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Daily response of drip water isotopes to precipitation in Liangfeng Cave, Guizhou Province, SW China

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ABSTRACT

Oxygen isotope ($\delta^{18}O$) is one of the most commonly used palaeoclimate proxies, and monitoring their modern evolutionary processes is very significant for palaeoclimate reconstruction. In this study, drip water samples are daily collected from two drip sites in Liangfeng Cave, Guizhou Province, SW China, between June 2008 and June 2010. The stable hydrogen and oxygen isotopes of these samples and the contemporary precipitation samples are measured. The relationships between the isotopes and the local air temperature, precipitation and relative humidity are analysed. The results show that the hydrogen and oxygen isotopic compositions of precipitation have obvious seasonal variations in the study area: lower in the rainy season and higher in the dry season. The local meteoric water line (LMWL) is $\delta D = 8.64\ \delta^{18}O + 17.44$. Precipitation is the only source of cave drip water, and its oxygen isotope signals are reflected in the two drip waters (SD: slower drip rate and previously called 1#, and FD: faster drip rate and previously called 5#). However, the amplitude of the drip water oxygen isotope variation is much smaller than that of the precipitation, i.e., homogenization occurs to some extent. However, there are significantly different responses to precipitation between the two drip sites. The response time of SD to precipitation is much longer than that of FD. The amplitude of oxygen isotope variation in SD, where the isotopic data deviate from the LMWL to a higher degree, is much smaller than that in FD. A comparison of these isotopic differences with previous research in the same cave indicates that the isotopic differences between the two drip waters result from different flow paths. The oxygen isotope signal in cave drip water perhaps mainly reflects summer monsoon information in the study area. The speleothems fed by drip waters (e.g. FD) with shorter response time to precipitation may be more suitable for high-resolution palaeoclimate research. Moreover, the *d*-excess from speleothem fluid inclusion has the potential to be used as an indicator of relative humidity of local air.

1. Introduction

Oxygen isotope ($\delta^{18}O$) is one of the most commonly used palaeoclimate proxies. Significant discoveries using oxygen isotopes have been made from ice cores, lake sediments, tree rings and other geological archives, but more important oxygen isotope indicators have been found during speleothem studies (e.g. Yuan et al., 2004; Wang et al., 2005, 2008; Fairchild et al., 2006; Zhang et al., 2008; Baker and Bradley, 2010; Orland et al., 2012). However, some interesting phenomena have been found during speleothem and drip water research. For example, the oxygen isotopic compositions of cave drip waters are significantly higher than those of local precipitation because of evaporation in semi-arid regions (Bar-Matthews et al., 1996). There is up to 4‰ (on average 1.4‰) oxygen isotope difference between two contemporary stalagmites separated by less than 10 m, and the oxygen isotope differences are up to 5‰ in Reed's Cave of the Black Hills in South Dakota, which was considered to be the result of different flow paths (Serefiddin et al., 2004). Speleothem oxygen isotopes show a negative anomaly caused by significant seasonal changes in precipitation signals (Rowe et al., 2012). However, there is >1‰ difference in oxygen isotopic compositions between two contemporary stalagmites in a single cave in Italy (Belli et al., 2013). In summary, in the formation process of speleothems or drip waters

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from atmosphere to cave, different caves, even different drip waters in the same cave, are not completely consistent with each other. Thus, monitoring and researching oxygen isotopes in modern cave drip waters are very important.

