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A comparative study on the stable isotopes from precipitation to speleothem in four caves of Guizhou, China

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ABSTRACT

Monitoring and sampling of soil waters, and cave drip waters were performed monthly at four caves of Guizhou, Southwest China, from April 2003 to May 2004, in order to comparatively study the control factors of stable isotope in drip waters and their corresponding speleothems. δD and $\delta^{18}O$ were measured for all samples including precipitation, soil waters, drip waters and modern speleothems. These results indicate that the amplitudes of the isotope values decrease gradually from precipitation to drip water in these caves, obviously suggesting the homogenization. Under certain conditions, it is possible to use speleothems to study high resolution (seasonal, even monthly) paleoclimatic changes in Liangfeng Cave (LFC) and Qixing Cave (QXC), but only low resolutions (more than a year) could be reached in Jiangjun Cave (JJC) and Xiniu Cave (XNC). The relationships between local meteoric water line (LMWL) and isotopic data of fluid inclusions in speleothems from the four caves can estimate local paleoclimate and paleoenvironment; however, it is debatable whether *d*-excess values can predict them. The effects of hydrological processes on the $\delta^{18}O$ values in drip waters cannot be ignored. Hydrochemistry may cause isotopic disequilibrium in the formation of speleothems.

1. Introduction

In the past few decades, many significant progresses have been made in using oxygen isotope compositions ($\delta^{18}O$) in speleothems to restore and reconstruct paleoclimate, which can be represented mainly in two aspects: paleotemperature (e.g. Griffiths et al., 2010; Wackerbarth et al., 2010; Zhang et al., 2008), and paleomonsoon or paleoprecipitation (e.g. Bar-Matthews et al., 2010; Breitenbach et al., 2010; Cai et al., 2010; Cosford et al., 2008; Dykoski et al., 2005; Hu et al., 2008; Liu et al., 2010; Tan et al., 2009).

However, some results (e.g. Breitenbach et al., 2010; Hu et al., 2008; Tan et al., 2009; Zhang et al., 2008) were calibrated by meteorological record. Serefiddin et al. (2004) displayed that among different coeval speleothems from the same cave, there is a significant difference of oxygen isotopes (up to 4‰), which may result from different drip water pathways or changes in catchment area; in modern drip waters from different sites, the difference is as much as 5‰, which presumably relates to subtle differences in routes. Many studies have shown that local precipitation, temperature, evaporation, water residence time and mixing between new and old waters can affect $\delta^{18}O$ values in drip water (Baldini et al., 2008; Bradley et al., 2010; Lachniet, 2009; Li et al., 2000; Riechelmann et al., 2011). The isotope fractionation processes occurring during precipitation of calcite inside the cave and on the stalagmite surface also have a large effect on speleothem stable isotope signals (Dorale and Liu, 2009; Dreybrodt and Scholz, 2011; Mühlinghaus et al., 2009; Mickler et al., 2004, 2006; Polag et al., 2010; Scholz et al., 2009; Wiedner et al., 2008).

Recently, Lachniet (2009) summarized previous studies about the factors on the $\delta^{18}O$ values in cave drip water: (1) primary controls of $\delta^{18}O$ in the atmosphere include temperature and relative humidity through their role in the multiple isotope "effects"; (2) variability and modifications of water $\delta^{18}O$ values in the soil and epikarst zones are dominated by evaporation, mixing, and infiltration of source waters; (3) the isotopically effective recharge into a cave system consists of those waters that participate in the precipitation of $CaCO_3$, resulting in different calcite deposition rates which may be biased to periods with optimal drip water saturation state.

Thus, oxygen isotope variations reflect a more complex array of processes including temperature driven changes in isotopic fractionation during calcite precipitation and changes in sources of moisture in the hydrological cycle (Dreybrodt and Scholz, 2011; Lachniet, 2009; McDermott, 2004; Moreno et al., 2010). No single dominant process, or simple set of processes affecting isotope signal, exists (Dayem et al., 2010). And in the sense, each cave is unique (Spötl et al., 2005).

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Therefore, an understanding of the processes that control equilibrium and kinetic fractionation of oxygen isotopes in water and carbonate species is essential for the proper interpretation of speleothem $\delta^{18}O$ as paleoclimatic and paleoenvironmental proxies, and is best complemented by cave monitoring such as infiltration, flow routing, drip seasonality and saturation state, and cave microclimate, among others (Lachniet, 2009).

The δD (δ^2H) and $\delta^{18}O$ values in precipitation and cave drip water have become focus of monitoring and researching modern environment, and some consensus have been achieved. In general, the δD and $\delta^{18}O$ values in precipitation have a significant seasonal variation (Cobb et al., 2007; Fuller et al., 2008; Pape et al., 2010); the δD and $\delta^{18}O$ values in soil water have a larger seasonal variation, which generally becomes less obvious with increasing soil depth (Cruz et al., 2005; Yonge et al., 1985); however, the δD and $\delta^{18}O$ values in drip water have a much lower seasonal variation (Cobb et al., 2007; Pape et al., 2010), and some are almost constant (Fuller et al., 2008; Yonge et al., 1985), which are homogenized (Cruz et al., 2005; Onac et al., 2008) or buffered (Perrin et al., 2003; Schwarz et al., 2008) to various extents. In humid areas, average isotopic compositions in drip water are mostly similar to the weighted average in local precipitation (Cobb et al., 2007; Fuller et al., 2008; Yonge et al., 1985). However, in arid or semi-arid areas, where evaporation is stronger, the δD and $\delta^{18}O$ values in drip water should be heavier to varying degrees than the weighted average in local precipitation (Ayalon et al., 1998; Bar-Matthews et al., 1996; Griffiths et al., 2010). The potential evapotranspiration (PET, i.e., the combination of evaporation and transpiration in the soil zone) have a significant effect on the $\delta^{18}O$ value of cave drip water (Riechelmann et al., 2011) and this impact has been modeled in a recent publication (Wackerbarth et al., 2010).

In short, under different climatic conditions or among different caves under the same climatic condition, the transmissions of isotopic signals have their own uniqueness, due to the complexity and uncertainty of various factors. Therefore, to interpret more accurately oxygen isotope signals in speleothem, more related researches must be carried out. In this study, we will comparatively discuss some potential factors that result in changes of oxygen isotope compositions in drip water and its corresponding speleothem on the basis of hydrogen and oxygen isotopic data in various waters from four caves, where climatic and environmental conditions are not exactly the same.

