, and the rock fractures here are not well devel-

oped. The overlying soil is relatively continuous, and the soil layer is 6–180 cm, averaging at ~ 33 cm; the vegetation is of a brushwood type. The climate in this area is largely controlled by the Indian and East Asian monsoons. The mean annual temperature (MAT) is ~16.6°C, the annual rainfall is 1176 mm, of which 77.5% falls in monsoonal seasons (April to September), and the average relative humidity of the atmosphere is 77%, according to data from a local weather station between April 2003 and May 2004.

1.2 Sampling methods

Samples of soil waters at the top of the cave system were collected using a 100 mL glass injector from 1 L boxes buried at a depth of 50 and 100 cm, respectively (Figure 1 (b)). Cave drip waters were collected in the main cave channel, and there were no temperature or moisture differences between each drip water site (Figure 1(c)).The speleothems, corresponding to the drip waters, were precipitated on a glass plate and collected from June 2003 to May 2004; soil and bedrock were collected near the soil waters sample sites. The detailed sampling times of soil water and drip water are listed in Table 1.

1.3 Test methods

Samples of soil and bedrock were triturated as fine powders less than 0.075 mm. The powdered samples (0.1–0.2 g) were placed into a low-pressure Teflon airproofed tin, exposed to a mixture acid of ultrapure $HF + HNO_3 + HCl$ to achieve acidolysis, and converted into perchlorates by evaporating to dryness. Soil (3–5 g) was triturated to a powder less than 2 mm and then leached using 1 mol/L NH_4Ac, with a buffer solution of pH 8. The solution was centrifuged and the supernatant was collected in a Teflon tin for enrichment. Finally, they were converted into perchlorates using same method as above for the soil exchangeable Sr isotope. Soil water and drip water were immediately filtered through 0.45 μm Millipore filters, then stored in acid-leached polyethylene bottles and acidified with ultrapure
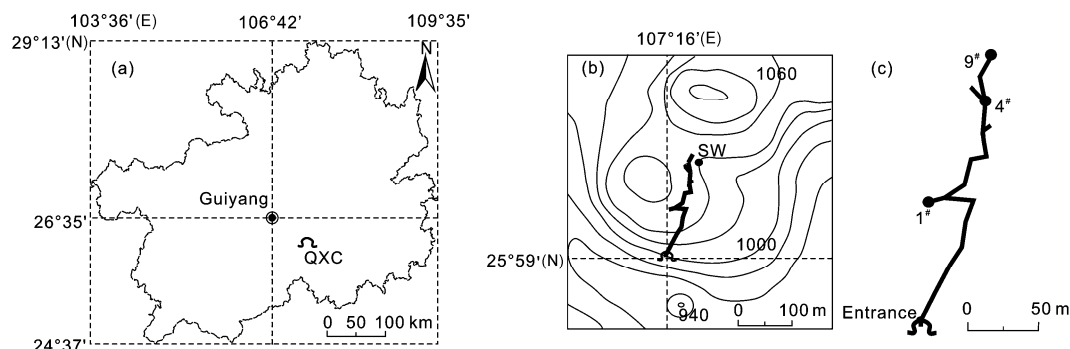

Figure 1   Qixing cave location (a); landform (b), cave orientation and sampling locations (b), (c); SW indicates soil water in (b). 1# indicates No. 1 drip water, and the rest are deduced by analogy in (c).

HNO_3. These samples were then evaporated to dryness in Teflon tins.

The separation of strontium from other major elements for isotopic analysis was achieved using a conventional ion-exchange technique using a Dowex 50W-8X 200–400 mesh resin in HCl media. The $^{87}Sr/^{86}Sr$ ratios were determined using a MC-ICP-MS (multiple collector inductively coupled plasma mass spectrometry, produced by Nu Instrument Ltd., UK), and normalized for fractionation to $^{86}Sr/^{88}Sr$=0.1194. A mean value of 0.710220 was determined by standard analysis of NIST-NBS987 (2σ= ±0.000029, n=24) during the measurement period of these samples. The strontium concentrations in soil water and drip water were measured by ICP-MS and the uncertainty was less than 5%.

All analytical processes were completed in the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences.

