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ORIGINAL ARTICLE

Influences of air CO_2 on hydrochemistry of drip water and implications for paleoclimate study in a stream-developed cave, SW China

Xiaoxiao Wang[1,2,3] · Yanhong Wu[1] · Licheng Shen[3]

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Abstract Cave air CO_2 is a vital part of the cave environment. Most studies about cave air CO_2 variations are performed in caves with no streams; there are few studies to date regarding the relationship of cave air CO_2 variations and drip water hydrochemistry in underground stream–developed caves. To study the relationship of underground stream, drip water, and cave air CO_2, monthly and daily monitoring of air CO_2 and of underground stream and drip water was performed in Xueyu Cave from 2012 to 2013. The results revealed that there was marked seasonal variation of air CO_2 and stream hydrochemistry in the cave. Daily variations of cave air CO_2, and of stream and drip water hydrochemistry, were notable during continuous monitoring. A dilution effect was observed by analyzing hydrochemical variations in underground stream and drip water after rainfall. High cave air CO_2 along with low pH and low $\delta^{13}C_{DIC}$ in stream and drip water indicated that air CO_2 was one of the dominant factors controlling stream and drip water hydrochemistry on a daily scale. On a seasonal scale, stream flows may promote increased cave air CO_2 in summer; in turn, the higher cave air CO_2 could inhibit degassing of drip water and make calcite $\delta^{13}C$ more negative. Variation of calcite $\delta^{13}C$ (precipitated from drip water) was in reverse of monthly temperature, soil CO_2, and cave air CO_2. Therefore, calcite $\delta^{13}C$ in Xueyu Cave could be used to determine monthly changes outside the cave. However, considering the different precipitation rate of sediment in different seasons, it was difficult to use stalagmites to reconstruct environmental change on a seasonal scale.

Keywords Carbon dioxide · Underground stream · Drip water · Paleoclimate reconstruction · Xueyu Cave

1 Introduction

The relationship between cave environment and the paleoclimate as recorded in speleothems is a major issue in speleology studies (Wei and Liu 2014). Indeed, cave environment is sensitive to changes in the external environment (Oster et al. 2012), and it can also reflect changes of global climate (Zhang et al. 2005). Such signs of climate change can be recorded in speleothems that are widely present in caves (Fairchild et al. 2006; Lambert and Aharon 2011), especially in the caves of the subtropical area in Southwest China, most of which are affected by the Southeast and Southwest Asia Monsoons from the Pacific and Indian Oceans, respectively (Yuan et al. 2004; Li et al. 2011; Zhang et al. 2014). Many factors can influence calcite precipitation processes in caves (Spötl et al. 2005; Sherwin and Baldini 2011) and cave air CO_2 levels. One such factor controls the partial pressures of CO_2 (PCO_2) and calcite saturation (SIc) in waters (Sherwin and Baldini 2011). Therefore, the study of cave CO_2 is an important approach to revealing speleothem growth and variations in paleoclimate proxydata extracted from speleothems.

To date, paleoclimate has mainly been reconstructed in dry caves because fewer parameters are altered compared

✉ Licheng Shen
xqimei@swu.edu.cn

Xiaoxiao Wang
wxx1989@escience.cn

[1] Institute of Mountain Hazards and Environment, Chinese Academy of Sciences, Chengdu 610041, China

[2] University of Chinese Academy of Sciences, Beijing 100049, China

[3] School of Geographical Sciences, Southwest University, Chongqing 400715, China

to caves with underground streams. Therefore, with a goal of understanding the mechanism by which climate change is recorded by $\delta^{13}C$ in speleothems, most studies on cave air CO_2 have been conducted in caves with no underground streams (Li et al. 2011). Nonetheless, many caves have underground streams, which are sensitive to changes in the external environment, especially with regard to rainfall. Previous studies have revealed that the level of karst groundwater rises within several hours after rainfall (Zhang et al. 2005; Liu et al. 2007). Cave air temperature decreases and cave air CO_2 varies sharply after rainfall, and a response in underground stream hydro-geochemistry is also evident (Pu et al. 2014). Troester and White (1984) studied underground stream PCO_2 and cave CO_2 in Tytoona Cave, Pennsylvania, and reported that cave air CO_2 was affected by degassing of an underground steam; CO_2 in the stream water was thought to be carried by infiltration water. Studies have also revealed the influences of CO_2 on carbon isotopic composition of drip water and calcite and on ionic composition of drip water (Hansen et al. 2013). Therefore, air CO_2 in a cave with a flowing underground stream may vary rapidly on a short time scale, and it is important to study variations in air CO_2 and in hydrochemistry of underground stream and drip water in these caves.

Our study was carried out in Xueyu Cave, which is located in Chongqing, SW China. A two-year study on cave air CO_2 and soil CO_2 was performed, and cave air CO_2 and underground stream and drip water hydrochemistry were monitored daily in November 2013 to determine the interaction between cave air CO_2 and underground stream and drip water. Implications for paleoclimatic study were also considered.

2 Study sites

Xueyu Cave (29°47′00″N, 107°47′14″E) is located in the basin of the Long River, a tributary of the Yangtze River, and is 17 km from the downtown of Fengdu County, Chongqing (Fig. 1a). The elevation of the cave entrance is approximately 233 m, and the outlet is approximately 55 m above the water level of the Long River. Xueyu Cave developed in the Fangdoushan anticline of the paralleled ridge-valley area of eastern Sichuan. The lithology is limestone of the Lower Triassic. The attitude of the bedrock layer is 320°∠43°, and the geologic structure line direction is NE. Xueyu Cave follows the strike of the bedrock layer, with a surveyed length of 1640 m; most parts of the cave are narrow, with deep passages (Pu et al. 2014). The cave can be divided into three layers (Pu et al. 2015), the underground stream flows through the middle and bottom layers, with several small waterfalls along the stream (Fig. 1b), and ultimately flows into the Long River. The temperature of the cave is approximately 16–18 °C, and the average temperature is 17.5 °C. Humidity in most parts of the cave is above 90 % year-round. With a subtropical climate, the local annual precipitation is 1072 mm, and the mean temperature is 17.5 °C. Affected by the Southwest and Southeast Asia Monsoons, most rainfall occurs in the rainy months, from April to October. The vegetation over the cave is evergreen broadleaf forest, coniferous forest, and bushwood, and the depth of the soil is approximately 1 m.

3 Field sampling and laboratory methods

On the 15th of every month (some data are absent), the cave air CO_2 concentration was monitored in the cave from January 2012 to November 2013 at sites S1–S4, distributed among the three layers, using a Testo 535 CO_2 detector (Testo Instruments Corp., Germany, 0–10,000 μatm, $\leq\pm3$ %). The measurements were carried out in the morning when there were no tourists in the cave. Hydrochemistry of the underground stream was monitored concurrently.