2. Study sites

Study areas are located in Guizhou province, southwest China (Fig. 1). The four caves studied are Liangfeng Cave (LFC), Qixing Cave (QXC), Jiangjun Cave (JJC) and Xiniu Cave (XNC), respectively. There are some differences in the geological backgrounds, the surface environments (such as soil and vegetation), and climate (such as precipitation and temperature) (Table 1), making response times of drip waters to local precipitation in the four caves largely different (Zhou et al., 2005). Sampling sites are shown in Fig. 1.

Fig. 1 indicates that the whole study area is located in the junction of two major summer monsoons in China (East Asian monsoon and Indian monsoon) (Wang and LinHo, 2002). LFC and QXC, closer to the effect sphere of East Asia monsoon, are affected more frequently by East Asia monsoon than JJC and XNC, which are near the effect regions of Indian monsoon, and vice verse (Fig. 1). This deduction is confirmed by isotopic and precipitation data of Guilin and Guiyang from IAEA. The peak of monthly rainfall in Guilin occurs earlier than that of Guiyang, and the $\delta^{18}O$ values in summer precipitation from Guilin are significantly heavier than those from Guiyang, i.e. the former (precipitation characteristics) maybe is controlled by the different monsoon systems, and the later (isotope difference) may be mainly altitude effect (Table 2 and Fig. 2).

3. Methods

Some sites were selected for sampling soil waters overlying LFC, QXC, JJC and XNC (similar order hereinafter). These sampling sites are at 50 cm depth from surface except that No. 1 in LFC and QXC are at 50 and 100 cm depth. The numbers of drip sites selected in the main channels of the caves were five, nine, four and three, respectively (Fig. 1).

All samples were collected between April 2003 and May 2004. Samples include precipitation, soil water, drip water (including the ceiling and the floor drip waters, but if there is no special description, "drip water" represents the floor drip water) and its corresponding modern speleothems, which were collected by a watch glass placed under the drip site in June 2003 and repossessed in June 2004. Thus, the precipitated calcite reflects the mean value of one year, and potential seasonal variability cannot be resolved. Except for precipitation (no water was collected in some winter months because of small precipitation intensity in winter in Guizhou, China) and speleothem, other samples were collected in April, June, July, August, September, October in 2003 and February or March, April, May or June 2004. The watch glass was taken away from drip site when drip water was collected using a glass container pre-cleaned by rinse using 2–3 N HCl, followed by deionized water, and finally dried at about 105 °C, after put back. In addition, environmental and climatic data such as air temperature and relative humidity in cave were recorded during the sampling time.

Oxygen isotope compositions in speleothems were determined by Stable Isotope Ratio Mass Spectrometer (Finnigan MAT-252) via a series of processes including triturated powder of less than 50 meshes for more quickly reacting with anhydrous phosphoric acid to get CO_2, and purified CO_2. The measurements reported here have a general precision of about ±0.3‰ for oxygen-18, at one standard deviation level. Hydrogen and oxygen isotopes in various water samples were determined by MultiFlow Continuous Flow Isotope Ratio Mass Spectrometer (IsoPrime-GC, UK), and revised using the standard waters (such as SLAP: Standard Light Antarctic Precipitation and GISP: Global Network of Isotopes in Precipitation). The measurements reported here generally have a long term precision of about ±0.1‰ for oxygen-18 and ±2‰ for deuterium, at one standard deviation level.

4. Results

4.1. Oxygen isotope composition in precipitation

Table S1 shows that the precipitation $\delta^{18}O$ values in the four cave regions range from −10.1‰ to 0.0‰, −13.4‰ to −0.5‰, −14.6‰ to −3.3‰ and −14.7‰ to −0.9‰, respectively; their arithmetic means are about −6.0‰ (n = 27), −7.0‰ (n = 39), −9.5‰ (n = 16) and −8.6‰ (n = 16), respectively; the weighted averages are about −7.9‰ (n = 27), −8.2‰ (n = 39), −10.8‰ (n = 16) and −10.7‰ (n = 16), respectively. That is, precipitation $\delta^{18}O$ averages are LFC > QXC > XNC ≥ JJC, which is lighter than data near the stations from IAEA (see Table 2). While this may result from incomprehensive sampling (no water was collected in some winter months (Table S1), which has a weightier isotope composition than that in summer, seen in Fig. 2) and/or inter-annual variation of oxygen isotope compositions in precipitation, the relations between different regions are consistent with those from IAEA data ($\delta^{18}O$ values in precipitation: Guilin > Guiyang, see Table 2).

4.2. Oxygen isotope composition in soil waters

The $\delta^{18}O$ values in all soil waters range from −8.6‰ to −2.0‰, about -5.8 ± 2.3‰ (n = 15) on average. In LFC, the average $\delta^{18}O$ value is about -5.5 ± 2.2‰ (n = 11) at 50 cm depth, and about -6.4 ± 2.6‰ (n = 4) at 100 cm. In QXC, the $\delta^{18}O$ values in soil waters vary between −8.8‰ and −2.8‰, and the average is about -5.7 ± 2.1‰ (n = 20) – about -5.8 ± 2.3‰ (n = 15) at 50 cm depth and about -5.3 ± 1.4‰ (n = 5) at 100 cm depth. In JJC, the $\delta^{18}O$ values in soil waters are between −9.0‰ and −4.4‰, and the average is about -6.4 ± 1.7‰ (n = 9) at 50 cm depth. In XNC, we only collected four soil water samples, and their $\delta^{18}O$ values are −10.1‰ (July 2003), −10.9‰ (August 2003), −10.1‰ (August 2003) and −6.3‰ (June 2004) (Table 3).