2 Results and discussion

2.1 $^{87}Sr/^{86}Sr$ ratios of all types of samples

The Sr isotopic compositions for different components in the QXC system are shown in Table 1 and Figure 2. We can see that the differences of $^{87}Sr/^{86}Sr$ ratios between samples are remarkable. The rainwater and bedrock (limestone) have low radiogenic $^{87}Sr/^{86}Sr$ values, while the soil has the most radiogenic $^{87}Sr/^{86}Sr$ values, whose dominant mineral is silicate [12]. The variations in $^{87}Sr/^{86}Sr$ ratio between the same types of sample are also significant, except for in soil and bedrock (only one sample). The $^{87}Sr/^{86}Sr$ values for the soil exchangeable fraction and soil water decrease with increasing soil depth, while the soil water Sr concentrations increase with depth. Meanwhile, cave drip water and the corresponding speleothems are less radiogenic ($^{87}Sr/^{86}Sr$) than those for soil and soil water. Figure 2 indicates that the $^{87}Sr/^{86}Sr$ ratios of soil exchangeable components fall between rainwater and soil, whereas the soil water $^{87}Sr/^{86}Sr$ values fall between values for the soil exchangeable fraction and soil. The values for cave drip water are all more radiogenic ($^{87}Sr/^{86}Sr$) than limestone, but less than soil water. Their speleothems $^{87}Sr/^{86}Sr$ values are similar to the corresponding drip waters.

2.2 $^{87}Sr/^{86}Sr$ ratios in soil waters

The previous study indicates in Guiyang that the $^{87}Sr/^{86}Sr$ ratios in rainwater range from 0.707934 to 0.709080, averaging at 0.708219, with a Sr concentration of 8.8 µg/L [13]. In the virgin forest in Maolan the $^{87}Sr/^{86}Sr$ ratios in rainwater ranged from 0.707463 to 0.712752, averaging at 0.709058, with a Sr concentration of 6.4 µg/L [14]. The QXC is located at the central site between Guiyang and Maolan, with a geological background (karst) and cultivated

Table 1 Sr concentrations and $^{87}Sr/^{86}Sr$ ratios of different components in the Qixing Cave

Sample	Date	Depth (cm)	Sr (µg/L)	$^{87}Sr/^{86}Sr$	$2\sigma(\times 10^{-6})$
Soil	2003-10-14	10–20	–	0.727317	23
	2003-10-14	30–40	–	0.727417	15
Soil exchangeable cation	2003-10-14	0–10	–	0.709704	13
	2003-10-14	30–40	–	0.709816	26
	2003-10-14	40–50	–	0.708944	15
Soil water	2004-05-27	50	14.4	0.710606	34
	2004-05-27	100	21.7	0.709746	12
Bedrock	2003-10-14		–	0.708059	18
1#	2003-09-13		14.5	0.709513	7
	2003-10-14		14.8	0.709567	7
	2004-02-26		17.8	0.709638	20
	2004-05-27		15.4	0.709554	13
Speleothem	2003-06-11– 2004-05-27		–	0.709561	13
4#	2003-08-14		27.0	0.709109	7
	2003-09-13		26.2	0.709054	5
	2004-02-26		23.4	0.709193	17
	2004-05-27		22.3	0.709201	11
Speleothem	2003-06-11– 2004-05-27		–	0.709043	28
9#	2003-08-14		42.9	0.708780	8
	2004-05-27		41.8	0.708742	11

"–" means no data.

style (scattered paddy fields) similar to Guiyang and Maolan. The $^{87}Sr/^{86}Sr$ ratio and Sr concentration in the rainwater can, therefore, be evaluated to be 0.708689 and 7.6 µg/L by the linear interpolation method in the QXC area.

