

Zaihua Liu
Hongchun Li
Chengfeng You
Naijung Wan
Hailong Sun

Thickness and stable isotopic characteristics of modern seasonal climate-controlled sub-annual travertine laminas in a travertine-depositing stream at Baishuitai, SW China: implications for paleoclimate reconstruction

Received: 14 March 2006
Accepted: 3 May 2006
Published online: 14 June 2006
© Springer-Verlag 2006

Z. Liu (✉)
School of Resources and Environmental
Sciences, Southwest University,
Chongqing 400715, China
E-mail: zliu@karst.edu.cn
Tel.: +86-773-5837340
Fax: +86-773-5837845

Z. Liu
The State Key Laboratory of
Environmental Geochemistry,
Institute of Geochemistry,
Chinese Academy of Science,
Guiyang 55002, China

H. Li
Department of Earth Sciences,
University of Southern California,
Los Angeles, CA 90089, USA

C. You · N. Wan
National Cheng Kung University,
Tainan 701, Taiwan, China

H. Sun
Karst Dynamics Laboratory, MLR,
Institute of Karst Geology, CAGS,
Guilin 541004, China

Abstract A continuous high-resolution (monthly) record of stable isotopes ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) in a well-laminated freshwater travertine deposited at Baishuitai, SW China from May 1998 to November 2001 was presented. The travertine exhibits clear annual bands with coupled brown/white color laminations. Throughout field investigation, it was found that the thin (1.5–2.2 mm), brown porous lamina was formed in the monsoonal rainy season from April to September, whereas the thick (5–8 mm), dense white lamina was formed in the dry season from October to March. The comparisons of lamina thickness and stable isotope signals in the travertine with the meteorological records allow us to constrain the relevant geochemical processes in the travertine formation under different climate conditions and to relate climate variables to their physicochemical proxies in the travertine record. Sympathetic variations in lamina thickness, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ along the sampled profile reflect changes in

hydrogeochemistry, showing that thin lamina and low $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values occur in warm and rainy seasons. The decreased amount of calcite precipitation and low $\delta^{13}\text{C}$ values during the warm and rainy seasons is caused by dilution of overland flow after rainfall. The low $\delta^{18}\text{O}$ values are believed to be related to the rainfall amount effect in subtropical monsoonal regions. This process is thought to be markedly subdued whenever the amount of rainfall is lower than a given threshold. Accordingly, distinct minima in lamina thickness, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are interpreted to reflect events with above-average rainfall, possibly heavy floods, and vice versa. This study demonstrates the potential of freshwater travertine to provide valuable information on seasonal or even monthly rainfall variations.

Keywords Travertine · Lamina thickness · Stable carbon and oxygen isotopes · Dilution · Rainfall amount effect · China

Introduction

Paleoclimate research has made appreciable progress in elucidating the response of important climate phenomena, such as the intertropical monsoons and the El Niño–Southern Oscillation, to internal (i.e., interaction among the atmosphere, oceans, land surface and ice

sheets) and external forcing (i.e., orbitally driven changes in solar radiation). To further improve the understanding of the complex dynamics of these climate processes, it is necessary to quantify how long-term fluctuations affect their high-frequency variability. Coral records in particular have proven to be capable of addressing this question (Charles et al. 1997;

Tudhope et al. 2001). To complement data retrieved from these marine archives, high-resolution terrestrial records are needed. Furthermore, quantitative or semiquantitative seasonal paleoclimate information for continental interiors is essential to verify climate model predictions (Montoya et al. 1998).

Among the various terrestrial records, speleothems have been of particular interest in studies of Quaternary climate change in recent years (Dorale et al. 1998; McDermott et al. 2001; Wang et al. 2001; Baldini et al. 2002; Frappier et al. 2002; Fleitmann et al. 2003; Yuan et al. 2004).

Speleothems form across a wide range of climatic zones, provide long, continuous, and commonly well-preserved records, and can be accurately dated over the last several hundred thousand years. Paleoenvironmental changes are potentially recorded in speleothems by a number of physical and chemical proxies, including variations in lamina thickness and their stable isotope compositions. However, due to their low growth rates on the order of 10^0 to 10^2 $\mu\text{m year}^{-1}$ (Baker et al. 1993), the temporal resolution achievable by conventional, i.e., mechanical, microsampling is usually limited to >10 years. In addition, the importance of site-specific effects for individual speleothem stable isotope records sets limits to their general reliability as archives of paleoenvironmental information (Bar-Matthews et al. 1996).

Despite the limitations of speleothems, other terrestrial records potentially offering high temporal resolution, such as freshwater tufas and travertines (Ford and Pedley 1996), have surprisingly received little attention. Several studies on freshwater tufas have demonstrated that valuable environmental information can be preserved in these deposits (Andrews et al. 1997; Ihlenfeld et al. 2003; Smith et al. 2004; Andrews and Brasier 2005). These previous studies, however, exclusively used tufa records, and paid no attention to the difference to travertine records (Liu et al. 2003). The problem is left in identifying the reasons for the formation of laminations in travertine, which is the basic issue when conducting high-resolution analyses. The purpose of this article is to investigate whether travertine can also provide useful annual or seasonal climate information suitable for high-resolution paleoclimate reconstruction. A continuous 4-year-long (1998–2001) stable isotope ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) record from a modern travertine was presented, and the relevant geochemical processes governing the observed variations in these parameters and the thickness of laminas in the travertine were discussed. Development of a reliable time series for the sample allows us to compare the physicochemical records with meteorological observations in order to define their climatic significance.