Studies of hydrogen and oxygen isotopes in cave drip water were carried out as early as 1985 (Yonge et al., 1985), and many important research achievements have been published (e.g. Cruz et al., 2005; Cobb et al., 2007; Pape et al., 2010; Wackerbarth et al., 2010; Riechelmann et al., 2011; Feng et al., 2012; Madonia et al., 2013). There are many complex factors influencing speleothem oxygen isotopes, including various isotopic effects (air temperature and relative humidity), effects from evaporation and mixing in the soil and the epikarst zone and the rate of deposition (Lachniet, 2009). The uniqueness and complexity of cave systems lead to great uncertainty of in the response of cave drip waters (or speleothems) to the climates overlying the caves (Bradley et al., 2010). Therefore, it is necessary to monitor and study cave drip waters in those regions in which many stalagmites studies have been carried out. However, in these cave monitoring processes, sampling frequencies are quarterly (e.g. Cobb et al., 2007), monthly (e.g. Li et al., 2000; Cruz et al., 2005; Luo and Wang, 2008; Pape et al., 2010; Riechelmann et al., 2011; Treble et al., 2013) or biweekly (e.g. Yonge et al., 1985; Oster et al., 2012). These sampling frequencies cannot accurately reveal the real information preserved in speleothems or drip waters in some regions, in which precipitation isotope signals and speleothem depositional rates strongly vary with time (seasonally or even an event time).

Therefore, we carried out a daily monitoring for two hydrological years in the Liangfeng Cave (LFC), which is situated approximately 8 km southeast of Dongge Cave (Yuan et al., 2004; Wang et al., 2005) in Guizhou Province, to identify the climate information contained by oxygen isotopes in cave drip waters more accurately. This cave has been monitored and studied for more than ten years (Zhou and Wang, 2005; Zhou et al., 2005; Luo et al., 2007, 2013a, 2013b; Luo and Wang, 2008, 2009; Xie et al., 2008). Through sampling drip water once every day, collecting precipitation during the sampling period and measuring the amount of precipitation, the air temperature and the air relative humidity, we analyse the response processes of the cave drip water to precipitation, and explore its palaeoclimatic significance by comparing the isotopic correspondence relationships between precipitation and cave drip water.

2. Materials and methods

2.1. Sampling site and local climate

The LFC (26°16′N, 108°03′E) is located in Yaosuo Village, Dongtang Town, Libo County, Guizhou Province, SW China. Background information on the cave can be found in a previous study (Luo and Wang, 2008). The lithology is mainly biogenic limestone of middle and late Carboniferous age, the thickness of the rock overlying the cave ceiling is approximately 100 m, and the soil is 0 cm–135 cm thick, with an average of approximately 27 cm. Rock fractures are well developed, and the vegetation type is primary karst forest. The mean annual temperature in Libo is approximately 18.6 °C, with hot summers and cold winters. Primary rainfall events occur from May to September (rainy season), and less than 14% of annual precipitation occurs between October and April of the following year (the dry season) in this study region. Drip site SD (previously called 1#) and FD (previously called 5#) (Luo et al., 2013a) are located in the main channel of the cave, and are separated by less than 20 m (Fig. 1). Their hydrological and geochemical characteristics are significantly different from each other (Table 1). Compared with FD, SD has a longer response time to precipitation, a slower drip rate and smaller amplitude of drip rate variation, a lower $^{87}Sr/^{86}Sr$ ratio and no water head variation. The flow type of SD is mainly matrix flow, but that of FD is preferential flow.

Table 1
Hydrogeochemical comparisons of two drip sites in Liangfeng Cave.

	SD	FD	References
$^{87}Sr/^{86}Sr$ ratio	Lower (0.708837 ± 10)	Higher (0.709177 ± 12)	(Zhu, 2011)
Water head variation	No	Yes	(Luo et al., 2013b)
Flow types	Matrix flow with preferential flow	Preferential flow with matrix flow	(Luo et al., 2013b)
Drip rate	Slower	Faster	(Luo et al., 2013b)
Amplitude of drip rate variation	Smaller	Larger	(Luo et al., 2013b)
$[SO_4^{2-}]$ (response time)	Lower and invariable (longer)	Higher and variable (shorter)	(Yang et al., 2012)

2.2. Sampling

From 24 June 2008 to 15 June 2010, drip water samples were daily collected at the SD and FD drip sites of the LFC. These samples were sealed in 10 ml glass bottles and stored at a low temperature (approximately 4 °C) until being processed. Simultaneously, rainwater samples were collected near the cave at every event by placing a rainwater harvesting anti-evaporation device on the roof of a local resident. Processing of precipitation samples was similar to that of drip water.