Soil CO_2 was also assessed in the morning of the 15th of every month using a GT901 infrared air pump CO_2 monitor (0–50,000 μatm, $\leq\pm1$ %. The soil CO_2 was sampled using tubes, and this device can pump out CO_2 when the sampling is performed) at depths of 30, 60, and 90 in Zhengjia and 20, 30, and 60 in Huoshiya (Fig. 1c). The vegetation types are bushwood and evergreen broadleaf forest, and the soil types are brunisolic and yellow soil in Zhengjia and Huoshiya, respectively. Calcite samples at the drip water site, S_{dw}, were collected on the 16th of every month using glass dishes (the dishes were placed just below the drip site for a month) for $\delta^{13}C$ testing (some data are absent, i.e., when there was no drip water).

Daily monitoring of cave CO_2 (S1–S4) and of underground stream water (S1, S3) and drip water (S_{dw}) was performed in November 2013. Water samples for cation analysis were collected using polyethylene bottles (50 ml) and then acidified with 1:1 nitric acid; anion analysis samples were collected with 500-ml high-density polyethylene bottles. Water samples for $\delta^{13}C_{DIC}$ measurement were collected in clean 10-ml high-density polyethylene bottles using 0.45 μm cellulose acetate membrane filters; the samples were spiked with 0.1 ml saturated $HgCl_2$ to prevent microbial activity (Taipale and Sonninen 2009). All water samples were stored refrigerated at 4 °C prior to analysis. The specific conductivity, pH, and water temperature were measured using a hand-held water quality meter measurement (Merck Corp., Germany; accuracy was 1 μS/cm, 0.01 pH, 0.1 °C). The HCO_3^- and Ca^{2+} concentrations of the water were measured in the field by titration with a Merck alkalinity and

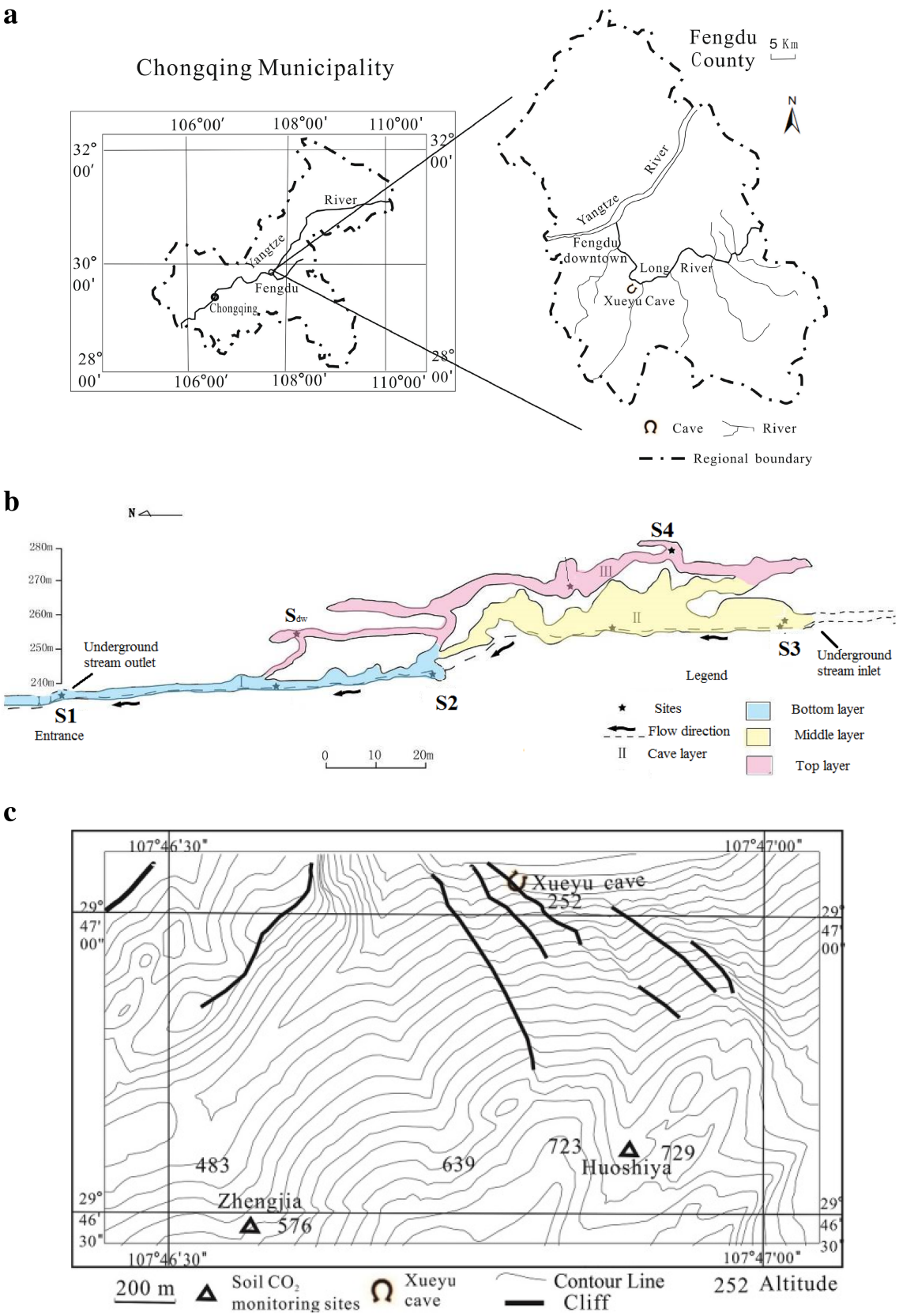

Fig. 1 **a** Location ofXueyu Cave, Fengdu County, Chongqing Municipality. **b** Section map ofXueyu Cave and monitoring sites in different layers (Wang 2010). **c** Location of soil CO_2 sampling sites

hardness portable testing kit (Merck Corp. Germany; accuracy was 0.1 mmol/l and 2 mg/l, respectively). A BS28-VP2 mini weather station (DavisCorp., USA) was placed approximately 500 m away from the entrance of Xueyu Cave to obtain rainfall and atmospheric temperature data (the accuracy was 0.01 mm and 0.1 °C, respectively). The discharge of the underground stream was monitored at 15-min intervals using a CTDP 300 (Greenspan Corp., Australia) multi-channel data logger during the daily monitoring in November 2013. At the same time, soil CO_2 was continuously monitored every 15 min in Zhengjia at a depth of 30 cm using a GT901 infrared air pump CO_2 monitor (the parameters of the monitor are presented above).