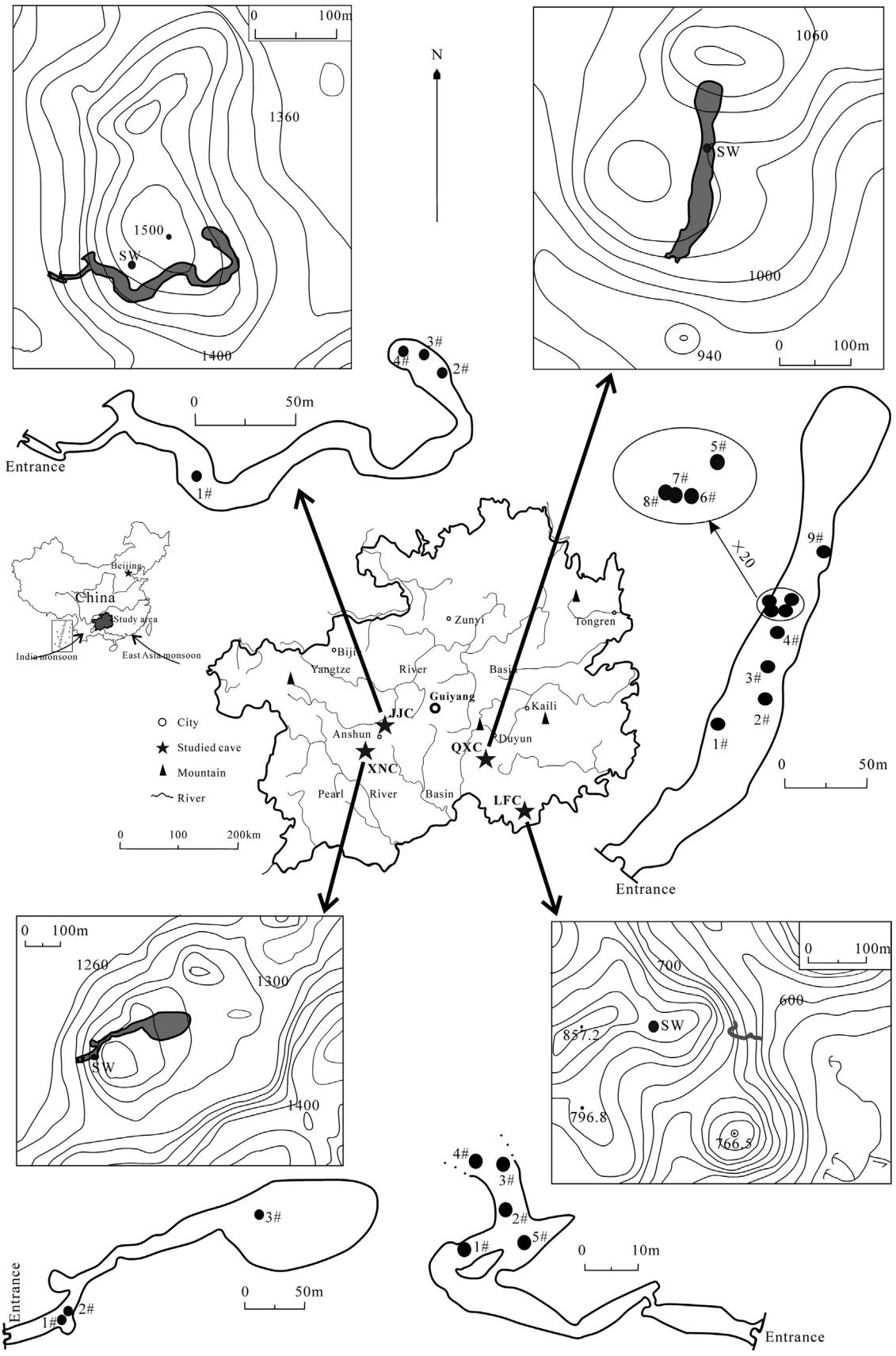

Fig. 1. Locations of the four caves (SW: soil water; 1#: drip water No. 1 and the rest may be deduced by analogy).

Table 1
General information of the four caves.

	LFC	QXC	JJC	XNC
Site	Libo	Duyun	Anshun	Zhenning
Longitude	108°03′E	107°16′E	106°04′E	105°47′E
Latitude	25°16′N	25°59′N	26°17′N	26°04′N
Altitude of cave entrance (m)	620	1020	1360	1300
Lithology	Limestone	Dolomitic limestone	Dolomite	Dolomite
Vegetation	Karst primary forest	Brushwood	Scrub tussock	Thorn tussock
Soil thickness mean (range) (cm)	27 (0–135)	33 (6–180)	26 (0–130)	21 (0–55)
Soil tightness	Loose	Tight	Very loose	Very tight
Soil texture	Loamy	Clay	Loamy	Clay
Soil porosity	Moderate	Small	Moderate	Small
Thickness of cave roof (m)	80–140	50–90	50–60	20–60
Bedrock fracture	Large	Small	Large	Small
MAT (°C)	18.6	16.6	14.0	15.4
AP (mm)	1 118.7	1 185.1	936.9	932.6
MCAP (°C)	15.1 ± 1.3	13.5 ± 1.7	14.5 ± 1.1	17.0 ± 1.2
MRH (%)	77.46 ± 3.15	76.99 ± 3.10	79.13 ± 4.23	77.44 ± 3.95
MCRH (%)	98 ± 2	98 ± 2	98 ± 2	99 ± 1

MAT: mean annual temperature; AP: annual precipitation; MCAT: mean cave air temperature; MRH: mean air relative humidity; MCRH: mean cave air relative humidity.

Table 2
The basic information and LMWL in Guilin and Guiyang of southwest China (data from IAEA).

Site	Longitude	Latitude	Altitude/m	MAP/mm	MAT/°C	Date	*n*	Weighted mean $\delta^{18}O$	Weighted mean δD	LMWL (*n* = 12)
Guilin	110.08E	25.07N	170	1531	19.0	1983/1–90/12	91/92	−6.2‰	−36‰	$\delta D = 8.5\delta^{18}O + 17.1$
Guiyang	106.43E	26.35N	1071	960	15.3	1988/2–92/12	58/58	−8.3‰	−52‰	$\delta D = 9.1\delta^{18}O + 24.3$

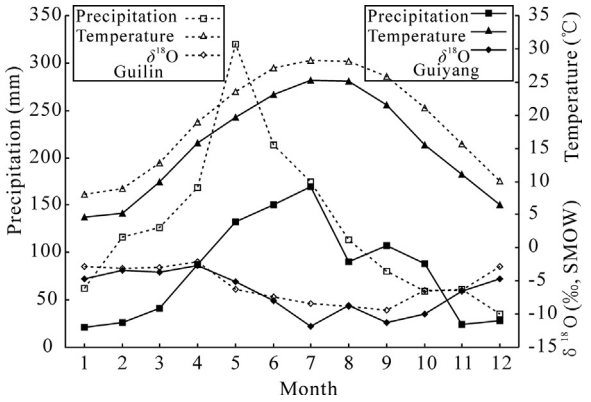

Fig. 2. The seasonal changes of precipitation, temperature and oxygen isotope values in precipitation in Guilin (1983–1990) and Guiyang (1988–1992) (all data from IAEA).