In addition, we monitored the monthly microenvironmental parameters (cave air relative humidity and temperature) in the cave from April 2011 to January 2013 (Fig. 2). We found that the cave air temperature was basically stable at approximately 15 °C except for January to April, which had lower temperatures. The relative humidity of the cave air was more than 95%, except for January to March, which had significantly lower values. There are no significant inter-annual changes in the cave air temperature and the cave air relative humidity.

2.3. Isotope measurements

The hydrogen and oxygen isotopic compositions of water samples were measured by using a stable isotope mass spectrometer (MAT 253) of the Finnigan Company performed in the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. All samples were continuously measured in batches in 2011. Two Standard Mean Ocean Water (SMOW) samples were inserted every ten samples to control measuring errors (2σ), which are $<0.5‰$ for hydrogen isotopes and $<0.2‰$ for oxygen isotopes. These isotope data are reported here in per mil units relative to SMOW.

3. Results

3.1. Precipitation isotopes

The hydrogen and oxygen isotopic compositions of precipitation of 114 samples from 2008 to 2010 (Fig. 3) were between −106‰ and 21‰ (average value −38‰), and −15.1‰ and 0.1‰ (average value −6.4‰), respectively. There is significant seasonal variation: values were lower in the rainy seasons and higher in the dry seasons (Fig. 4a). The local meteoric water line (LMWL) obtained by these precipitation samples is very close to the LMWL of Guilin from IAEA (International Atomic Energy Agency) from 1983 to 1990

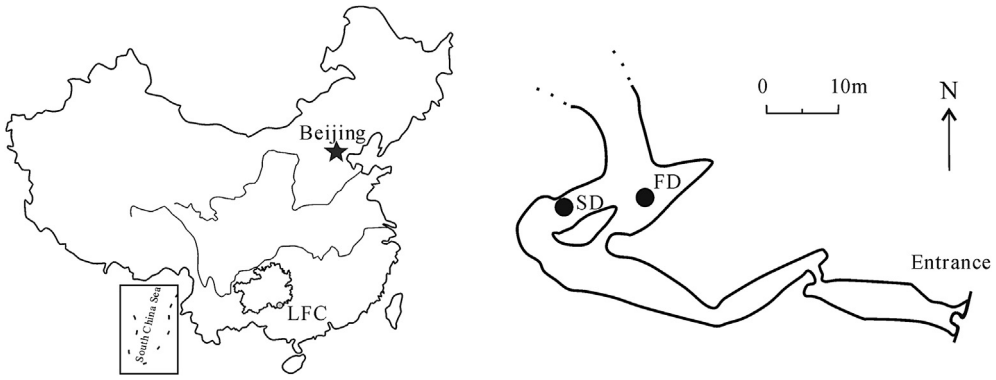

Fig. 1. Sketch of location and drip sites of Liangfeng Cave.

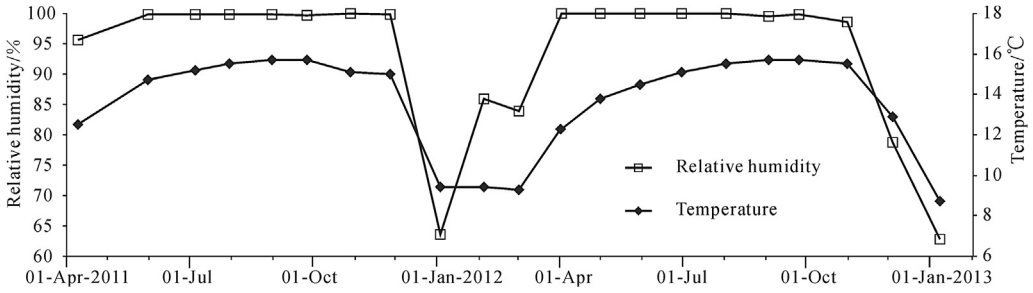

Fig. 2. Cave air relative humidity (%) and temperature (°C) in Liangfeng Cave.