Cations in the water samples were assessed at the Geochemistry and Isotopic Laboratory of Southwest University using an Optima 2100DV ICP-OES (Perkin-ElmerCorp. USA), with an accuracy of 0.001 mg/l; analytical errors were within ±5 % compared with the standard error. Anions were analyzed using ion chromatography within 1 % error (compared with standard error) at the Water Environmental Laboratory of the School of Geographical Sciences, Southwest University. $\delta^{13}C$ of the sediments was measured using a Delta VPlus gas isotope mass spectrometer combined with a KielIV automated carbonate device at the Geochemistry and Isotope Laboratory of the School of Geographical Sciences, Southwest University. The international standard NBS19 and laboratory standards NCKU1 and SWU1 were measured after every five and seven samples, with a long-term 1r precision of 0.06 ‰. Water $\delta^{13}C_{DIC}$ was analyzed on a Delta plus XL with a 1r external precision of 0.15 ‰ at the Testing and Analysis Center, Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Science. Water temperature, pH, Ca^{2+}, Mg^{2+}, HCO_3^-, K^+, Na^+, Cl^-, and SO_4^{2-} were used to calculate PCO_2 and SIc with the program WATSPEC (Wigley 1977). IBM SPSS Statistics 22 and OriginPro 2015 were used for the statistical analysis.

4 Results

4.1 Atmospheric temperature and rainfall in the area of Xueyu Cave

Cave air temperature in closed caves is always the same as the local annual mean temperature (Sebela and Turk 2011; Casteel and Banner 2015; Lobo et al. 2015). According to our study in Xueyu Cave, cave air temperature was stable, ranging from 16.0 to 18.0 °C, with an average temperature of 17.5 °C. Consistent with the subtropical monsoon climate in the area, the lowest atmospheric temperature during our study period was in January (1.1 °C) and the highest in August (39.9 °C). In 2012, the average temperature outside the cave rose higher than the average temperature inside the cave in April and sank lower in November (Fig. 2). In 2013, the external temperature became higher than the inner cave mean temperature at an earlier date. Rainfall showed two peaks in 2012, appearing in May and September, but there was only one rainfall peak in 2013 (Fig. 2). More precipitation occurred in late spring and early summer, with less rainfall in July and August due to the subtropical anticyclone.

4.2 Seasonal variations of soil CO_2, cave air CO_2, and underground stream hydrochemistry

Soil CO_2 varied seasonally in our study (Fig. 3), it was high in summer and low in winter. The highest concentration was approximately 40,000 μatm, and the lowest was approximately the same as the atmospheric CO_2 concentration. The variations in soil CO_2 paralleled those in atmospheric temperature. Differences in soil CO_2 concentration between the two sites were observed, with the concentration much higher (1000 μatm) at Huoshiya than at Zhengjia.

Corresponding to seasonal fluctuations of atmospheric temperature and soil CO_2, cave air CO_2 varied seasonally (Fig. 4a). Cave air CO_2 was high in summer and low in winter. The highest CO_2 concentration in the cave was more than 10,000 μatm, and the lowest was approximately 400 μatm. The air CO_2 increased in April and decreased in November, with a trend similar to that of atmospheric temperature. The CO_2 concentration was lowest at the downstream site (S1), which might be due to ventilation near the cave entrance (Linan et al. 2008; Sanchez-Canete et al. 2013).

Consistent with the variations of soil CO_2 and cave air CO_2, hydrochemistry of the underground stream in Xueyu Cave showed seasonal variations (Fig. 4b–h). Values of pH were low in summer and high in winter, with a range of 6.73–8.60. Spc, Ca^{2+}, and HCO_3^- showed almost an inverse trend (high in summer and low in winter) compared with the variation of pH. Influenced by high temperature and less rainfall in August 2012, concentrations of Ca^{2+} and HCO_3^- and Spc dropped noticeably. Contrary to the variations in 2012, Spc, Ca^{2+}, and HCO_3^- increased consistently through 2013. Water temperature (Tw) was stable during our two-year study; the average water temperature of the stream was 16.4 °C. Partial pressure of CO_2 (PCO_2) in the stream was consistent with the variations of Spc, Ca^{2+}, and HCO_3^- in 2012, whereas PCO_2