From systemically monitoring the results of oxygen (hydrogen) isotope compositions in a series of samples in the QXC, the soil water originates directly from local precipitation [15], suggesting that rainwater is an important sources for Sr in the soil water. Therefore, the Sr in soil water is not only derived from the soil layer, but also originates partly from precipitation. The $^{87}Sr/^{86}Sr$ ratios in soil waters at 50 and 100 cm depths are 0.710606 and 0.709746, respectively, which fall in between the values for rainwater and soil water (Figure 2), and suggest a decrease with the increasing of soil depth. Conversely, the Sr concentrations in soil water increase with the soil depth, with levels of 14.4 and 21.7 µg/L, respectively. This may suggest that the effect of the bedrock dissolution with low $^{87}Sr/^{86}Sr$ signal (Figure 2) on $^{87}Sr/^{86}Sr$ ratios in the soil water increase with soil depth. The Sr isotopes in the soil water (Table 1 and Figure 2) suggest a disequilibrium between the soil exchangeable Sr and the soil water. The soil water samples are more radiogenic ($^{87}Sr/^{86}Sr$) than those in rainwater and soil exchangeable cation (Table 1 and Figure 2). This implies that when rainwater with a lower $^{87}Sr/^{86}Sr$ ratio falls down into the soil layer, the seepage water is affected by the chemical weathering of silicate [12] with more radiogenic $^{87}Sr/^{86}Sr$.
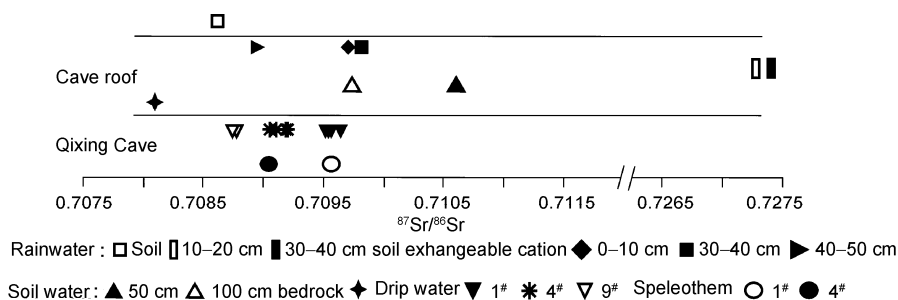
Figure 2   [87]Sr/[86]Sr variations of each components in the Qixing Cave system (rainwater Sr isotopic data from [13,14], refer to sec. 2.2. 1[#] represents No. 1 drip water, the rest are also deduced by analogy).

This results in an increase in [87]Sr/[86]Sr ratio in the soil water. However, an incomplete exchange process may occur between soil waters and soil exchangeable cations, since the migration rate of seepage water is rapid, leading to an isotopic disequilibrium between soil waters and the exchange pool [16]. A similar conclusion was also drawn by other research groups [17].

In summary, the Sr concentrations and isotopic signals in soil water result from interactions between the silicate and the soil exchangeable cations in the soil layer, when rainwater with a low [87]Sr/[86]Sr ratio infiltrates the soil layer. Soil water results from interactions between different components and the soil system is very complicated. Soil water is a direct source for drip water and can, therefore, be used as an end-member which represents the soil system overlying the QXC. The soil layer is relatively continuous, but its thickness is inconsistent (6–180 cm), averaging at 33 cm. Furthermore, variations in [87]Sr/[86]Sr ratio in the soil exchangeable pool and soil are not distinct at soil depths more than 10 cm from the interface between the bedrock and soil. This suggests the minimal effect of bedrock dissolution with low [87]Sr/[86]Sr values. It is, therefore, reasonable that the soil water at the 50 cm depth could be studied as an output end-member to represent the soil layer overlying the cave, whose [87]Sr/[86]Sr ratio is 0.710606.

2.3   Sources in drip waters and their implications

In the QXC, the mean [87]Sr/[86]Sr ratios in the 1[#], 4[#] and 9[#] are 0.709568, 0.709139 and 0.708761, respectively (Table 2), which fall in between the soil water and bedrock levels. There is a remarkable positive linear correlation between the [87]Sr/[86]Sr ratios and the reciprocal of the Sr concentrations (1/Sr) in drip waters (Figure 3). Although a previous study [7] notes that there is a PCP process when the seepage water transfers in the vadose zone overlying the QXC, the partition coefficients for Mg and Sr (Tr/Ca$_{CaCO_3}$ = K$_{Tr}$ (Tr/Ca)$_{solution}$, Tr denotes Mg or Sr) are considerably smaller than 1 in solution [18,19]. This means the Sr concentrations in seepage water are not significantly affected by any PCP processes. The strong positive relationship between [87]Sr/[86]Sr

ratios and 1/Sr in drip water (Figure 3) suggest that the ions in drip water are predominantly from the soil layer (soil water) and bedrock overlying the cave. Importantly, this is consistent with the two end-members model. The model can be used to calculate the relative contribution rates of soil water and bedrock to drip water [20,21].