($\delta D = 8.52\ \delta^{18}O + 17.11$), as well as that from Li et al. (2000) ($\delta D = 8.8\ \delta^{18}O + 19.5$).

3.2. Hydrogen and oxygen isotopes of cave drip waters

The oxygen isotope values in the two drip waters are between −7.8‰ and −6.6‰ (Figs. 4b,c and 5a,b), and the hydrogen isotope values are between −54‰ and −44‰ (Fig. 5a and b). There are very significant correlations (Fig. 5c and d) between the hydrogen isotopes and the oxygen isotopes of all precipitation and drip water samples.

From comparative analysis of contemporary meteorological records (average daily temperature, daily precipitation and air relative humidity) and the precipitation isotope values, we found the following results: (1) Overall, oxygen isotope values are correlated between the two drip waters and precipitation, i.e., isotopes are lighter in the rainy seasons and heavier in the dry seasons (Fig. 4a–c). (2) The amplitude of variation in the SD drip water oxygen isotopes is slightly smaller than that in FD, and its response to precipitation is significantly slower (approximately a month) than that of FD (Fig. 4a–c). (3) The *d*-excess values of drip waters are mostly near to or less than 10‰, showing an increasing trend with time (Fig. 4d and e). (4) The isotopes of all drip waters are concentrated within a very small range of precipitation isotope values (Figs. 5c and 4d). (5) The majority of the drip water isotopic data were plotted on the low right of the LMWL (Fig. 5a and b). The deviation from the LMWL in SD was greater than that in FD, and the slope of the regression line of SD was significantly greater than that of FD (Fig. 5a and b). (6) The oxygen isotopes in FD gradually become heavier with time, which is similar to the changes in the *d*-excess in all drip waters. However, this is not true for SD (Fig. 4c–e).

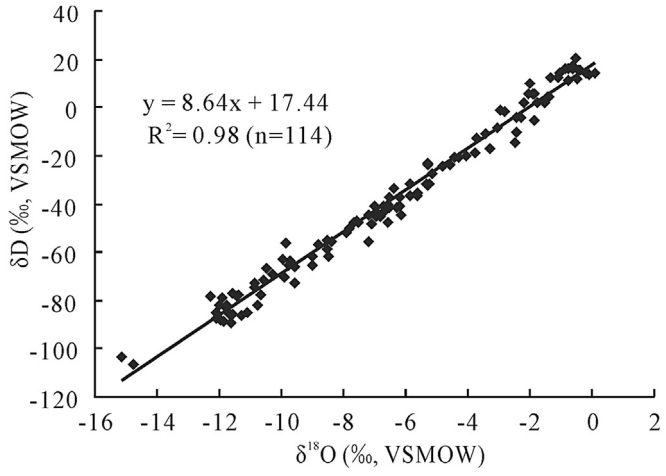

Fig. 3. Relationship (LMWL) between hydrogen and oxygen isotopes of precipitation in the study area.

4. Discussion

4.1. Cave drip water sources

Although the isotopes in the SD and FD plot almost on an approximate straight line of precipitation isotopes (correlation coefficient >0.98) (Fig. 5c and d), very significant differences are still present (Fig. 5a and b). Those isotopes of the two drip waters mostly plot on the low right of the LMWL, especially SD. This suggests that the cave drip waters are derived from the local meteoric water (Luo and Wang, 2008). However, there are different extends of hydrogeochemical impacts on different drip sites (Table 1) in the process from the surface to the cave, which results in the abovementioned isotopic differences. This confirms that hydrological geochemical processes affect the hydrogen and oxygen isotopic compositions of drip waters to varying degrees (Riechelmann et al., 2013; Treble et al., 2013; Luo et al., 2013a).