4.3. Oxygen isotope composition in drip waters

Table 5 shows that the drip water $\delta^{18}O$ values in the four caves range from −8.3‰ to −5.7‰, −8.3‰ to −4.3‰, −9.2‰ to −6.8‰, and −9.2‰ to −6.8‰, respectively, and their averages are −7.0 ± 0.6‰ (*n* = 39), −6.8 ± 0.7‰ (*n* = 70), −8.2 ± 0.7‰ (*n* = 33), and −7.9 ± 0.5‰ (*n* = 27), respectively.

4.4. Oxygen isotope composition in modern speleothems

Table 4 shows that the $\delta^{18}O$ values in modern speleothems are basically equivalent within LFC and within XNC, ranging from −7.0‰ to −6.7‰ (average −6.8 ± 0.1‰, *n* = 5) and −8.3‰ to −7.7‰ (average −8.0 ± 0.3‰, *n* = 3), respectively. However, in QXC and JJC, there are very significant inter-cave differences. These modern speleothems can be classified into two groups according to $\delta^{18}O$ values. 1#, 2#, 6#, 7# and 8# in QXC are classified into Group I, with high $\delta^{18}O$ values (between −4.9‰ and −4.0‰) and an average of −4.4 ± 0.4‰ (*n* = 5), and 3#, 4#, 5# and 9# into Group II, with low $\delta^{18}O$ values (between −6.1‰ and −5.5‰) and an average of −5.8 ± 0.3‰ (*n* = 4). Similarly, 2# and 3# in JJC are classified into Group I, both with a $\delta^{18}O$ value of −6.9‰, and 1# (−7.8‰) and 4# (−9.0‰) into Group II, with an average of −8.4 ± 0.9‰ (*n* = 2). There is a difference over 1.5‰ between Group I and Group II for both QXC and JJC.

In addition, we found that cave air temperatures were lower (more than 3 °C) than mean annual temperature (MAT) in the LFC and QXC, but not in other two caves (Table 1). LFC is ventilated seasonally, and other three caves were not found.

5. Discussion

5.1. Local meteoric water line

Fig. 3 shows that δD and $\delta^{18}O$ data from soil waters plot near or on top left of the Local Meteoric Water Lines (LMWL) from isotopic data in the LFC and QXC regions, but near or on bottom right of the LMWLs (or WML) in the JJC and XNC regions. Some researchers found similar results (Carrasco et al., 2006; Cruz et al., 2005; Vaks et al., 2003). According to Fig. 3, both relations between isotopic data and LWMLs (or WML) possibly result from re-condensation and re-evaporation or secondary evaporation, and the effects of water–rock interaction are not obvious. These stable isotopic characteristics exhibit different climatic characteristics in the two sub-regions (southeast Guizhou and western-centre Guizhou). That is, in the LFC and QXC region, where atmosphere is more stable with weaker wind and more sunny days, which will promote the loss of ground heat, the "secondary condensation water" (as dew drops) recharges soil water under higher vegetation cover, thereby supplying deeper percolation water (as drip water) (Ingraham and Matthews, 1988, 1990, 1995; Liu et al., 2004). As a result, the partial isotope data in drip waters plot on the top left of LMWL (Cui et al., 2009; Liu et al., 2005, 2007; Scholl et al., 2002). On the contrary, in the JJC and XNC area, where atmosphere is more active with stronger wind and more cloudy days, which will prevent rapid loss of ground heat, the partial isotope data in soil waters and drip waters plot on the bottom right of LMWL due to re-evaporation effect (Fig. 3).

Table 3
Hydrogen and oxygen isotope compositions in soil water.

Cave	Sampling date	Sample	$\delta^{18}O$ (‰)	δD (‰)	*d*-Excess
LFC	07/11/03	50(1)[a]	−6.8	−48	6.4
		100(1)	−6.4	−33	18.8
	09/15/03	50(1)	−8.0	−53	10.2
		100(1)	−8.2	−57	8.3
	10/16/03	50(1)	−6.9	−52	3.4
		50(2)	−7.9	−55	8.0
		50(3)	−8.6	−55	13.7
		100(1)	−8.3	−56	11.0
	03/03/04	50(1)	−4.7	−25	12.9
		50(1)	−2.0	0	16.1
	04/15/04	50(5)	−3.4	−13	14.1
		100(1)	−2.7	−10	11.6
	05/30/04	50(1)	−3.3	−12	13.8
		50(3)	−4.6	−26	10.4
		50(4)	−4.7	−25	13.1
QXC	07/15/03	50(1)	−7.1	−55	1.5
		100(1)	−6.7	−40	13.1
	08/14/03	50(1)	−7.6	−49	11.6
		50(2)	−8.2	−56	10.0
	09/13/03	50(1)	−8.4	−53	14.3
		50(2)	−8.7	−61	8.5
		50(3)	−8.1	−51	13.9
		100(1)	−6.9	−51	4.2
	10/14/03	50(2)	−6.8	−56	−2.1
	02/28/04	50(1)	−3.2	−13	12.7
		50(2)	−2.8	−11	11.2
		100(1)	−4.0	−22	9.6
	04/14/04	50(1)	−3.1	−17	8.3
		50(2)	−3.0	−7	16.7
		50(3)	−3.4	−12	15.7
		100(1)	−3.9	−20	11.2
	05/28/04	50(1)	−4.3	−23	11.2
		50(2)	−7.3	−43	15.7
		50(3)	−5.5	−31	13.0
		100(1)	−5.1	−28	12.9
JJC	08/21/03	50(1)	−8.0	−51	13.7
	09/18/03	50(1)	−9.0	−46	25.1
	10/19/03	50(1)	−8.4	−62	5.3
	03/09/04	50(1)	−4.4	−20	15.3
		50(3)	−6.1	−34	15.0
		50(4)	−6.1	−19	29.7
		50(5)	−5.8	−25	20.7
	06/06/04	50(1)	−4.9	−31	7.9
		50(3)	−4.8	−20	18.8
XNC	07/16/03	50(1)	−10.1	−69	11.7
	08/19/03	50(1)	−10.9	−64	23.4
		50(3)	−10.0	−66	14.5
	06/03/04	50(2)	−6.3	−37	13.5

[a] Sampling depth in cm (number of sampling site), *d*-excess = δD-8δ^{18}O.