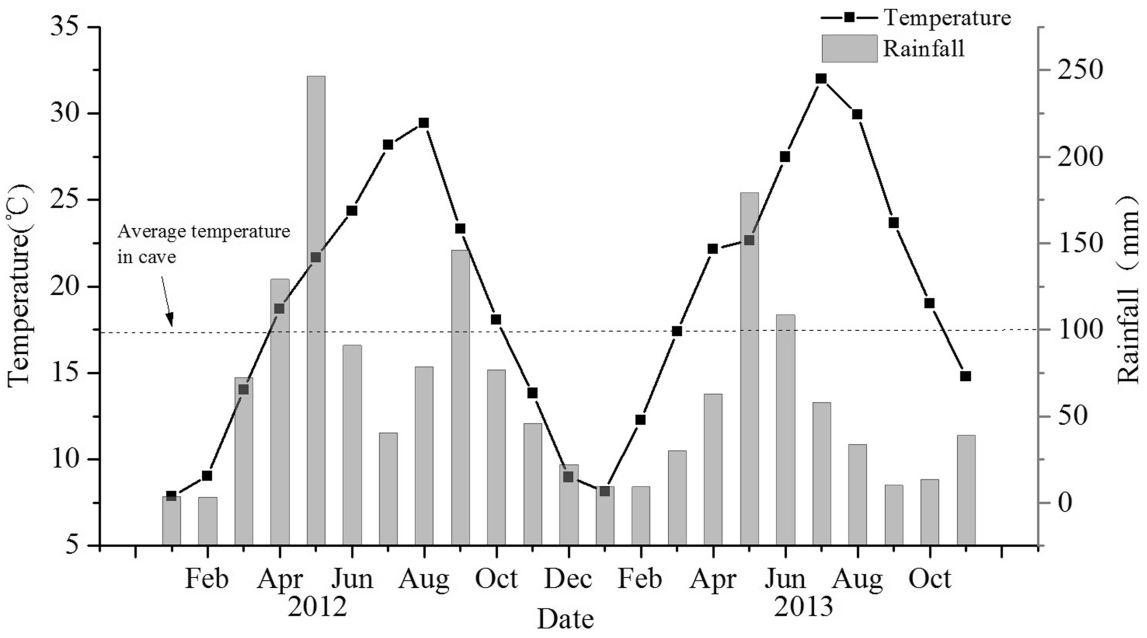

Fig. 2 Atmosphere temperature and rainfall in the area of Xueyu Cave

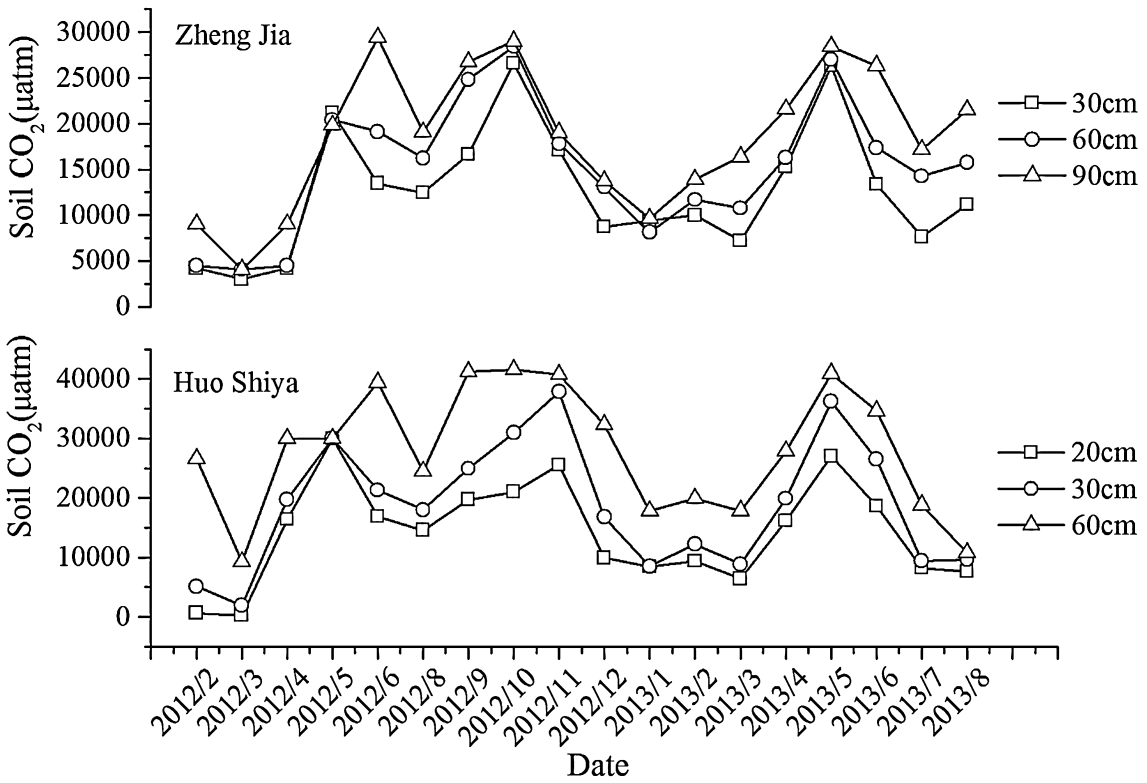

Fig. 3 Seasonal variations of soil CO_2 in Zhengjia and HuoShiya

showed an inverse trend in 2013. Saturation index of calcite (SIc) varied differently compared with the variation of PCO_2—it was low in summer and high in winter. Overall, seasonal variations of stream hydrochemistry, soil CO_2, and cave air CO_2 were notable during our study period.

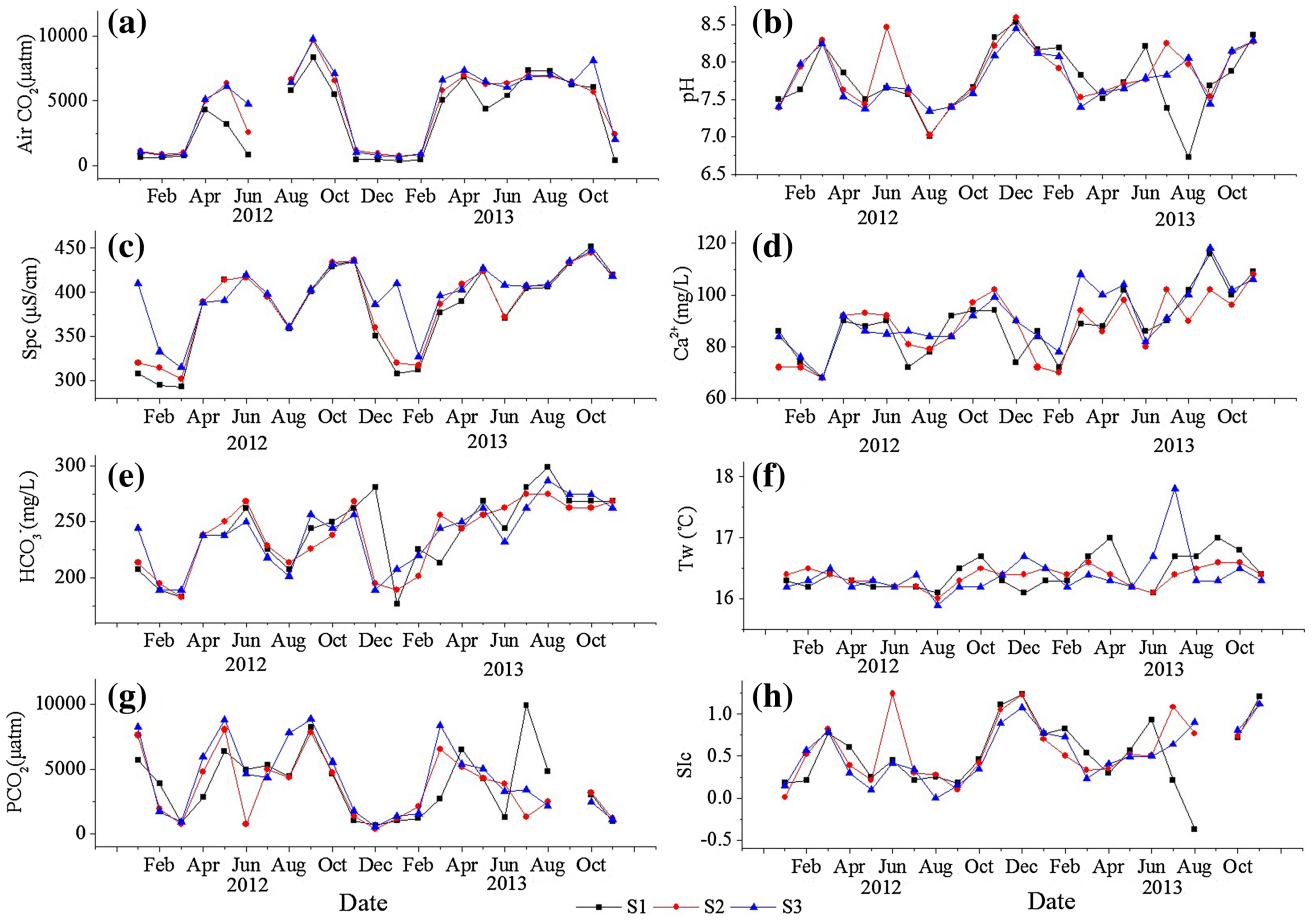

Fig. 4 Seasonal variations of air CO_2 and underground stream hydrochemistry in Xueyu Cave