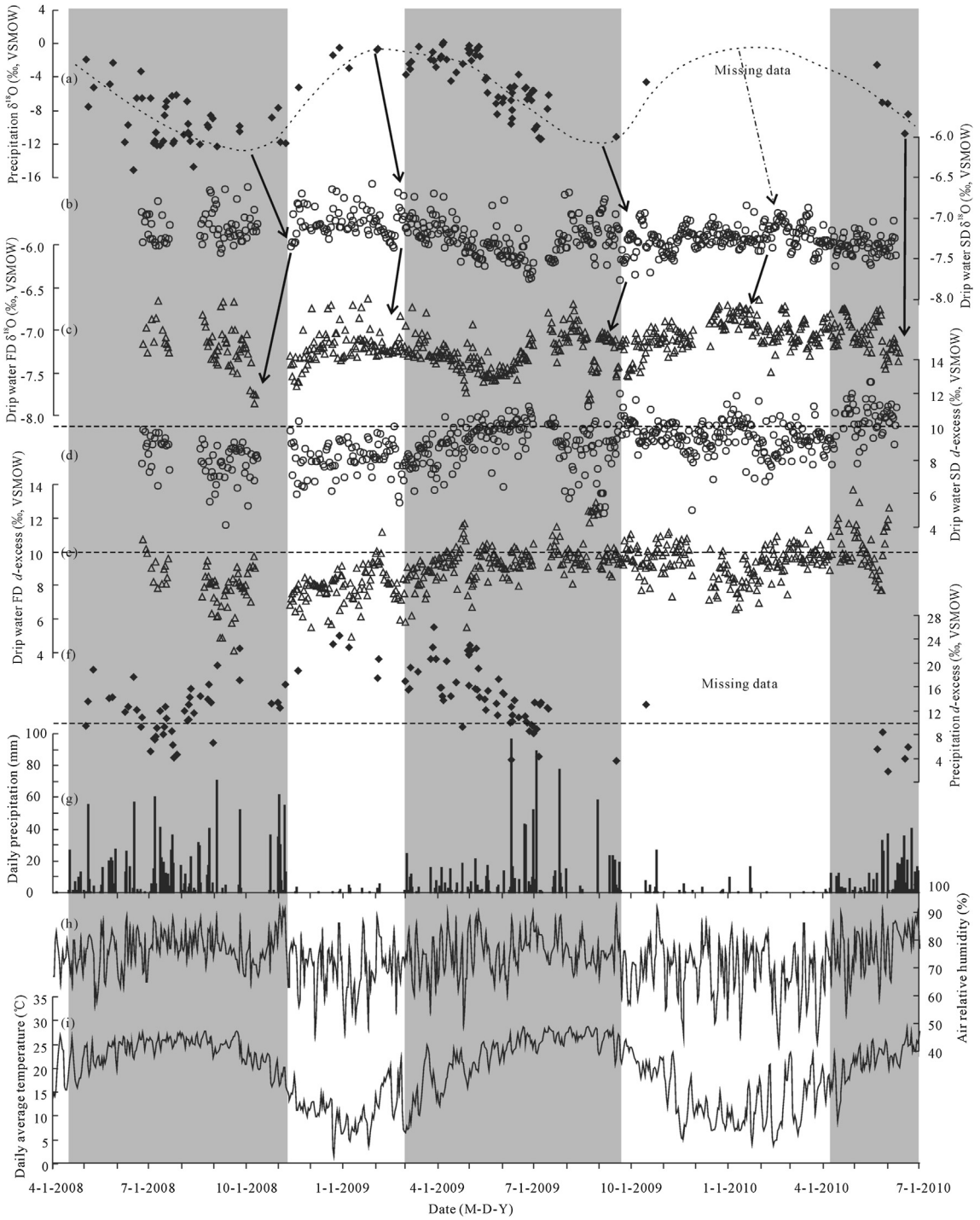

Fig. 4. Relationships between oxygen isotope and *d*-excess in precipitation and drip waters and precipitation amount and temperature in the study area (shaded areas indicate the wet season, the other for the dry season) (a: $\delta^{18}O$ values of precipitation; b: $\delta^{18}O$ values of SD drip water; c: $\delta^{18}O$ values of FD drip water; d: *d*-excess of SD drip water; e: *d*-excess of FD drip water; f: *d*-excess of precipitation; g: daily amount of precipitation; h: air relative humidity; i: average daily temperature).