General settings

The travertine sample (Fig. 1) for this study was collected in November 2001 from a site (B-4, Fig. 2) in a canal put in use in May 1998 at Baishuitai, SW China. The location lies ~ 50 km south of the Shangri-La Town, in the vicinity of Gudu village (Fig. 2). The area is characterized by a subtropical monsoon climate, with $>75\%$ of the annual precipitation occurring during the rainy season from April to September.

Discharge of the spring 1–3, which supplies the canal (Fig. 2), is perennial but varies seasonally in response to the monsoonal rainfall distribution. The spring drains a karst catchment located to the west and southwest of the sampling site. The size of the catchment area is ~ 10 km^2 . Its elevation ranges from 2,800 to 4,000 m above sea level. The lithology of the karst mountain area consists of Middle Triassic limestone and Lower Triassic shale and sandstone. The area is covered by a brown residual clay soil of variable and eastward increasing thickness of 0–0.8 m. The vegetation in the catchment is characteristic of virgin forests and comprises mainly C3 plants (shrubs, trees). Apart from ~ 3 km^2 fossil travertine deposits within the karst terrain, modern travertine deposition commences only along the canal and downstream of springs 1–1 and 1–2 (Fig. 2). The sample analyzed in this study (Fig. 1) was deposited on a dead brushwood branch in the canal, ~ 2 km from the spring 1–3 (Fig. 2). Water flow rates at this site are moderately fast, making both microenvironmental effects (Andrews et al. 1997) and erosive episodes unlikely. Periodical

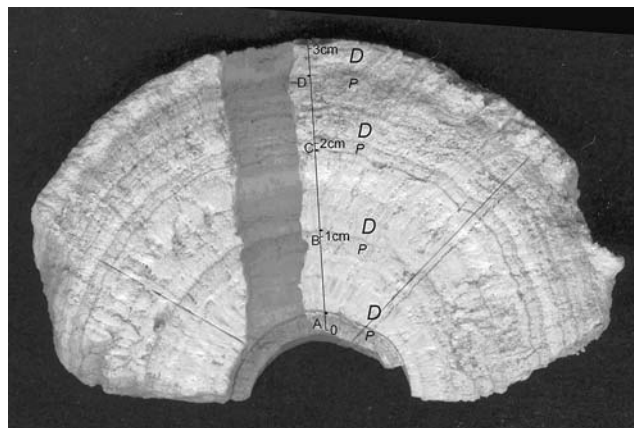
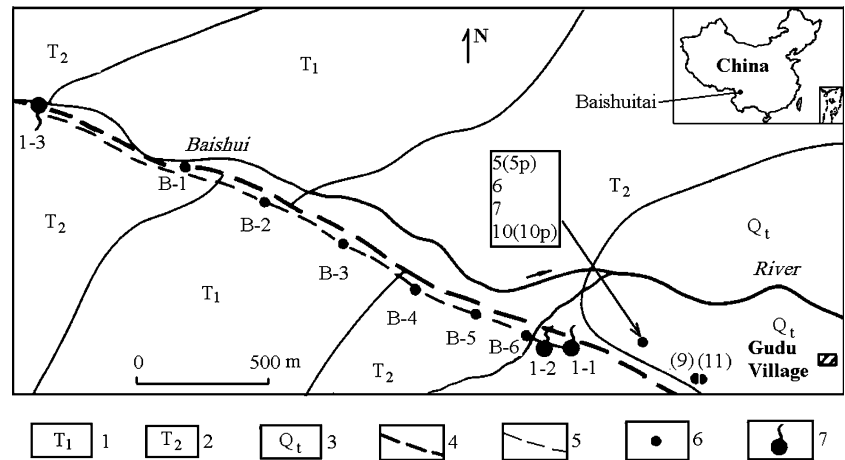


Fig. 1 The modern laminated travertine deposit (Sample B4) formed between May 1998 and November 2001 in the Baishuitai canal, showing alternation of thin brown-colored (with porous texture P) and thick white-colored (with dense texture D) laminas. A couplet comprising a thin and a thick laminas is assumed to represent one annual cycle. The top outer surface corresponds to November 25, 2001, when the sample was collected. A, B, C and D are the laminas formed in the rainy seasons of 1998, 1999, 2000 and 2001, respectively

Fig. 2 Distribution of springs and travertine deposits at Baishuitai, SW China (after Liu et al. 2003) 1 Lower Triassic shale and sandstone; 2 Middle Triassic limestone; 3 Quaternary travertine; 4 Fault; 5 Canal; 6 Travertine sampling spots; 7 Spring



drying out of the site during dry seasons is not probable because the water level is buffered by the travertine barrages, which dam up the water behind their structures. Other details of the site description can be found in the reference of Liu et al. (2003).

Air temperature and precipitation records

The meteorological information, which is necessary for an interpretation of the lamina thickness and isotope records in terms of their climatic significance, was obtained from the Shangri-La Bureau of Meteorology, Yunnan, China. Complete records of daily and monthly average air temperature and total daily and monthly precipitation, however, are only available for Shangri-La Weather Station, which is nearest (about 50 km) to the sampling location, with elevation of 3,300 m. Though the general climate (e.g., seasonal rainfall and air temperature patterns) is similar between the sampling location and the weather station, there exist possibly some differences in absolute temperature and precipitation. So, the climate information at the Shangri-La Weather Station can be used only for qualitative or semiquantitative interpretation of the isotope records and lamina thickness in terms of their climatic significance. For quantitative purpose, meteorological information in the catchment area has to be obtained by future monitoring. Figure 3 shows the daily precipitation and daily air temperature from 1998 through 2001, when the travertine sample was formed, recorded at Shangri-La Weather Station. Figure 4 summarizes the monthly precipitation and monthly averaged air temperature from 1998 through 2001 recorded at Shangri-La Weather Station. It can be seen that the rainy season generally starts from April, and ends in September each year, during which the air temperature is also high, belonging to typical Asian monsoon climate. Figure 5 shows the statistics of annual, rainy (April–September)

and dry (October–March) seasons' air temperature and precipitation. It's clear that the year 2000 is abundant in precipitation but lowest in air temperature.