4.3 Daily variations of cave air CO_2 and of underground stream and drip water hydrochemistry

Existing in a relatively closed space, cave air CO_2 can be temporarily stored within the cave, and thus affect carbon exchange at the water–air interface. In our study, cave air CO_2 rose to more than 10,000 μatm from 30th October to 9th November 2013, with a slight decrease on 6th November (Fig. 5a). The value then fell quickly and air CO_2 became lower than the original CO_2 concentration (4740 μatm on average) on November 17th. We found air CO_2 concentrations downstream (S1) were affected by gas exchange between the interior and exterior, as this site was close to the cave entrance. Thus, it was reasonable that CO_2 variations between S1 and the other sites were larger during the decreasing period (Fig. 5a). Midstream site S2 was located near a waterfall, with water flowing from the middle layer to the bottom layer of the cave. The air CO_2 concentration was higher at S2 than at the other three sites on November 17th, a time when the air CO_2 declined at all the monitoring sites in the cave. Not far from upstream site S3 was the inlet of the underground stream, and the cave air CO_2 at S3 was almost the same as that of S2 during our continuous study. However, the air CO_2 concentration at the midstream site (S2) was lower than at the upstream site (S3) on November 17th, which might be due to the dynamic degassing of stream water at S2, whereas the stream water flowed calmly at S3. S4 was located at the top layer, the variation of air CO_2 was slow and gradual. The air CO_2 at S4 reached a peak 1 day later in comparison with the other three monitoring sites; air CO_2 at S4 declined simultaneously with S2 and S3 after peaking.

The hydrochemistry of the underground stream was monitored simultaneously with air monitoring. Synchronization of HCO_3^-, Spc, and Ca^{2+} of the groundwater stream increased from Nov 3rd to Nov 10th and then decreased (Fig. 5). The low pH, low SIc, low $\delta^{13}C_{DIC}$, and high PCO_2 of stream water occurred at almost the same time on Nov 9th. When water flowed into the cave, spatial variations of water temperature were found: it was higher at S1 (downstream site) and lower at S3 (upstream site). The pH decreased from 8.20 to 7.30 before Nov 9th, with little fluctuation, and

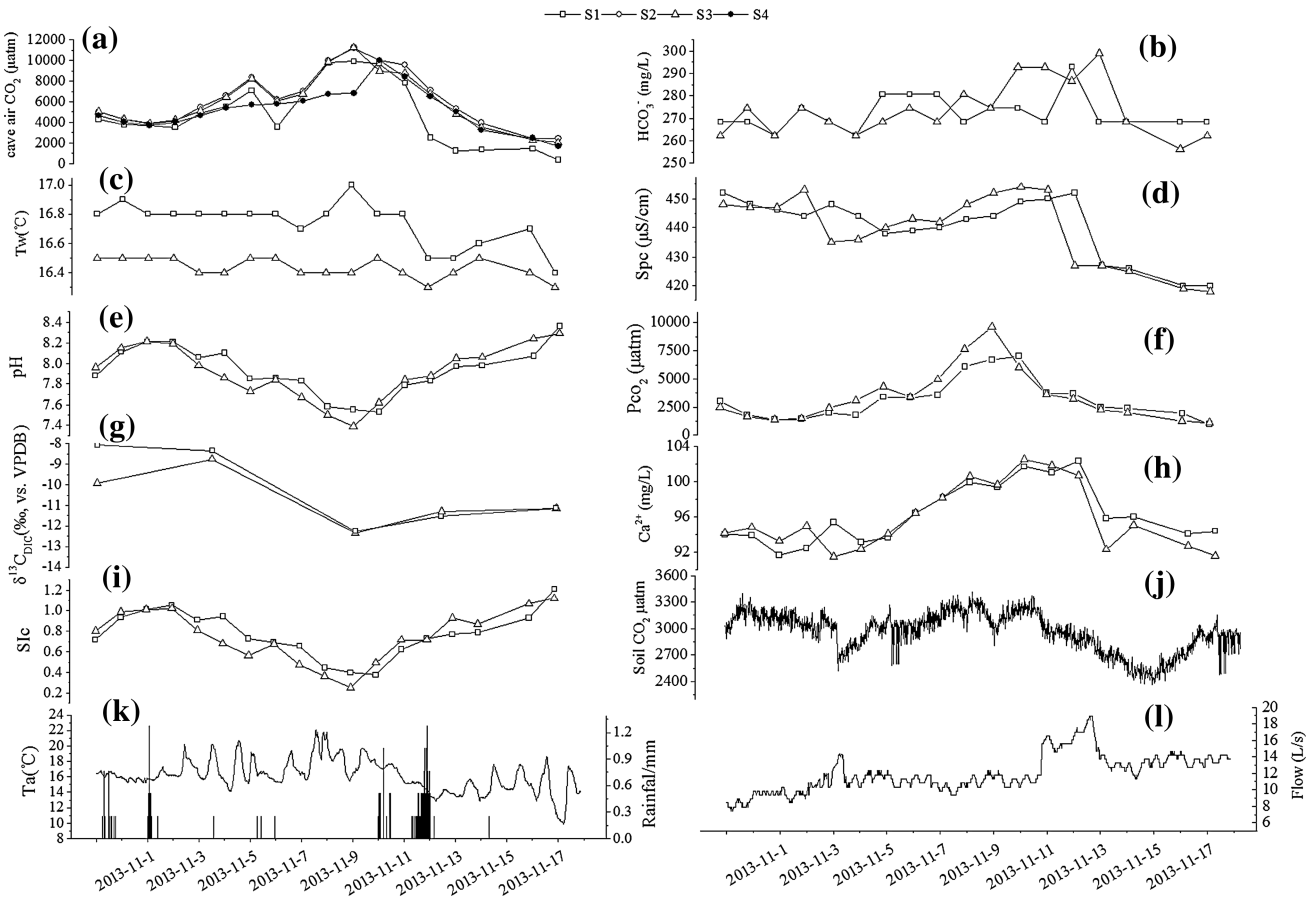

Fig. 5 Daily variations of air CO_2 (**a**), underground stream hydrochemistry (**b**, **c**, **d**, **e**, **f**, **g**, **h**, **i**) in Xueyu Cave, soil CO_2 at 30 cm depth at Zhengjia (**j**), atmosphere temperature and rainfall (**k**), and stream flow (**l**)

increased again to 8.30. Rain water pH during the study was 7.96 and it was lower than pH of the stream water. The curve of PCO_2 showed a same shape as that for air CO_2, reaching a peak value when the cave air CO_2 was highest on Nov 9th.

Drip water hydrochemistry was stable before the second rainfall on Nov 12th. After Nov 12th, Tw, pH, Ca^{2+}, and HCO_3^- increased and Spc and $\delta^{13}C_{DIC}$ decreased (Fig. 6). The average Tw, pH, Spc, Ca^{2+}, and HCO_3^- of drip water were 17.4 °C, 7.98, 733.81 μS/cm, 185.56 mg/l, and 449.87 mg/l, respectively, during our study.