Here, we have assumed that the mass fraction of Sr derived from soil water (S) at 50 cm depth soil is X (%), and that of bedrock dissolution (R) is $(1–X)$ (%). That is, the [87]Sr/[86]Sr ratios in drip water (D), as a component mixture from soil water and bedrock dissolution, can be expressed as

$$\left(^{87}Sr / ^{86}Sr \right)_D = X \left(^{87}Sr / ^{86}Sr \right)_S + (1-X)\left(^{87}Sr / ^{86}Sr \right)_R . \quad (1)$$

We then get

$$X = \left[\left(^{87}Sr / ^{86}Sr \right)_D - \left(^{87}Sr / ^{86}Sr \right)_R \right] \Big/ \\ \left[\left(^{87}Sr / ^{86}Sr \right)_S - \left(^{87}Sr / ^{86}Sr \right)_R \right] \times 100\% . \quad (2)$$

The relative proportions from the two main sources for 1[#], 4[#] and 9[#] have been estimated and presented in Table 2 using eq. (2). There are distinct differences in the relative contributions from soil water and bedrock dissolution
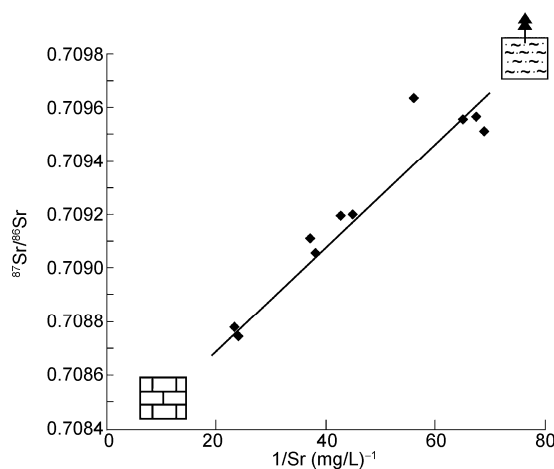

Figure 3   The linear positive relationship between ([87]Sr/[86]Sr) and (1/Sr) for drip water.

Table 2 Relative proportions from two sources and $\delta^{13}C_{DIC}$ values in drip water

	1#	4#	9#
$^{87}Sr/^{86}Sr_{mean}$	0.709568	0.709139	0.708761
$X_{bedrock}$ (%)	40.8	57.6	72.4
X_{soil} (%)	59.2	42.4	27.6
$\delta^{13}C_{DIC}$ (‰)	−4.5 (−6.6–−2.7)	−8.6 (−9.5–−7.0)	−9.3 (−9.8–−9.2)

for different drip waters. This may suggest that the extent of interaction between seepage water and bedrock is different along different flow-routes, due to different residence times in the unsaturated zone overlying the cave [22].

Table 2 shows that the soil water affects the drip water in all drip sites, although the relative contribution rates from soil water vary at different drip sites. There is no obvious variability in the structure of the bedrock overlying the cave with speleothems growing over a relative short time scale (less than several hundred thousand years). This suggests the corresponding flow path of seepage water for drip water has not obviously changed over the past several hundred thousand years, which means the relative proportion from bedrock dissolution to drip water is also unchanged. However, the strontium isotopic compositions in bedrock are generally constant, and the $^{87}Sr/^{86}Sr$ ratios in drip waters are inherited well by their corresponding speleothems (Table 1 and Figure 2). This may suggest that the Sr isotopic signals in drip water/speleothem primarily record the Sr isotopic signals in soil. A similar conclusion has also been reported by other researchers [22]. In this study area, the weathering crust (soil) of carbonate is mainly made up of silicate [12], which has more radiogenic strontium (high $^{87}Sr/^{86}Sr$ ratio) than carbonate [23]. Therefore, if the chemical weathering intensity of soils overlying a cave increases, then more silicate components would be dissolved and more Sr ions in the soil water would originate from silicate components. In short, the Sr isotopic signals in cave drip water/speleothem can reflect the chemical weathering intensity of the soil, and act as an indicator of monsoon intensity in the study area [3,24].