Analytical method

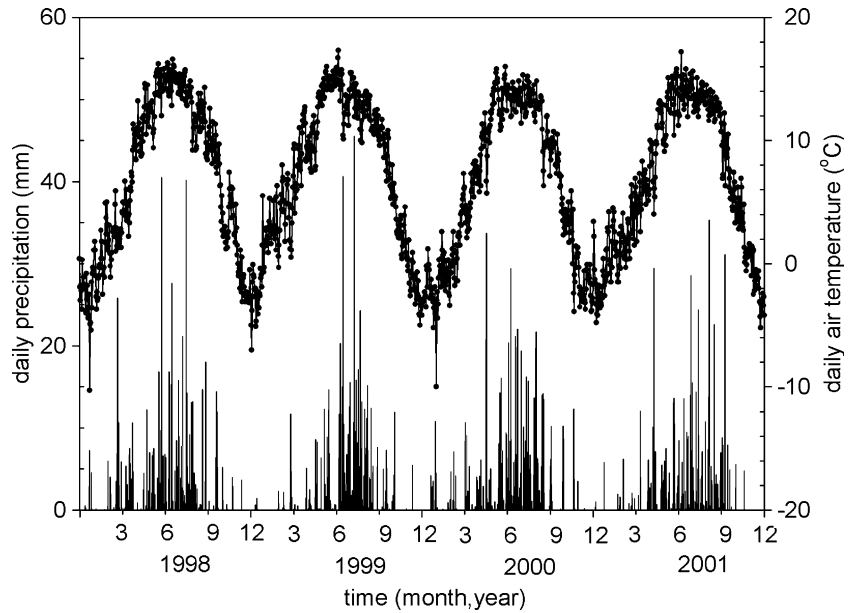
A total of 118 stable isotope samples were subsampled from the B-4 travertine by a micromill along the growth axis with an interval of 0.25 mm. About 10 µg powder of each sample was put into an individual reaction vial of a Kiel-III automatic carbonate device connected Finnigan DELTA Plus XP IRMS at National Cheng Kung University, Taiwan, China, to react with pure H_3PO_4 at 70°C. The generated CO_2 was then purified and sent to the IRMS for $\delta^{18}O$ and $\delta^{13}C$ analyses. The results were reported to against VPDB standard at 25°C. The IRMS has been calibrated with NBS standards of NBS-19 (limestone), NBS-18 (carbonatite) and LSVEC (lithium carbonate). The IRMS working conditions with a working standard, Ultiss (limestone), for every seven samples were also monitored. Based on the measurements of NBS19 ($n = 39$) and Ultiss ($n = 324$), the external analytical uncertainty is 0.021‰ for $\delta^{13}C$ and 0.047‰ for $\delta^{18}O$ (1 σ standard deviation).

Results and discussion

Thickness of the laminas in the travertine

The crosscut sample exhibits laminated textures consisting of alternated porous darker (brown)- and dense lighter (white)-colored laminas (Fig. 1), with the boundaries between laminas normally appearing undulating and obscure. The thickness of a single lamina mostly ranges from 1.5 to 8 mm. In the sample, a couplet is defined by alternations of porous and dense laminas (Fig. 1), which correspond to darker- and

Fig. 3 Daily precipitation (*bar chart*) and air temperature (*dotted line*) from 1998 through 2001 recorded at Shangri-La Weather Station



lighter-colored lamina (Fig. 1), respectively. In the description below, they are referred as porous lamina and dense lamina, respectively. Porous lamina was of lightly calcified texture. Dense lamina show micritic occurrence.

In May 1998, when the canal was put into use, a thin, porous lamina (A in Fig. 1) started developing and grew until September 1998 (0~2.2 mm in Fig. 1), when the rainy season ended, then was succeeded by a thick dense lamina that had begun to develop on the top of lamina

A. The dense lamina continued to grow until March 1999 (~6.6 from 2.2 to 8.8 mm in Fig. 1), when the 1999 rainy season started. The dense lamina was again covered by a porous lamina (B in Fig. 1), which grew during a period from April to September 1999 (~1.9 from 8.8 to 10.7 mm in Fig. 1). In the October 1999, a dense texture was again present on the surface (~8 from 10.7 to 18.7 mm in Fig. 1). In April 2000, when rainy season started, the porous lamina started forming (~1.5 from 18.7 to 20.2 mm in Fig. 1) till the end of the rainy

Fig. 4 Monthly precipitation (*bar chart*) and monthly-averaged air temperature (*dotted line*) from 1998 through 2001 recorded at Shangri-La Weather Station