5 Discussion

5.1 Rainfall and hydrochemistry of underground stream and drip water

In previous works, underground stream and drip water were found to be sensitive to rainfall events; hydrochemistry variations on yearly, seasonal, and daily scales have been reported, especially variations in underground stream and drip water hydrochemistry during a storm event (Zhang et al. 2005; Liu et al. 2007). Considering the dualistic structure of karst systems, underground stream and drip water hydrochemistry responds quickly to rainfall events: a massive influx of rainwater into the epikarst zone after soil infiltration flushes out "old water" in cracks, a process known as "piston flow" (Pu et al. 2014). The "fresh water" will then flow into the stream, affecting hydrochemistry of underground stream and drip water. Subsequent rainfall will then cause a dilution effect with respect to hydrochemistry.

Seasonal hydrochemistry variation of the underground stream was mainly controlled by atmospheric temperature and rainfall, with pH and SIc low in summer and high in winter. In contrast, Spc, HCO_3^-, and PCO_2 were high in summer and low in winter. Rainfall might have been a major factor influencing the variation of stream hydrochemistry when considering monthly variation of stream hydrochemistry in 2012, which varied in coordination with rainfall. However, variation of rainfall could not explain the variation of stream hydrochemistry in 2013. Due to the rapid changing of stream hydrochemistry, daily monitoring

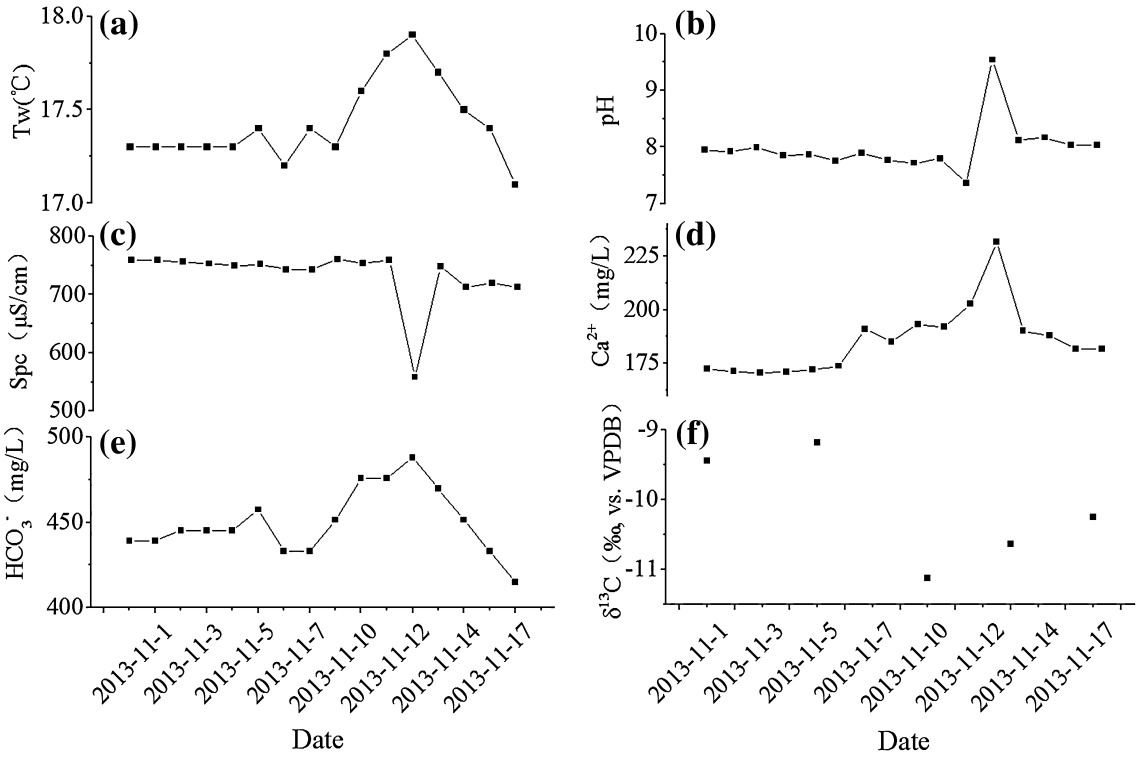

Fig. 6 Daily variations of drip water hydrochemistry

was need to study rainfall's effects on hydrochemical variations.

During our daily study from Oct 30th to Nov 17th (Fig. 5), two rainfall events occurred, with precipitation of 4 and 22 mm. The discharge of underground streams showed an obvious response to rainfall (Fig. 5l), and response time was approximately 4 h, as we previously reported (Wang et al. 2013). Piston flow and dilution effect were observed after the two rainfall events. The higher pH, SIc, and Spc, and lower PCO_2 values before Nov 3rd reflect the "old water," which was pushed out by the first rainfall. There was sufficient retention time in the epikarst zone for "old water" to react with bedrock, and the dissolved CO_2 in water was consumed, resulting in an increase in pH and SIc, and a reduction in PCO_2. With decreased erosive ability, the stream hydrochemistry varied indistinctively between upstream and downstream sites under the influence of "old water."The discharge of the underground stream reached its first peak on Nov 3rd, with lower Spc, Ca^{2+}, and HCO_3^- values, showing a response time for stream discharge after a small rainfall event of approximately 2 days. The rain water had enough time to dissolve CO_2 when it infiltrated through the soil, and the solution of soil CO_2 in rain water could be observed by the reduction in overlaid soil PCO_2 (Fig. 5j). The second rainfall during our study was on Nov 10th and 11th, and dilution effect of the rainfall was evident with decreases in HCO_3^-, Ca^{2+}, and Spc on Nov 13th. The response time of stream discharge was less than one day, revealing that the response time was related to the amount of rainfall. Though soil CO_2 dropped after the second rainfall, which might mean soil CO_2 had dissolved in rainwater, PCO_2 decreased for the remainder of the time series after Nov 9th. pH, SIc, and $\delta^{13}C_{DIC}$ showed no decreasing trend. The peaks of pH, PCO_2, and air CO_2 occurred concurrently, but at a time that was not consistent with a rainfall event, indicating hydrochemistry of the stream was not influenced only by rainfall, but also by cave air CO_2.

Hydrochemistry of drip water was almost unaffected by the first rainfall, showing no evident variation after Nov 3rd (Fig. 6). This might be due to less rain water infiltrating through the bedrock. Dilution effect of the second rainfall is shown in Fig. 6: water temperature, pH, Ca^{2+}, and HCO_3^- concentrations increased, and Spc decreased after the second rainfall.