It is necessary to explore more evidence to support the climatic characteristics in the LFC and QXC region, which have been confirmed preliminarily by some facts. For example, Table 1 shows that cave air temperatures are lower (more than 3 °C) than mean annual temperature (MAT) in the two caves. These cave air temperatures were measured during the sampling time (daytime), from March to October, when temperature is higher in a day and a year, respectively. This shows that the true cave temperature maybe is lower than the average temperature in Table 1. This is inconsistent with the general viewpoint that cave temperature is close to local MAT, which may be caused by large temperature difference between day and night (from Local weather stations). During the sunshiny day, the temperature soars under the direct sunlight, which is conducive to heat loss at night, so the temperature drops fleetly. While the duration of high temperature is generally much shorter than that of low temperature, solar energy loses quickly before it has a chance to be transmitted to the deeper layer (as cave) with the buffer effects of vegetation, soil, bedrock overlying the cave on heat transmission, and as a result, the cave temperature is lower than the MAT. Possibly, it is just the opposite situation in other two caves.

5.2. *d*-Excess (δD-8$\delta^{18}O$)

Overall, the deuterium excesses (*d*-excess = δD-8δ^{18}O) in precipitation are high (mostly more than 10‰) during the dry and early rainy seasons (November to next April), and low (mostly less than 10‰) during the rainy and early dry seasons (May to October) in the four cave regions, and average *d*-excess values are LFC ≈ QXC < JJC ≈ XNC (Table S1 and Fig. 4). These seasonal variations and regional differences are by and large consistent with those from IAEA stations near these caves (Guilin and Guiyang), indicating that there are obvious differences of moisture sources among the four cave regions. That is, LFC and QXC, which are closer to Guilin, maybe are affected more strongly by moisture source from the East Asian monsoon; however, JJC and XNC, which are located in southwestern Guiyang, maybe are also influenced by moisture sources

Table 4
Average $\delta^{18}O_{SMOW}$ values in drip waters, $\delta^{18}O_{PDB}$ values in their corresponding speleothems, and speleothem $\delta^{18}O_{PDB}$ (‰) calculated using the formula from the literature (O'Neil et al., 1969) under oxygen isotopic equilibrium condition.

Cave (CAT/°C)	Sample	Drip water $\delta^{18}O$ (‰)	Speleothem $\delta^{18}O$ (‰)	Calculated speleothem $\delta^{18}O$ (‰)
LFC (15.2 ± 1.3)	1#	−7.0	−6.7	−6.7
	2#	−7.3	−6.7	−7.0
	3#	−6.9	−6.8	−6.6
	4#	−6.9	−7.0	−6.6
	5#	−6.8	−6.7	−6.5
QXC (13.5 ± 1.7)	1#	−6.6	−4.0	−5.9
	2#[a]	−6.7	−4.9	−6.0
	3#	−6.8	−5.9	−6.1
	4#[a]	−6.9	−5.5	−6.2
	5#	−6.9	−6.1	−6.2
	6#[b]	−6.6	−4.4	−5.9
	7#	−6.9	−4.0	−6.2
	8#[b]	−6.8	−4.9	−6.1
	9#[a]	−6.9	−5.6	−6.2
JJC (14.5 ± 1.1)	1#[a]	−7.8	−7.8	−7.3
	2#[a]	−8.0	−6.9	−7.5
	3#[a]	−8.3	−6.9	−7.8
	4#	−8.6	−9.0	−8.1
XNC (17.0 ± 1.2)	1#	−7.7	−8.1	−7.8
	2#	−7.8	−7.7	−7.9
	3#	−8.2	−8.3	−8.3

CAT expresses the average temperature in the cave (n = 9); the $\delta^{18}O$ value in drip water is arithmetic mean (n = 9).
[a] It is deposit on the top of drip water' corresponding stalagmite.
[b] Speleothem from 2002 to 2003.

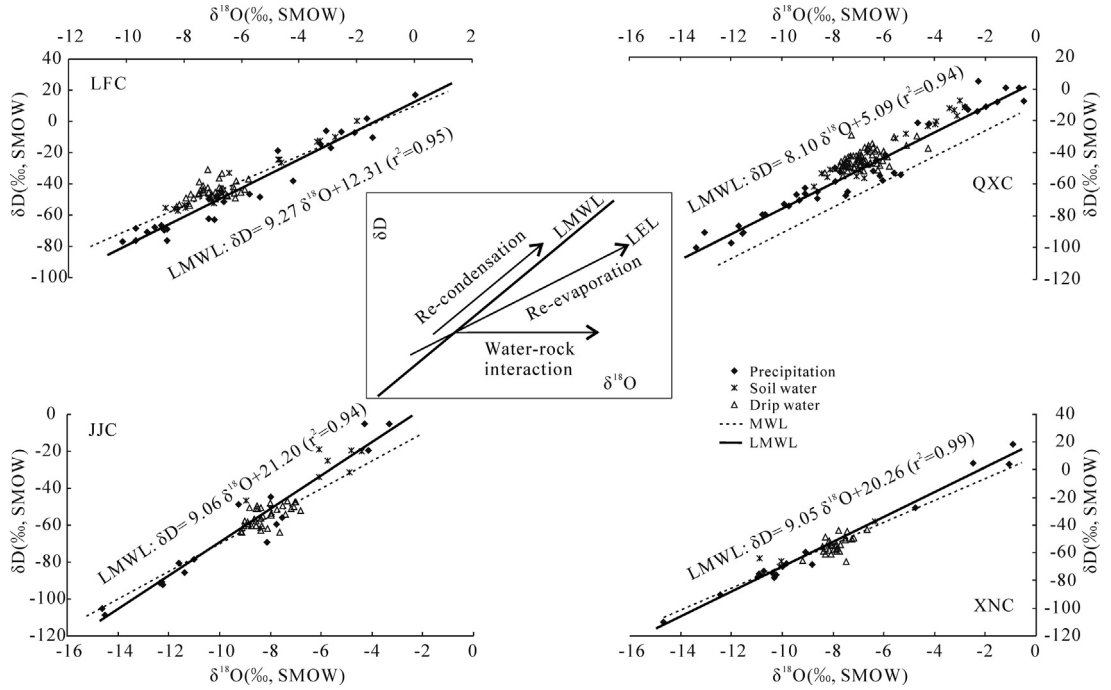

Fig. 3. The relationships between isotopic compositions in various waters and LMWLs derived from our local precipitation isotope data (or WML), respectively. LEL: local evaporation lines.

from the local secondary evaporation and Indian monsoon, besides the East Asian monsoon (Fig. 1) (Johnson and Ingram, 2004).