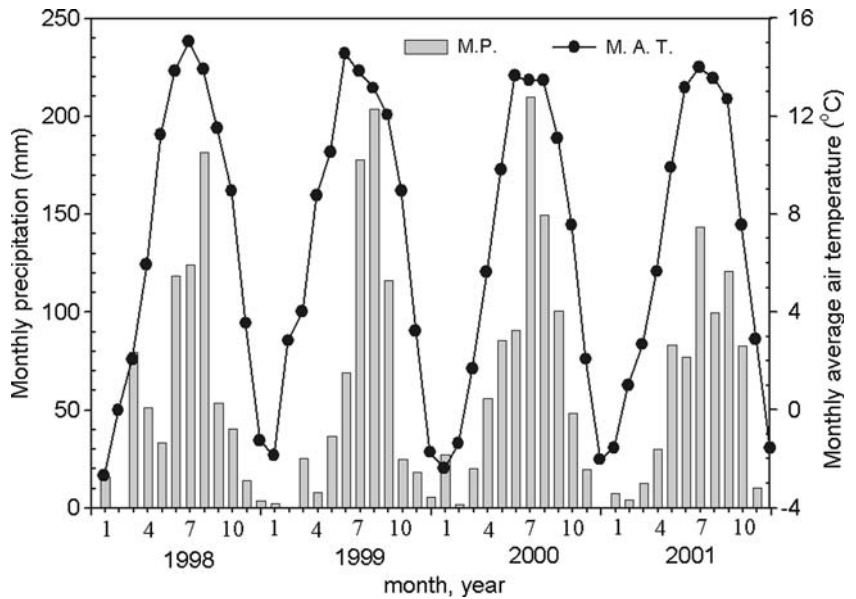
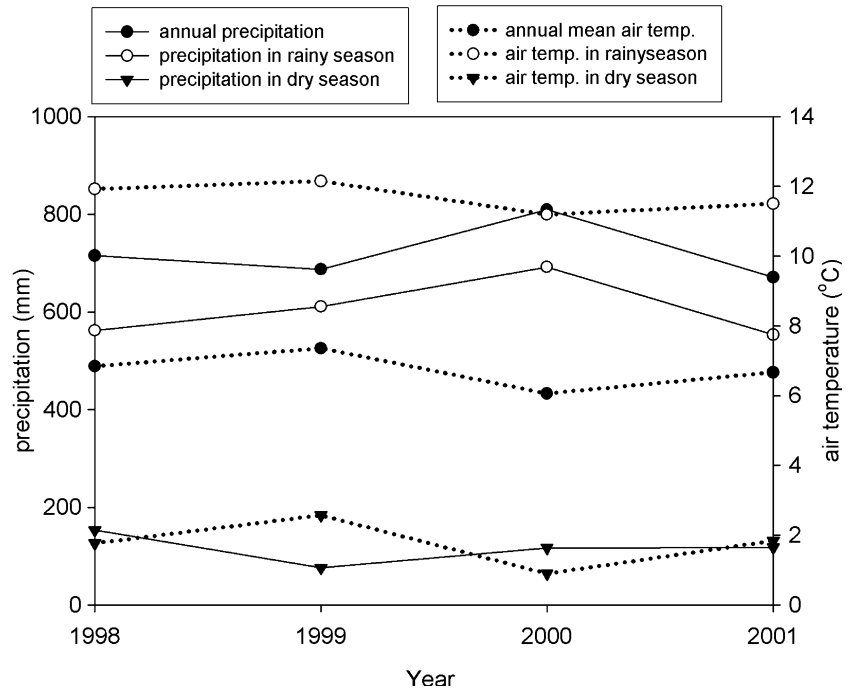


Fig. 5 The annual, dry and rainy seasons' air temperature and precipitation at Shangri-La Weather Station from 1998 to 2001



season. Then to March 2001, another dense lamina was formed (~5 from 20.2 to 25.2 mm in Fig. 1), and then 1.8 mm porous lamina deposited in the rainy season of 2001. On the top is the incomplete dense lamina from October to November 2001, when the sample was collected. Overall, by in situ observation, it was found that the lighter dense laminas were deposited in autumn–winter dry season (October–March), and the brown porous laminas in spring–summer rainy season (April–September). These observations show that the lamination of travertine is also annual, like tufas (Kano et al. 2003). In the laminated travertine at B-4 in Fig. 2, the annual growth rate was about 6.5–9.9 mm.

Laminated structure was also found in tufas in SW Japan by Kano et al. (2003). They found that the annual layering pattern was primarily controlled by changes in the rate of calcite precipitation. The concentration of dissolved CaCO_3 , which correlates with the precipitation rate, was high in summer–autumn (June–October) and low in winter–spring (November–May), owing to changes in the partial pressure of CO_2 in underground air. The seasonal precipitation rate was high in summer–autumn and low in winter–spring, which is consistent with the seasonal lamination pattern seen in the tufas. Moreover, the textures of collected samples show that the laminations consist of densely calcified summer–autumn laminas and lightly calcified winter–spring laminas. They inferred that the increased precipitation rate stimulated thick calcite encrustation on cyanobacterial filaments to produce the dense textures. As the relevant

processes are temperature dependent, the seasonal lamination pattern at Shirokawa was thought to generally apply to other laminated tufas deposited in temperate climates.

However, as has been shown above, a reversed pattern happened at the Baishuitai. The thin lightly calcified lamina was deposited in spring–summer strong rainy season (April–September), while thick dense calcified laminas in autumn–winter dry season. The reason is explained below.

Seasonal dilution, underground processes and seasonal pattern of water chemistry

Chemical processes associated with tufa/travertine deposition have been largely researched and reviewed (Ford and Pedley 1996). It has been suggested that the most basic conditions are the supersaturated water, and a high concentration of $[\text{Ca}^{2+}]$ and $[\text{HCO}_3^-]$. The depositional system at Baishuitai satisfies these basic conditions (Liu et al. 2003). However, in the past study (You 2003), an important finding was the seasonal variation seen in water chemistry (Table 1). In particular, important chemical variables such as $[\text{HCO}_3^-]$, $[\text{Ca}^{2+}]$ and $[\text{Na}^+]$ show a regular seasonal pattern (Table 1), which may have been controlled originally by weather conditions. Air temperature and rainfall influence various physicochemical processes, such as soil CO_2 production, dissolution of limestone, CO_2 outgassing, dilution and