It is well known that $d\text{-excess} = \delta D - 8\delta^{18}O$ (Dansgaard, 1964), and that the *d*-excess values of precipitation depend on the temperature and air relative humidity in the moisture source region (Merlivat and Jouzel, 1979). Fig. 4f indicates that the *d*-excess values of precipitation show significant seasonal variation in the Liangfeng Cave area, being lower in the rainy seasons and higher in the dry seasons. The lowest *d*-excess values occurred during July, and the highest during January. In addition, the *d*-excess values of precipitation are substantially greater than the global average (10‰), except when they are less than or approximately equal to 10‰ (Craig, 1961) in the middle of the rainy season (June–August). This suggests that precipitation mainly originates from marine air masses in the rainy season, and local moisture sources gradually increase until the dry season. However, the *d*-excess values of drip waters are mostly in the vicinity of or less than 10‰ (Fig. 4d and e), which suggests that drip waters of different periods mainly originate from precipitation during the rainy season (lower *d*-excess).

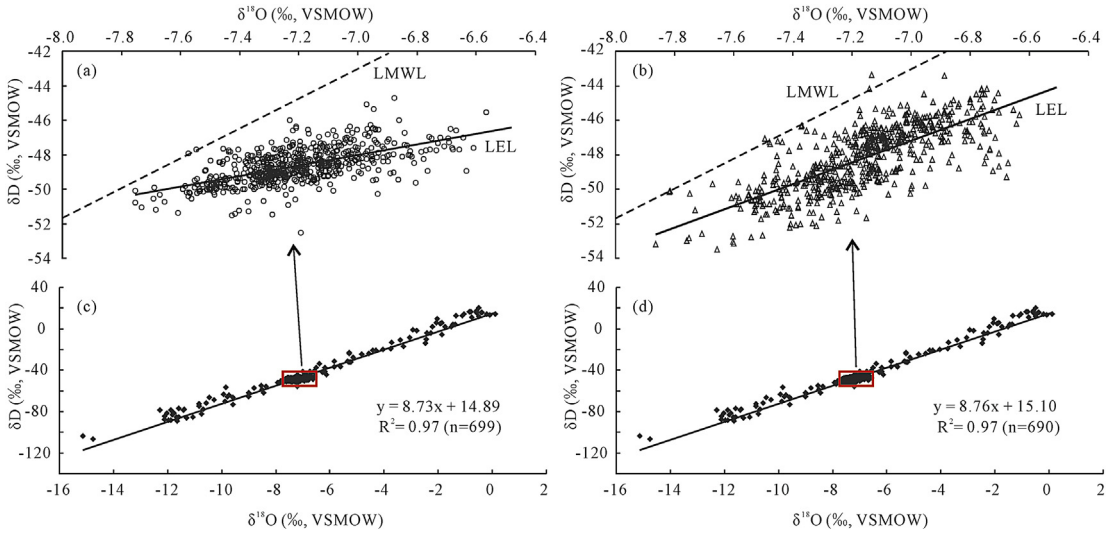

Fig. 5. Relationships between isotopic compositions of drip waters and local meteoric water line (LMWL) (red boxes are ranges of isotopic compositions in the drip waters; LEL is the local evaporation line; a: relationship between LMWL and SD drip water isotopes; b: relationship between LMWL and FD drip water isotopes); c: relationship between precipitation isotopes and SD drip water isotopes; d: relationship between precipitation isotopes and FD drip water isotopes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.2. Response of cave drip water to precipitation

The response of drip water to precipitation mainly depends on the effect of the flow path (Tooth and Fairchild, 2003). In this study, the responses of the two drip waters to precipitation are, overall, similar to each other (Fig. 4). The oxygen isotope variations in the two drip waters are less than 1.5‰, i.e. there is a high degree of homogenization; however, these drip waters also roughly record seasonal variation signals in precipitation isotopic compositions with very significant seasonal variations (heavier in the dry season and lighter in the rainy season).