The average *d*-excess values in soil waters overlying four caves are 11.5 ± 3.9‰ (n = 16), 10.7 ± 4.8‰ (n = 0), 17.1 ± 5.5‰ (n = 3) and 16.8 ± 7.7‰ (n = 8), respectively (Table 3), most of which are higher than those in precipitation in the corresponding regions and have no regular seasonal variations. However, their average *d*-excess values well inherit the differences in precipitation among the four cave regions. These results show that soil water is affected by evaporation near the surface and the *d*-excess signals in precipitation are recorded by soil waters overlying the four caves.

There are some *d*-excess differences (about 5‰) among drip waters from the same cave, and the average *d*-excess values in the four caves are 10.8 ± 5.5‰ (n = 39), 10.3 ± 5.4‰ (n = 70), 10.3 ± 4.8‰ (n = 33) and 8.9 ± 4.9 (n = 27), respectively (Table S2). However, these average *d*-excess values are not the same with those in precipitation and soil waters, which have significant regional characteristics. This indicates that the cave drip water may be controlled

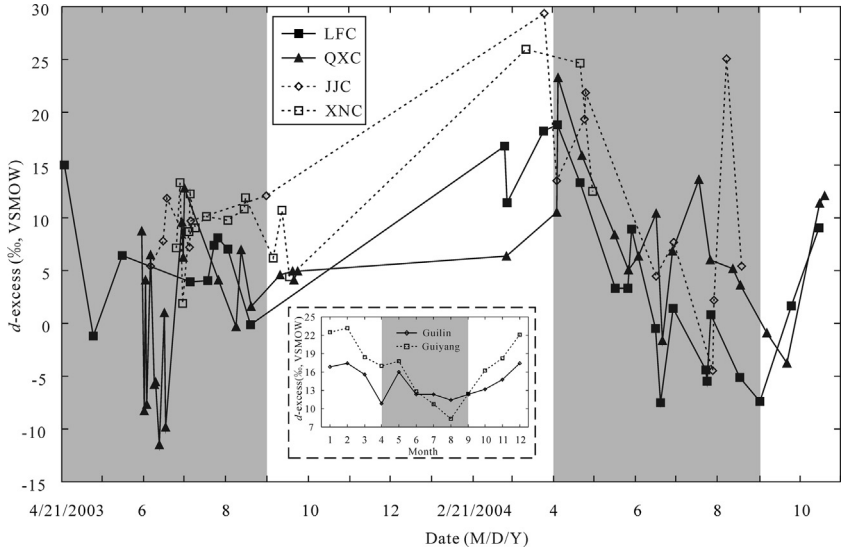

Fig. 4. Seasonal variations of deuterium excess (*d*-excess) in precipitation (shaded areas for the rainy season, April to September).

chiefly by summer precipitation, which has a lower *d*-excess, and that the effect of evaporation is not very significant. These results clearly show that the effects of moisture sources on precipitation and evaporation on soil water are not passed into drip waters in the form of *d*-excess signals, because the regulation and storage capacities of medium reservoirs overlying the caves are very strong.

Thus, there are very obvious *d*-excess differences from various moisture sources in precipitation and soil waters among the four cave regions, and the *d*-excess may be mainly controlled by temperature (Lambert and Aharon, 2010; Luz et al., 2009), which will affect re-condensation and re-evaporation processes. For instance, the *d*-excess values are lower when temperature is higher, and vice verse. However, the significant differences of *d*-excess values and their seasonal variations are not found in these caves. Therefore, unlike in other places (McGarry et al., 2004), the *d*-excess of fluid inclusions in speleothems may not be suitable as a proxy of moisture source and temperature in these regions.

5.3. Local evaporation lines

After comparing the $\delta^{18}O$ values in drip waters with local weighted average values in precipitation, we can find that oxygen isotope compositions of drip waters are heavier than their corresponding weighted average values in precipitation to various degrees (up to 0.3–0.9‰), which may result from local surface evaporation. However, Fig. 3 shows that the evaporation lines (LELs) are very close to the LMWLs in the four caves. That is, there are no obvious LELs, or LELs coincident with LMWL in this study area. In addition, according to the analysis of *d*-excess in Section 4.2, the effect of evaporation on the isotopic compositions of drip water may be weakened by the regulation and storage capacities of medium reservoirs overlying the caves. Thus, evaporation has an influence on drip water, but only to a small extent. This is consistent with the higher air relative humidity in this region (Table 1).

5.4. Seasonal variations

Fig. 2 shows that, in these study areas, there is a significant seasonal variation of the oxygen isotope compositions in precipitation (generally lighter from June to September, and heavier from November to next April, while May and October are interims) and the $\delta^{18}O$ values in Guilin are close to those in Guiyang in dry seasons, but are relatively higher in rainy seasons. This mainly reflects the characteristics of the water vapor source – the light precipitation mainly origins from the water vapor of summer monsoon, but the heavy precipitation origins from the water vapor of local evaporation in this region (Johnson and Ingram, 2004), which is also illustrated by the seasonal changes of *d*-excess in Fig. 4. In addition, Fig. 2 also shows that precipitation is remarkably larger in Guilin than Guiyang at the first half year; it is close each other after July when the East Asian monsoon becomes stable. These suggest that Guilin is affected more frequently by East Asia monsoon (occurs earlier) than Guiyang where is near the effect regions of Indian monsoon (occurs later). Correspondingly, the monthly average temperatures are lower in Guiyang than those of Guilin, both of which show a seasonal variation with high temperature in summer and low temperature in winter.

Moreover, seasonal change characteristics of $\delta^{18}O$ values in precipitation in the four cave areas are also higher in rainy season than those in dry season (Fig. 5). Although the amplitudes of $\delta^{18}O$ values in soil waters are significantly lower than those of precipitation, their seasonal changes are broadly similar to those of precipitation, indicating that soil waters respond rapidly to precipitation, and are mixed by the "old water" (previous water in the media). However, only in LFC and QXC do $\delta^{18}O$ values in drip waters have significant seasonal variations, but not in JJC and XNC, especially XNC with the lowest amplitude (about 1.5‰). Their average $\delta^{18}O$ values in drip waters are close to each other among the different drip sites within each cave. Previous studies show that the $\delta^{13}C$ values in drip waters have no significant seasonal changes in the four caves, except for LFC, and that there are very remarkable differences among the different drip waters in both QXC and JJC, due to the different hydro-geochemical effects (Luo et al., in press, submitted for publication). Therefore, the hydro-geochemical processes cannot completely explain the seasonal variations of oxygen isotope composition in drip waters. In fact, this is also proved by Fig. 3. Consequently, to further explain the seasonal variations, more systematic observations and researches need to be done.