Table 1 The seasonal pattern of water chemistry at Baishuitai

Site	Season	pH	Water temp.	SpC ($\mu\text{s/cm}$)	$[\text{Ca}^{2+}]^{\text{a}}$ (mg/l)	$[\text{HCO}_3^-]^{\text{b}}$ (mg/l)	Na^+ (mg/l)	SIc ^c	PCO_2^{d} (ppmv)
Sp1-3	Rainy	6.78	11.1	989	188.80	675.61	7.39	0.14	87,498
	Dry	6.60	10.8	988	188.60	674.92	5.67	-0.05	131,826
B-1	Rainy	7.52	13.8	754	141.80	513.46	2.77	0.70	12,560
	Dry	7.30	9.4	888	168.60	605.92	5.61	0.55	23,334
B-2	Rainy	7.93	15.3	737	138.40	501.73	2.71	1.10	4,797
	Dry	7.65	9.9	865	164.00	590.05	5.63	0.88	10,162
B-3	Rainy	8.11	16.3	691	129.20	469.99	2.38	1.23	2,971
	Dry	7.92	9.9	834	157.80	568.66	5.16	1.11	5,223
B-4	Rainy	8.13	16.9	691	129.20	469.99	2.17	1.26	2,857
	Dry	7.93	9.9	827	156.40	563.83	5.60	1.12	5,058
B-5	Rainy	8.15	16.4	613	113.60	416.17	1.91	1.18	2,415
	Dry	7.96	9.6	789	148.80	537.61	5.60	1.10	4,497
B-6	Rainy	8.16	16.7	604	111.80	409.96	2.18	1.18	2,333
	Dry	7.94	9.2	766	144.20	521.74	5.06	1.06	4,560

The data are from You (2003)

^{a,b} $[\text{Ca}^{2+}]$ and $[\text{HCO}_3^-]$ were calculated by linear relation between them and spc (Liu et al. 2006)

^cCalcite saturation index in water ($\text{SIc} = \log \text{IAP}/K$, where IAP is ionic activity product and K is the calcite equilibrium constant). If $\text{SIc} > 0$, supersaturation occurs and travertine will deposit; if $\text{SIc} < 0$, water is aggressive to calcite; and if $\text{SIc} = 0$, the equilibrium reaches

^dCalculated CO_2 partial pressure of water by WATSPEC (Wigley 1977)

precipitation of calcite. These processes take place in different environments of a tufa/travertine depositional system. To explain the seasonal pattern, the processes along the passage of rainwater through a series of environments will be discussed. A high $[\text{HCO}_3^-]$ and $[\text{Ca}^{2+}]$ is basically due to the dissolution of limestone and requires an elevated PCO_2 level in the percolating water. Water PCO_2 increases by passing through a soil layer and a deep source CO_2 (Liu et al. 2003). The PCO_2 of air within the soil rises to < 0.1 atm in normal climates (Ford and Williams 1988), due to the respiration of roots and decomposition of organic matter. However, for endogenic system, PCO_2 of air could be much higher (Liu et al. 2003). More uptake of CO_2 causes more dissolution of CaCO_3 because the dissolution of CO_2 decreases the pH of the water and increases its aggressiveness in dissolving CaCO_3 . Soil PCO_2 is higher in summer, because higher temperatures increase the effects of biological activity (Drake and Wigley 1975). However, when the canal water is supplied mainly with conduit flow or overland flow (referring to the flow when rainfall rates exceed infiltration rates), the $[\text{HCO}_3^-]$ and $[\text{Ca}^{2+}]$ in rainy summer could be lower than that in winter due to the dilution effect of rainwater. This latter case is possibly similar to the seasonal pattern seen in the data sets (Table 1). Though the deposition of calcite could decrease the concentration of HCO_3^- and Ca^{2+} in water, the dilution effect of overland flow in rainy summer season on $[\text{HCO}_3^-]$ and $[\text{Ca}^{2+}]$ was more important, which was verified by much lower concentration of more conservative ions (e.g., Na^+ , Table 1) in rainy season.

Depositional rate and layering pattern of the travertine

Seasonal layering of the travertine at Baishuitai (Fig. 1) is inferred to result from seasonal changes in precipitation rate (Kano et al. 2003). According to Buhmann and Dreybrodt (1985), the rate decreased with a temperature, $[\text{HCO}_3^-]$ and $[\text{Ca}^{2+}]$ decrease. According to Table 1,

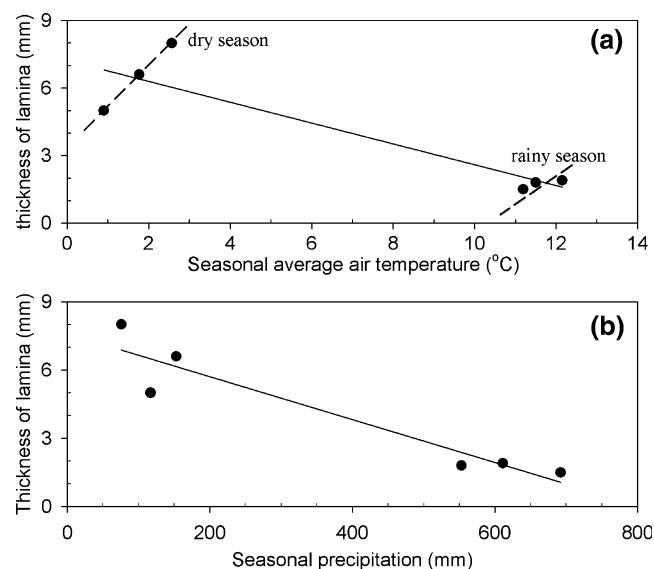


Fig. 6 Correlation between lamina thickness and seasonal average air temperature (a) and seasonal precipitation (b). Note: the first and last laminae formed in 1998 rainy season and 2001 dry season were not considered here due to their incompleteness

$[\text{HCO}_3^-]$ and $[\text{Ca}^{2+}]$ were lower in rainy season (April to September) due to the dilution effect by rainwater. Although the higher temperature increased the depositional rate in both dry season and rainy season (Fig. 6a, dashed lines), the lower values for $[\text{HCO}_3^-]$ and $[\text{Ca}^{2+}]$ overtook the effect of temperature and overall decreased the precipitation rate in the rainy season. This is indicated by the fact that lamina thickness formed in the rainy season is much less than that in dry season (Fig. 6), and shows negative correlation with seasonal precipitation (Fig. 6b).