2.4 The relationship between $^{87}Sr/^{86}Sr$ ratios and $\delta^{13}C_{DIC}$ values in drip water

Our previous studies have indicated that $\delta^{13}C_{DIC}$ signals could be affected by bedrock (carbonate) dissolution and PCP processes in the unsaturated zone overlying the QXC, when soil water transforms to drip water [7]. Site 1#, with a heavier $\delta^{13}C_{DIC}$ value is classified as Group I, with a $\delta^{13}C_{DIC}$ value 4.5‰–5.7‰ heavier than that in soil water. This suggests that $\delta^{13}C_{DIC}$ value for 1# is dominated mainly by bedrock dissolution and PCP processes. However, the $\delta^{13}C_{DIC}$ values in the 4# and 9# of Group II were only 0.6%–1.6‰ heavier than that of soil water, which is less affected by bedrock dissolution and PCP processes [7]. Due to the bed-

rock having a higher $\delta^{13}C$ value (1.8‰) and the preferential degassing of $^{12}CO_2$ over $^{13}CO_2$ in the PCP process, the $\delta^{13}C_{DIC}$ value in drip water would increase when both processes are occurring. It is impossible to distinguish the effects of bedrock dissolution and PCP processes based on the $\delta^{13}C_{DIC}$ values of drip water, using only C isotope and hydrological data. Unlike the C stable isotopes (^{13}C and ^{12}C), Sr has a higher relative atomic mass, and the ratio of ^{87}Sr and ^{86}Sr is lower. Consequently, there is negligible Sr isotopic fractionation in the processes of seepage water movement and transformation in the unsaturated zone overlying the cave. The $^{87}Sr/^{86}Sr$ ratio is primarily controlled by the relative proportions of different sources. Sr isotope signals ($^{87}Sr/^{86}Sr$ ratio), which are usually used as tracing sources in the geochemical field, are a potential tool to distinguish between bedrock dissolution and PCP processes.

In this study, the Sr isotope composition reveals that there is not a one-to-one positive correlation between the $\delta^{13}C_{DIC}$ values in drip water and the contribution rates of bedrock dissolution. By contrast, the $\delta^{13}C_{DIC}$ value in 1# is the heaviest (−4.5‰), where the contribution rate from bedrock dissolution is the lowest. In 9#, bedrock dissolution is the highest, and its $\delta^{13}C_{DIC}$ value is the lightest (−9.3‰). The contribution rate from bedrock dissolution in 4# is higher than that in 1#, and lower than that in 9#, but its $\delta^{13}C_{DIC}$ value is significantly lighter than that for 1# by up to 4‰ and a little heavier than that for 9# (Table 2). Therefore, according to the relationship between $^{87}Sr/^{86}Sr$ ratio and the $\delta^{13}C_{DIC}$ values in drip water, when seepage water moves from the soil layer into the cave, the effect of inorganic carbon from the bedrock dissolution is not the main factor that results in different $\delta^{13}C_{DIC}$ values across the different drip sites of QXC. This suggests that PCP processes are the main factor in the processes discussed above. Similar conclusions were drawn by other scientists [25,26].

3 Conclusions

This study indicates that the differences in $^{87}Sr/^{86}Sr$ ratio across different components are distinct in the QXC, which provides a good opportunity for analyzing the relationship between them. On the basis of the remarkable differences in $^{87}Sr/^{86}Sr$ ratio between different drip waters and previous studies [8,9], the different flow paths of seepage water result in a variation in residence times and hydro-geological processes in the unsaturated zone overlying the cave. This would affect the sources of drip water, leading to the different relative proportions from bedrock dissolution for 1#, 4# and 9#, which were 40.8%, 57.6% and 72.4%, respectively. Although the $^{87}Sr/^{86}Sr$ ratios between the drip water and its corresponding speleothem are a little different in 4#, the speleothem fundamentally inherits the Sr isotopic signals from the drip water. In addition, the source of the drip

waters and their corresponding speleothems are derived predominantly from the soil layer and bedrock overlying the cave. There are few other sources in this study area, suggesting that the different relative proportions from the soil layer and bedrock may result from changes to the $^{87}Sr/^{86}Sr$ ratios in the drip water and speleothem. As a result, it is feasible to use Sr isotopic signals in the speleothem as an indicator for the chemical weathering intensity of soil, and consequently as a monsoon proxy in this study area. It is, however, necessary to systemically investigate the effects of hydrogeological processes on climatic and environmental signals in the unsaturated zone overlying the cave, when using $^{87}Sr/^{86}Sr$ ratios in the speleothem model past climates and environments. The relationship between $^{87}Sr/^{86}Sr$ ratios and $\delta^{13}C_{DIC}$ values in drip waters indicates that the $\delta^{13}C_{DIC}$ values in drip water are controlled principally by a PCP process, and are less affected by bedrock dissolution.

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