5.5. Transmission of isotopic signals

According to the analyses in Section 4.4 and Fig. 5, we find that the intensities (amplitudes) of isotopic signal gradually decrease from precipitation to soil water, and to drip water, which may result from the homogenization of the media overlying the cave (Cruz et al., 2005).

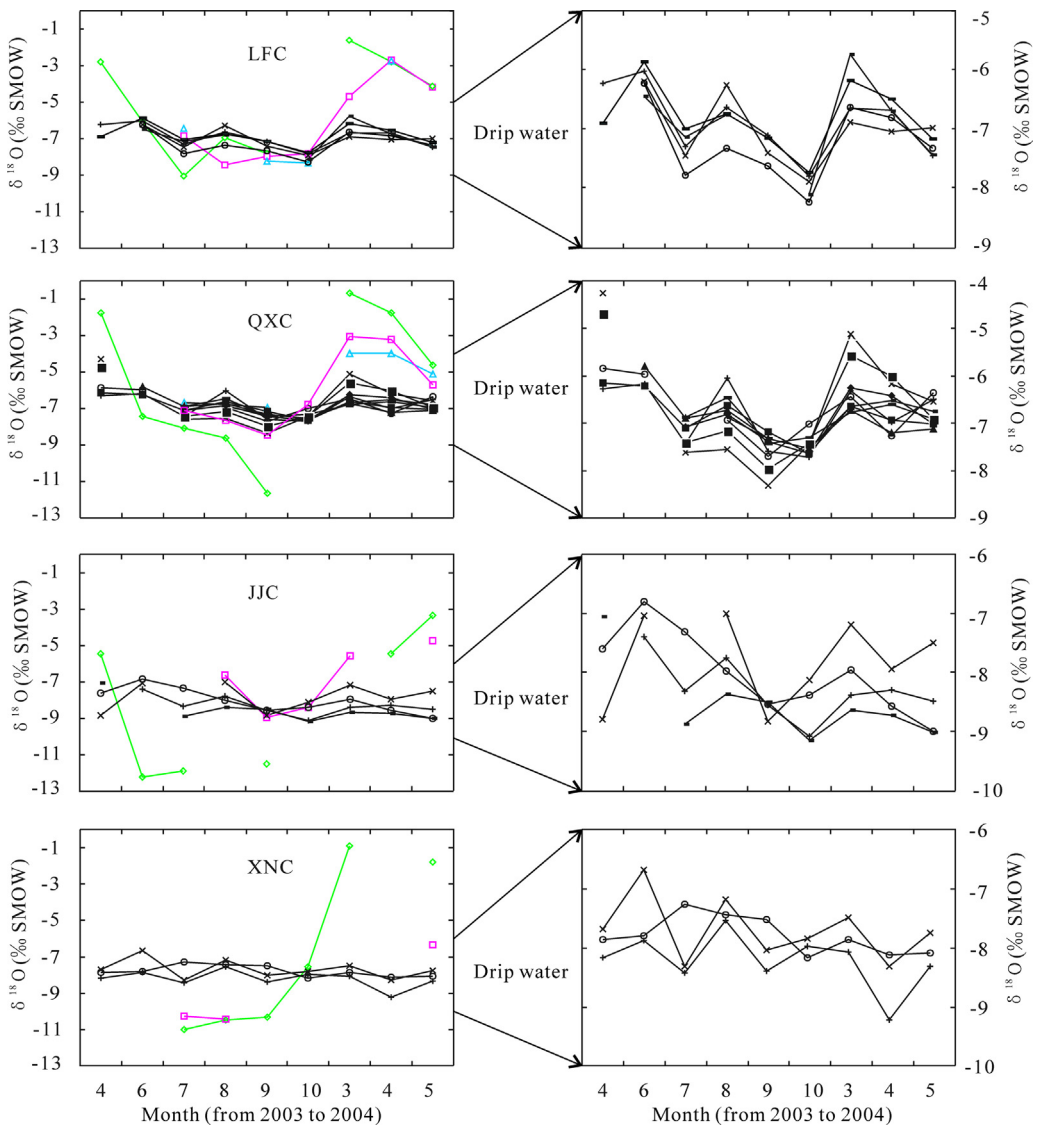

Fig. 5. The temporal changes of oxygen isotope compositions in various types of waters ((◇) precipitation; (□) soil water at 50 cm soil depth; (△) soil water at 100 cm soil depth; (×) 1#; (○) 2#; (+) 3#; (_) 4#; (−) 5#; (■) 6#; (♦) 7#; (▪) 8#; (▲) 9#). The proper dates of *X*-axis can be seen in Table S2.

Fig. 5 shows that there are no significant differences of average $\delta^{18}O$ values among different drip waters from the same cave (Table 4), which is not similar to the literature (Serefiddin et al., 2004). This difference (1‰) can be explained solely by karst hydrology (Baker and Bradley, 2010). There is a certain degree of variation in $\delta^{18}O$ values among coeval drip waters from the same cave (Table 4), which is expressed as follows:

(1) In LFC, only the $\delta^{18}O$ values in 2# drip water from July to September are higher (about 0.5‰) than other drip waters, which just correspond to the facts that the drip rate and its amplitude of variation are lowest, and that the drip water responds slowest to precipitation events in 2# with highest SO_4 concentration (Luo et al., in press). Therefore, the relatively lighter oxygen isotope composition may be related to these hydro-geochemical characteristics, and the threshold precipitation that drip water can respond in 2# may be higher than other drip sites; (2) the amplitudes of $\delta^{18}O$ values are largest in the 1# and 6# from QXC, which correspond to the seasonal variations of drip rate (high in rainy seasons and low in dry seasons); but the lowest amplitudes of $\delta^{18}O$ values correspond to the larger drip rates and their amplitudes in the 4# and 5# in QXC (Luo et al., in press), which is difficult to understand; (3) the non-seasonal amplitude of $\delta^{18}O$ values is largest in the 1# from JJC, which just corresponds to non-seasonal variation of drip rate, various water head and shortest response time to precipitation (Luo et al., in press; Zhou et al., 2005); (4) in XNC, the amplitude of $\delta^{18}O$ values is lowest in 2#, which also corresponds to lowest drip rate and its amplitude, poor connectivity of flow paths and constant water head (Luo et al., in press; Zhou et al., 2005).