Variations in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the laminated travertine

The carbon isotopic composition ($\delta^{13}\text{C}$) of the sample shows a regular cyclical change (Fig. 7). Three clear cycles and one subtle cycle in 2000 are present within the 30-mm-thick travertine. The thickness of the cycles ranges from 6.5 to 9.9 mm, and the maximum variation in $\delta^{13}\text{C}$ is 1.8‰ from the minimum 5.2‰ to the maximum value of 7.0‰ (vs. PDB). However, the subspecimens on the 17.2- and 27.2-mm horizons recorded exceptionally high $\delta^{13}\text{C}$ values. The oxygen isotopic composition ($\delta^{18}\text{O}$) also shows a cyclical change, which covaries basically with $\delta^{13}\text{C}$ (Fig. 7). The amplitude of the changes ranges from 0.6 to 2.6‰. The maximum and minimum values are -9.7‰ and -12.3‰ , respectively. There are two exceptional peaks located also at the 17.2- and 27.2-mm horizons. From the 19.5- to the 25.9-mm horizons, the curve is relatively flat and low (Fig. 7). The cycles of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ correlate with the laminations. The porous laminas (*P* in Fig. 1), which formed in spring–summer rainy seasons, record the lower $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, and dense autumn–winter laminas (*D* in

Fig. 1) formed in dry season record higher $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values.

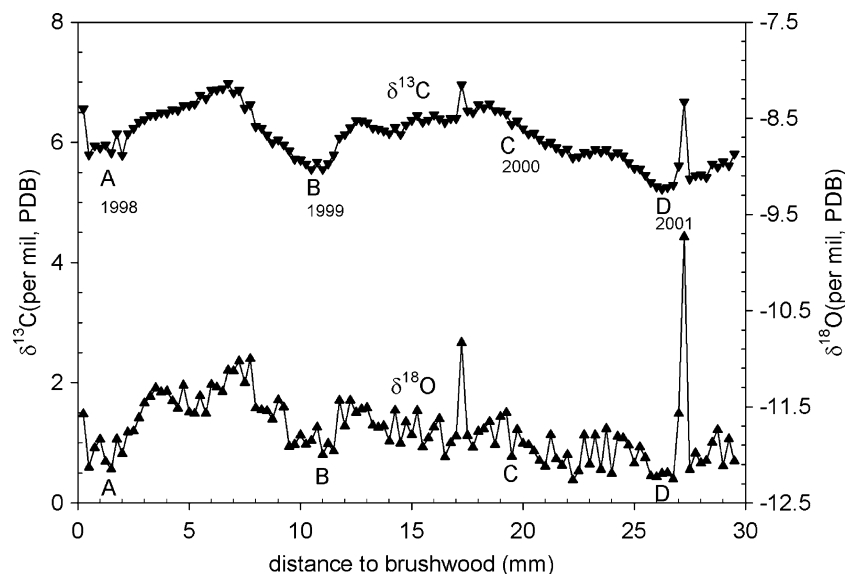
The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ curves of the sample show similar patterns of change. This similarity can be seen in a cross-plot of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of all measured subspecimens that yield a large correlation coefficient (0.75; Fig. 8).

Reasons for seasonal changes in carbon and oxygen isotopic compositions

Matsuoka et al. (2001) found that the $\delta^{18}\text{O}$ curve in a laminated tufa, SW Japan reflects seasonal changes in water temperature, and cyclic variation in $\delta^{13}\text{C}$ was controlled by seasonal changes in the $\delta^{13}\text{C}$ of dissolved inorganic carbon in groundwater, which is probably caused by groundwater degassing. However, the travertine deposits at Baishuitai were mainly related to endogenic CO_2 source, which has much higher $\delta^{13}\text{C}$ values ($> -10\text{‰}$) than soil CO_2 ($< -20\text{‰}$), and contributes to higher $\delta^{13}\text{C}$ values of HCO_3^- (-1.2‰ for the spring) and travertine (Liu et al. 2003). Therefore, the lower values in travertine $\delta^{13}\text{C}$ in rainy season should mainly be related to the dilution effect by overland flow after rainfall, which is mainly influenced by soil water, and so has lower $\delta^{13}\text{C}$ values. Due to the dilution effect, $\delta^{18}\text{O}$ values in travertine in rainy season should also be low, account of the monsoon rainfall amount effect (Dansgaard 1964; Rozanski et al. 1992; Zhang et al. 2002). According to Zhang et al. (2002), the $\delta^{18}\text{O}$ values of rainwater in summer rainy season (-15.25‰) could be about 3‰ lower than those in winter dry season (-12.38‰) in nearby stations.

The strong correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values (Fig. 8) supports the hypothesis that the dilution by

Fig. 7 Results of high-resolution analysis of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for the travertine sample. Cut interval of the sub-specimens is 0.25 mm. Data are plotted versus distance from growth center, where a brushwood branch was as start point of calcite nucleation.