5.2 Carbon exchange at water–air interface on daily and seasonal scales

The exchange of carbon between an underground stream and cave air can be reflected in hydrochemistry variations (Troester and White 1984). The high cave air CO_2 with low pH, low SIc, low $\delta^{13}C_{DIC}$, high Ca^{2+}, and high PCO_2 of stream water occurred at almost the same time on Nov 9th with no preceding rainfall event (Fig. 5), indicating the variations of stream hydrochemistry were affected by cave

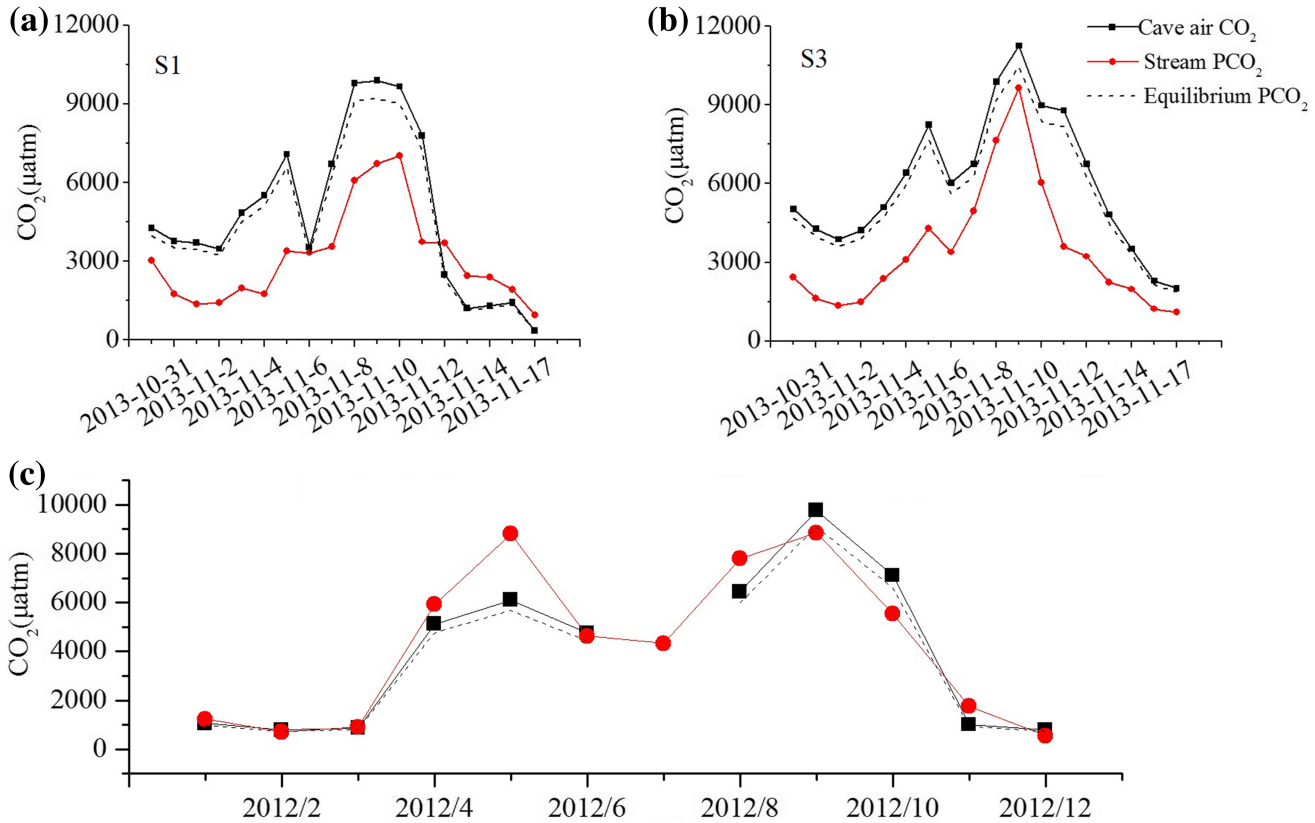

Fig. 7 Daily (**a**, **b**) and monthly (**c**) cave air CO_2, stream PCO_2, and calculated equilibrium PCO_2 in stream water

air CO_2, especially carbon exchange at the water–air interface. Equilibrium PCO_2 in stream water was calculated to determine carbon exchange at the water–air interface (Fig. 7a, b). Outgassing of stream water would be expected if PCO_2 were higher than equilibrium PCO_2 and air CO_2 should dissolve into water when equilibrium CO_2 is higher than stream PCO_2. Cave air CO_2 and equilibrium CO_2 were always higher than stream PCO_2 at the upstream site (S3), suggesting more cave air CO_2 was dissolved in stream water and cave air CO_2 controlled pH, SIc, PCO_2, and $\delta^{13}C_{DIC}$ variations. The relationship between stream PCO_2 and equilibrium CO_2 at the downstream site (S1) was almost the same as the upstream site (S3) before Nov 12th, but Stream PCO_2 was higher than equilibrium CO_2 at the downstream site(S1)after Nov 12th, indicating that outgassing of the stream might have occurred, with the downstream site being affected by ventilation near the cave entrance.

Stream PCO_2 was mainly affected by cave air CO_2 during our daily study, but the situation was different on a seasonal scale. Monthly stream PCO_2, cave air CO_2 and calculated equilibrium PCO_2 are shown in Fig. 7c. Stream PCO_2 was higher than cave air CO_2 during the period of cave air CO_2 increasing and lower than cave air CO_2 during the declining period. The increase in cave air CO_2 in Xueyu Cave might have been promoted by degassing of stream water during summer, when more soil CO_2 would be carried into the cave by more rain water. A higher concentration of CO_2 promoted by the underground stream could inhibit degassing of drip water and make drip water $\delta^{13}C_{DIC}$ more negative in summer compared with that in caves with no stream.

Carbon exchange between cave air and drip water was inferred by the variation of drip water $\delta^{13}C_{DIC}$ during our daily study (Fig. 6). Drip water $\delta^{13}C_{DIC}$ became more negative when cave air CO_2 concentration was high, showing the same variation as stream water $\delta^{13}C_{DIC}$, indicating drip water $\delta^{13}C_{DIC}$ was affected by cave air CO_2 variations. We could suppose that the rising cave air CO_2 promoted by the underground stream in summer could make drip water $\delta^{13}C_{DIC}$ more negative and inhibit degassing of drip water, in turn influencing calcite precipitation and leaving calcite $\delta^{13}C$ more negative.