These corresponding relations suggest that those oxygen isotopic characteristics may be controlled mainly by precipitation with significant seasonal variation (Figs. 2 and 5), and the $\delta^{18}O$ values in drip waters are affected to various extents by hydrological processes, which may depend on the flow path of the seepage water overlying the caves. These speculating conclusions are still primary, and more work need to be done to draw more convincing conclusions.

The differences of $\delta^{18}O$ values between the ceiling and the floor drip waters are shown in Fig. 6. These differences are almost within measurement precision of ±0.1‰ even during March and April with lower air relative humidity, suggesting that the $\delta^{18}O$ value in drip water is not affected significantly by evaporation in the dripping process. That is to say, the $\delta^{18}O$ value signal basically does not change in the dripping process.

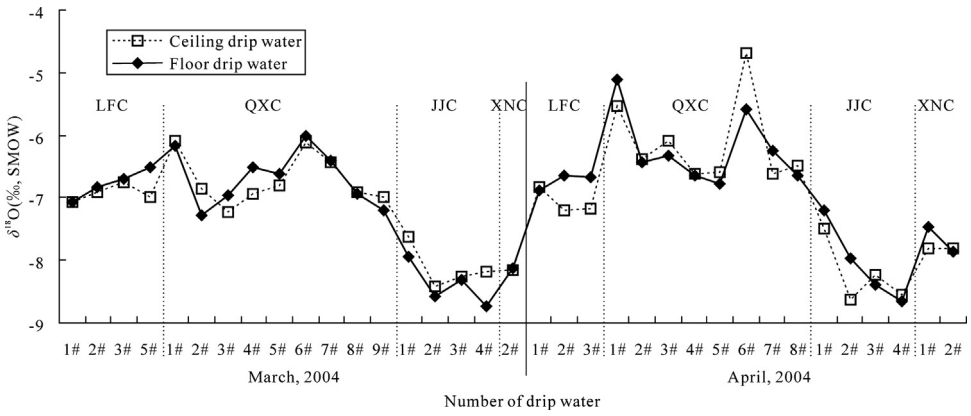

Fig. 6. The comparisons of $\delta^{18}O$ values in the ceiling drip waters and the floor drip waters.

The evolution of oxygen isotope signal is actually a deposition process under the equilibrium or disequilibrium from drip water to speleothem. Table 4 shows that in LFC, the calculated speleothem $\delta^{18}O$ values are very close to measured speleothem $\delta^{18}O$ values, respectively; in QXC, the calculated speleothem $\delta^{18}O$ values are very close among different drip sites each other, but their differences of speleothem $\delta^{18}O$ between the calculated values and their corresponding measured values are significant in Group I (1#, 2#, 6#, 7# and 8#); in JJC, the differences of speleothem $\delta^{18}O$ values are remarkable, with higher calculated speleothem $\delta^{18}O$ value than their corresponding measured values in Group I (2# and 3#) and lower in Group II (1# and 4#); in XNC, the calculated speleothem $\delta^{18}O$ value are also very close to measured speleothem $\delta^{18}O$ values, respectively.

In short, all studied speleothems from LFC and XNC are deposited in equilibrium condition, and those from Group II in QXC basically are also in equilibrium, but other speleothems, including all in JJC and Group I in QXC, are in disequilibrium. The $\delta^{18}O$ values in Group I from QXC and JJC are heavier than the equilibrium $\delta^{18}O$ (calculated speleothem $\delta^{18}O$) values, which are affected significantly by the bedrock dissolution and prior calcite precipitation (PCP) processes, and leading to heavier $\delta^{13}C$ values in drip waters and their corresponding speleothems (Luo et al., in press, submitted for publication), these could attribute to $\delta^{13}C$ and $\delta^{18}O$ are simultaneously influenced by disequilibrium effects (Mühlinghaus et al., 2009; Scholz et al., 2009). Water itself contains O, which leads to the isotopic differences between oxygen and carbon in the formation of speleothem. However, the rapid calcite precipitation and/or rapid CO_2 degassing (Mickler et al., 2004) in the bedrock dissolution and PCP processes all may result in an isotopic disequilibrium in the deposition process of speleothems (heavier $\delta^{18}O$ values). The $\delta^{18}O$ values in speleothems from 1# and 4# (Group I of JJC), are lighter, maybe due to rapid formation of speleothems (Luo et al., in press).

6. Conclusions

The oxygen isotope signals in precipitation have remarkable seasonal changes with lighter oxygen/hydrogen isotopic values in rainy seasons and heavier values in dry seasons, and similar seasonal variations also are showed in soil waters in the four cave regions. However, only in drip waters from LFC and QXC do oxygen/hydrogen isotopes inherit the signals of isotopic seasonal changes from precipitation, while such significant seasonal variations are not shown in drip waters from other two caves (JJC and XNC). Although more studies about the seasonal variations of oxygen isotopes in drip waters still need to be concerned, we can draw that under certain conditions, it is possible to use speleothems to research high resolution (seasonal, even monthly) paleoclimatic changes in LFC and QXC, but only lower resolution (more than year) could be reached in JJC and XNC, particularly in XNC.

In LFC and QXC regions, because of the recharges of "secondary condensation water" (as dew drops), the partial isotope data in drip waters plot on the top left of LMWL. On the contrary, in JJC and XNC, the partial isotope data in drip waters plot on the bottom right of LMWL due to re-evaporation effect. Therefore, these relationships between LMWL and isotopic data (hydrogen and oxygen) of fluid inclusions in speleothems (as stalagmites) from these caves are potential to estimate the local paleoclimate and paleoenvironment.

We found that the effects of moisture sources on precipitation and evaporation on soil water were not passed well into drip waters in the form of *d*-excess signals, that is, the *d*-excess values of drip waters are not coincident with corresponding precipitation and soil waters. Thus, it is debatable whether *d*-excess values of fluid inclusions in speleothems (as stalagmites) from these caves can predict the local paleoclimate and paleoenvironment. In addition, compared with oxygen isotopic compositions in different drip waters within the same cave, the effects of hydrological processes on the oxygen isotopic compositions in drip waters should not be ignored. Comparing oxygen isotope compositions in drip waters with their corresponding speleothems, we found that not all speleothems can accurately record temperature changes even within the same cave. That is, hydrochemistry may result in isotopic disequilibrium in the formation of speleothems.

Consequently, the controls on oxygen isotope are not simpler than those on carbon isotope in speleothem, a result which was not generally believed before. The variations of oxygen isotope may reflect a series of more complex processes in cave drip water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemer.2012.05.002.

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