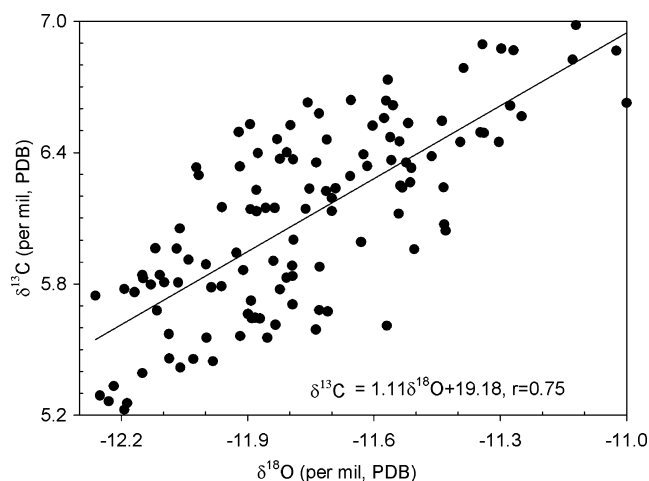


Fig. 8 Cross-plot of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of all measured subspecimens

rainwater is the main factor producing the seasonal change of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

Anomalies in isotopic values recorded in the laminated travertine

As have been seen in Fig. 7, the present travertine records two types of anomalies in isotopic values: the prominent peaks seen in 17.2- and 27.2-mm horizons, and irregular changes seen in the year 2000 lamina (the 18.7- to the 25.2-mm horizons). These peaks may be associated with a very special phenomenon, which happened in dry weather and increased the ^{18}O in water and ^{13}C in HCO_3^- . This significant isotopic increase could be the result of strong evaporation, and resultant degassing, which selectively removes H_2^{16}O and $^{12}\text{CO}_2$. This event probably resulted from a change in hydrological conditions such as variations in water flow during winter or summer. Another anomaly, irregularity in the cycle in the year 2000 lamina (the 18.7- to the 25.2-mm horizons), is characterized by the abnormal shapes of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ curves, each having a relatively low value in autumn–winter lamina. This is associated with the relatively thin, porous lamina (Figs. 1, 6). Meteorological data from Shangri-La Weather Station show a wet year in 2000 (Fig. 5), which had a $\sim 12\%$ increase in annual precipitation, and explains the low isotopic values and thin lamina.

Conclusions

Like tufas (Matsuoka et al. 2001; Ihlenfeld et al. 2003), travertines with annual laminations are also useful tools

for high-resolution paleoclimate analysis. Based on the study of the laminated travertine at Baishuitai, it concludes:

1. The laminated travertine represents an alternation of porous spring–summer lamina and dense autumn–winter lamina (Fig. 1). The lamination pattern is primarily controlled by seasonal changes in the calcite precipitation rate, which correlates positively with $[\text{Ca}^{2+}]$, $[\text{HCO}_3^-]$ and water temperature. A decrease in $[\text{Ca}^{2+}]$ and $[\text{HCO}_3^-]$ in spring–summer rainy season mainly resulted from the dilution by rainwater, overtook the effect of temperature increase from autumn–winter season to spring–summer season. So, the thickness of the spring–summer lamina was less than that of the autumn–winter laminas. Therefore, *on the seasonal scale* in a year, lamina thickness is a measurement of rainfall (negatively!) but not temperature (Fig. 6b). The temperature effect could be found in the positive relation between autumn–winter dry season lamina thickness and the autumn–winter seasonal temperature, and between spring–summer rainy season lamina thickness and the spring–summer seasonal temperature (Fig. 6a).
2. The laminated travertine records cyclic variations in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. Isotope records correlate well with the seasonal lamination pattern, consisting of dense autumn–winter and porous spring–summer laminas (Fig. 7). In addition to seasonal changes of water temperature (Matsuoka et al. 2001), the $\delta^{18}\text{O}$ curve may also reflect the rainfall amount effect due to the dilution by rainwater in the spring–summer season. Variations in $\delta^{13}\text{C}$, which correlate well with $\delta^{18}\text{O}$ ($r = 0.75$; Fig. 8), are controlled by spring–summer seasonal dilution in $\delta^{13}\text{C}$ of spring $[\text{HCO}_3^-]$, which is mainly related to deep source CO_2 , and much higher than that of epikarst spring $[\text{HCO}_3^-]$, the latter being controlled by soil CO_2 (Liu et al. 2000). Extreme climatic events, such as drought and floods, appear as anomalies in both the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ curves (Fig. 7). These findings should be generally applicable to the interpretation of travertine records in the subtropical monsoon belts and mid to high latitudes with distinct rainfall seasons.

In conclusion, by combining the analysis of lamina thickness, textures, stable isotopes and trace elements (Ihlenfeld et al. 2003), with appropriate dating methods, it is expected that travertine can provide important information on the terrestrial paleoclimate change.

Acknowledgments This work was supported by the National Natural Science Foundation of China (Grant Nos. 40372117 and 40572017), Ministry of Science and Technology of China (Grant No. 2005DIB3J067), Ministry of Land and Resources of China (Grant No. 9806).