The bedrock in the study area has a very low $^{87}Sr/^{86}Sr$ ratio (Zhu, 2011). This ratio is also low in the SD drip water (Table 1). The unchanged water head, the main flow type being matrix flow, the smaller drip rate and the longer response time by the SO_4^{2-} tracer (Table 1) indicate that the response of SD to precipitation is slower than that of FD, and the storage capacity of the reservoir overlying SD may be much larger than that of FD. Comparing the isotope response relationships to precipitation with the hydrogeochemical characteristics of the two drip sites (Table 1), we found that FD could very quickly respond to the precipitation changes, but SD was relatively slow (approximately a month), with a relatively small magnitude of isotopic changes. In other words, the information from the isotope response of drip water to precipitation is entirely consistent with these conclusions, which are drawn from various hydrologic and geochemical indicators during previous studies (Zhu, 2011; Yang et al., 2012; Luo et al., 2013b). This suggests that the different hydrogeochemical processes of the two drip sites are likely responsible for their different response times and oxygen isotope values.

4.3. Implications for speleothem palaeoclimatic studies

The responses of the two drip waters in the LFC to precipitation are significantly different, which is highly consistent with previous findings. This suggests that the oxygen isotopic compositions of drip waters from different flow paths differ to varying degrees, which is of great significance for comparative studies of oxygen isotopes of different stalagmites from the same cave. The drip waters of different stages mainly originate from precipitation in the middle of the rainy season, which suggests that, regardless of whether speleothems are formed in the rainy or dry season, their oxygen isotopic compositions will still mainly record the summer precipitation signal. The oxygen isotope signals from stalagmites and other deposits mostly reflect information on the summer monsoon in this study area.

This study also shows that the oxygen isotope compositions of FD (but not SD) drip water are significantly heavier after August 2009, but the *d*-excess values of the two drip waters have similar characteristics (Fig. 4c–e). This may be associated with the longer dry season and lower air relative humidity during the second hydrological year (Fig. 4g and h). On the one hand, the stalagmites fed by drip sites with a faster response to precipitation (e.g. FD) might retain better high-resolution (such as seasonal) climatic information. On the other hand, despite the finding of a previous study (Luo et al., 2013a) that the *d*-excess value from drip waters (or stalagmite fluid inclusions) may not be suitable as an indicator of water source and temperature, in this study we found that the *d*-excess value may be a good indicator of air relative humidity. Furthermore, the deviation in the SD isotopic data from the LMWL was greater than that of FD (Fig. 5), which may result from greater evaporation intensity caused by lower drip rates (Table 1) (Day and Henderson, 2011).

5. Conclusions

In the LFC area, the hydrogen and oxygen isotopic compositions of precipitation show obvious seasonal variations (lighter in the rainy season and heavier in the dry season), and the LMWL is $\delta D = 8.64\,\delta^{18}O + 17.44$. Precipitation is the only source of drip water in the study cave. The isotopic signals from the two drip waters reflect seasonal variations in precipitation isotopes, but the magnitudes of the changes are much smaller than those of precipitation. The response patterns between the two drip sites are significantly difference: the response time of SD is much slower than that of FD, which has a larger change in the magnitude of isotopes with time. In addition, the deviation in the SD isotopic data from the LMWL is greater than that in the FD data, which suggests that it results from greater evaporation intensity caused by the lower drip rate in the SD. Comparing the results with previous

studies, the isotopic differences between the two drip waters mainly resulted from different flow paths. We also found that the drip water oxygen isotopes mainly reflected summer monsoon information in the study area, and speleothems fed by those drip waters that have a faster response to precipitation (e.g. FD) may be more suitable for high-resolution palaeoclimate research by comparative analysis. In addition, the *d*-excess value stored in stalagmite fluid inclusions may be a good indicator of local air relative humidity.

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