5.3 Implications for speleothem paleoclimate studies

Speleothem $\delta^{13}C$ has been used to reconstruct paleoclimate (Li et al. 2011; Finne et al. 2014), and variations in $\delta^{13}C$ in stalagmites have been used to reflect changes in local vegetation (Meyer et al. 2014). Monitoring $\delta^{13}C$ of drip water and calcite on artificial substrates underneath drip sites is becoming more important when studying the

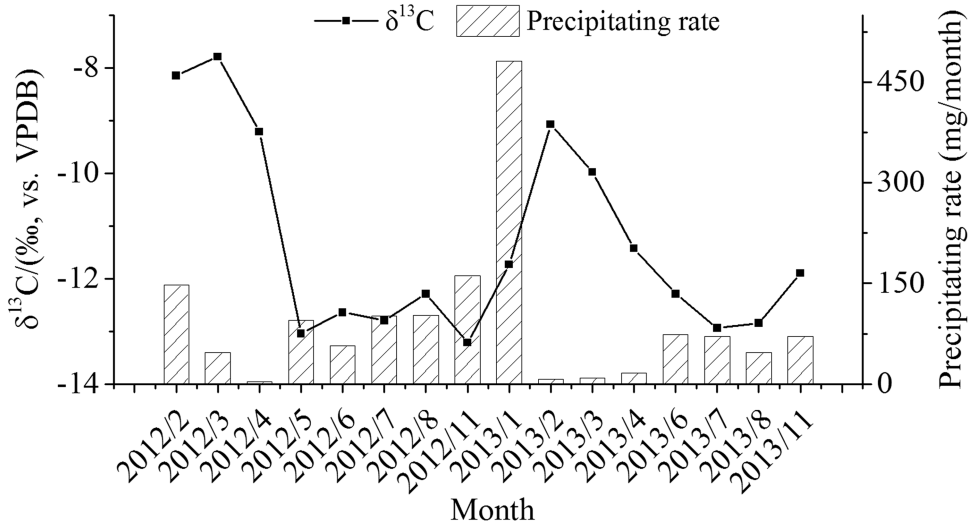

Fig. 8 Monthly sediment precipitating rate and calcite $\delta^{13}C$ under dripping site Sdw (some data absent)

recording mechanism of calcite $\delta^{13}C$ (Luo et al. 2014; Prasanna et al. 2014). Previous studies have shown that $\delta^{13}C_{DIC}$ of drip water is affected by many factors, such as isotopic composition of soil CO_2, bedrock weathering, and in-cave processes (Oster et al. 2012; Meyer et al. 2014). Isotope fractionation occurs during limestone dissolution, calcite deposition, and CO_2 exchange between drip water and cave atmosphere (Spötl et al. 2005; Dreybrodt and Scholz 2011; Lambert and Aharon 2011). Isotope equilibrium fractionation, which is temperature-dependent, between drip water and calcite is approximately 1 ± 0.2 ‰ (Mook et al. 1974; Romanek et al. 1992), but the kinetic fractionation associated with CO_2 degassing when drip water drops from the cave ceiling could cause deviations in calcite carbon isotope composition (Meyer et al. 2014).

Variation of $\delta^{13}C_{DIC}$ in drip water could be reflected by calcite $\delta^{13}C$, as discussed in previous studies (Dreybrodt and Scholz 2011). However, the variation of drip water $\delta^{13}C_{DIC}$ might be faster than calcite precipitating rate; daily changes in drip water $\delta^{13}C_{DIC}$ might not be reflected in calcite $\delta^{13}C$. Therefore, it remains unclear whether daily variations of cave air CO_2 could be recorded in calcite, as daily precipitation of calcite during our continuous monitoring was not observed.

Monthly $\delta^{13}C$ data of sediment during our study are presented in Fig. 8. $\delta^{13}C$ showed seasonal fluctuations in sediment: high in winter and low in summer. Variations of $\delta^{13}C$ in sediment were opposite to variations of monthly temperature, soil CO_2, and cave air CO_2. High cave air CO_2 concentrations in summer can inhibit degassing of drip water, with light carbon (^{12}C) being incorporated into calcite and making calcite $\delta^{13}C$ more negative (Dreybrodt and Scholz 2011). When cave air CO_2 concentration decreased in winter, degassing of drip water was rapid and calcite $\delta^{13}C$ became more positive. Similar to the seasonal variation in degassing of drip water, sediment precipitation was rapid in winter and slow in summer. The highest rate of precipitation of sediment appeared in January 2013 in our study (Fig. 8). The precipitation rate was not only controlled by cave air CO_2 but also by rainfall. In summer, more rainfall and higher soil CO_2 can result in higher concentrations of Ca^{2+} in drip water (Pu et al. 2015), but high air CO_2 concentrations in the cave inhibited $CaCO_3$ deposition. Low cave air CO_2 concentration favored $CaCO_3$ deposition in winter (Spötlet al. Spötl et al. 2005), but less Ca^{2+} was carried by reduced drip water (even no drip water in winter months during our study). Accordingly, the precipitation rate in January 2013 might be due to more drip water with a higher Ca^{2+} concentration when cave air CO_2 was low, but the situation was different in different years due to the variations of rainfall and cave air CO_2. Affected by different monthly precipitation rates, stalagmites under the drip water might consist primarily of sediment precipitated in months when the precipitation rate was high.

In summary, monthly sediment $\delta^{13}C$ in Xueyu Cave (Fig. 8) reflected seasonal variation of soil CO_2 and cave air CO_2. Variation of calcite $\delta^{13}C$ in our study was consistent with previous studies (Meyer et al. 2014), indicating calcite $\delta^{13}C$ in Xueyu Cave could be used to reflect environmental change outside the cave. However, considering different precipitation rates of sediment from drip water in different seasons, it was difficult to use stalagmites to reconstruct past seasonal changes.

6 Conclusion

Seasonal variations of air CO_2 in Xueyu Cave were notable: cave air CO_2 increased in April and decreased in November. Cave air CO_2 variation was consistent with

variations of atmosphere temperature and soil CO_2. Affected by outside temperature and rainfall, hydrochemistry of the underground stream showed seasonal variation. Daily variations of cave air CO_2, stream and drip water hydrochemistry were also notable in Nov 2013. The high cave air CO_2 with low pH, low SIc, low $\delta^{13}C_{DIC}$, high Ca^{2+}, and high PCO_2 of stream water occurring at almost the same time on Nov 9th revealed that air CO_2 was a dominant controlling factor on a daily scale of the stream hydrochemistry when there was no rainfall. On a seasonal scale, CO_2 carried by the underground stream in summer might accelerate the increase in air CO_2 in Xueyu Cave; higher CO_2 concentration inhibited outgassing of drip water and made calcite $\delta^{13}C$ more negative. Seasonal variation of $\delta^{13}C$ in sediment was inconsistent with atmosphere temperature, soil CO_2, and cave air CO_2, indicating calcite $\delta^{13}C$ in Xueyu Cave could reflect seasonal changes of the external environment. Considering the different precipitation rate of sediment across seasons, it was difficult to use stalagmites to reconstruct past environment change on seasonal scale.

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