References

- Andrews JE, Brasier AT (2005) Seasonal records of climatic change in annually laminated tufas: short review and future prospects. *J Quaternary Sci* 20:411–421
- Andrews JE, Riding R, Denn PF (1997) The stable isotope record of environmental and climatic signals in modern terrestrial microbial carbonates from Europe. *Palaeogeogr Palaeoclimatol Palaeoecol* 129:171–189
- Baker A, Smart PL, Edwards RL, Richards A (1993) Annual growth bandings in a cave stalagmite. *Nature* 364:518–520
- Baldini JUL, McDermott F, Fairchild IJ (2002) Structure of the 8200-year cold event revealed by a speleothem trace element record. *Science* 296:2203–2206
- Bar-Matthews M, Ayalon A, Matthews A, Sass E, Halicz L (1996) Carbon and oxygen isotope study of the active water-carbonate system in a karstic Mediterranean cave: implications for paleoclimate research in semiarid regions. *Geochim Cosmochim Acta* 60:337–347
- Buhmann D, Dreybrodt W (1985) The kinetics of calcite dissolution and precipitation in geologically relevant situations of karst areas. 1 *Open Syst Chem Geol* 48:189–211
- Charles CD, Hunter DE, Fairbanks RG (1997) Interaction between the ENSO and the Asian monsoon in a coral record of tropical climate. *Science* 277:925–928
- Dansgaard W (1964) Stable isotopes in precipitation. *Tellus* 16:436–468
- Dorale JA, Edwards RL, Ito E, González LA (1998) Climate and vegetation history of the Midcontinent from 75 to 25 ka: a speleothem record from Crevice Cave, Missouri, USA. *Science* 282:1871–1874
- Drake JJ, Wigley TML (1975) The effect of climate on the chemistry of carbonate groundwaters. *Water Resour Res* 11:958–962
- Fleitmann D, Burns SJ, Mudelsee M, Neff U, Kramers J, Mangini A, Matter A (2003) Holocene forcing of the Indian monsoon recorded in a stalagmite from Southern Oman. *Science* 300:1737–1739
- Ford TD, Pedley HM (1996) A review of tufa and travertine deposits of the world. *Earth Sci Rev* 41:117–175
- Ford TD, Williams PW (1988) Karst geomorphology and hydrology. Unwin Hyman Academic, London
- Frappier A, Sahagian D, González LA, Carpenter SJ (2002) El Niño events recorded by stalagmite carbon isotopes. *Science* 298:565
- Ihlenfeld C, Norman MD, Gagan MK, Drysdale RN, Maas R, Webb J (2003) Climatic significance of seasonal trace element and stable isotope variations in a modern freshwater tufa. *Geochim Cosmochim Acta* 67:2341–2357
- Kano A, Matsuoka J, Kojo T, Fujii H (2003) Origin of annual laminations in tufa deposits, southwest Japan. *Palaeogeogr Palaeoclimatol Palaeoecol* 191:243–262
- Liu Z, Yuan D, He S, Zhang M, Zhang J (2000) Geochemical features of the geothermal CO₂-water-carbonate rock system and analysis on its CO₂ sources. *Sci China (D)* 43:569–576
- Liu Z, Zhang M, Li Q, You S (2003) Hydrochemical and isotope characteristics of spring water and travertine in the Baishuitai area (SW China) and their meaning for paleoenvironmental reconstruction. *Environ Geol* 44:698–704
- Liu Z, Li Q, Sun H, Wang J, Wu K (2006) Diurnal variations of hydrochemistry in a travertine-depositing stream at Baishuitai, Yunnan, SW China. *Aquat Geochem* 12:103–121
- Matsuoka J, Kano A, Oba T, Watanabe T, Sakai S, Seto K (2001) Seasonal variation of stable isotopic compositions recorded in a laminated tufa, SW Japan. *Earth Planet Sci Lett* 192:31–44
- McDermott F, Matthey DP, Hawkesworth C (2001) Centennial-scale Holocene climate variability revealed by a high-resolution speleothem $\delta^{18}\text{O}$ record from SW Ireland. *Science* 294:1328–1331
- Montoya M, Crowley TJ, Storch H (1998) Temperatures at the last interglacial simulated by a coupled ocean-atmosphere climate model. *Paleoceanography* 13:170–177
- Rozanski K, Araguas-Araguas L, Gonfiantini R (1992) Relation between long-term trends of oxygen-18 isotope composition of precipitation and climate. *Science* 258:981–985
- Smith JR, Giegengack R, Schwarcz HP (2004) Constraints on Pleistocene pluvial climates through stable-isotope analysis of fossil-spring tufas and associated gastropods, Kharga Oasis, Egypt. *Palaeogeogr Palaeoclimatol Palaeoecol* 206:157–175
- Tudhope AW, Chilcott CP, McCulloch MT, Cook ER, Chappell J, Ellam RM, Lea DW, Lough JM, Shimmield GB (2001) Variability in the El Niño–Southern Oscillation through a glacial–interglacial cycle. *Science* 291:1511–1517
- Wang YJ, Cheng H, Edwards RL, An ZS, Wu JY, Shen C, Dorale JA (2001) A high-resolution absolute-dated Late Pleistocene monsoon record from Hulu Cave, China. *Science* 294:2345–2348
- Wigley TML (1977) WATSPEC. A computer program for determining the equilibrium of aqueous solutions. *Br Geomorphol Res Group Tech Bull* 20:1–46
- You S (2003) The evolution of hydrochemistry and carbon and oxygen isotopes in Baishuitai Travertine scenic area and its environmental significance. Master degree thesis, Guangxi Normal University
- Yuan D, Cheng H, Edwards RL, Dykoski CA, Kelly MJ, Zhang M, Qing J, Lin Y, Wang Y, Wu J, Dorale JA, An Z, Cai Y (2004) Timing, duration, and transitions of the last interglacial Asian monsoon. *Science* 304:575–578
- Zhang X, Nakawo M, Yao T, Han J, Xie Z (2002) Variations of stable isotopic compositions in precipitation on the Tibetan Plateau and its adjacent regions. *Sci China* 45:481–493