

Hydrochemical and isotope characteristics of spring water and travertine in the Baishuitai area (SW China) and their meaning for paleoenvironmental reconstruction

Z. Liu · M. Zhang · Q. Li · S. You

Abstract A method of combining hydrochemical data logging and in situ titrating with measurement of stable carbon and oxygen isotopes was used to reveal the hydrochemical and isotopic characteristics in the Baishuitai travertine scenic area of SW China. It was found that the travertine-forming springs have a very high concentration of calcium and bicarbonate, and accordingly very high CO₂ partial pressures, which are not likely to be produced by biological activity in soil alone. Further analysis of the stable carbon isotopes of the springs shows that the high pressure of CO₂ is mainly related to an endogenic CO₂ source. That means the Baishuitai travertine is endogenic in origin. This is contrast to the commonly accepted saying that the travertine deposition in this study simply is a product of warm and humid conditions in a karst ecological environment. Rapid CO₂ degassing from the water is triggered by the much higher partial pressures in water than that of the surrounding air. Consequently, as the waters flow downstream of the spring the pH increases, the waters become supersaturated with respect to calcite, and travertine is deposited. The preferential release of ¹²CO₂ to the atmosphere results in a progressive increase of

travertine $\delta^{13}\text{C}$ downstream. This is concluded with a preliminary discussion of variation in travertine-forming water temperatures, according to differences in stable oxygen isotopic compositions of the travertine formed in different epochs at Baishuitai. It was found that the change in water temperature is as high as 13 °C, i.e., from 23 °C at about 2500 years B.P., to 10 °C at present. This may mainly reflect that the effect of geothermal source on water temperature is decreasing. The problems involved in paleoenvironmental reconstruction with endogene travertine are also discussed. They are the impacts of “dead carbon” in radiocarbon dating and the enrichment in ¹³C of travertine by endogenic CO₂ and degassing of CO₂ from water, which has to be considered in paleovegetation reconstruction when using $\delta^{13}\text{C}$ data of the endogene carbonate deposits.

Keywords Hydrochemistry · Stable carbon and oxygen isotopes · Endogenic CO₂ sources · Endogene travertine · Paleoenvironment reconstruction · Baishuitai, Yunnan Province, SW China

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Introduction

Baishuitai is in southeastern Zhongdian County, Yunnan Province, SW China, about 100 km from the county town. The altitude ranges from 2,380 m to 2,600 m a.s.l. Baishuitai Springs, which are abundant in calcium, flow out from the mountainside of Mahuishan in a forested area, which is near Gudu Village (Fig. 1). About 100 m from the springs, a travertine platform with layered CaCO₃ has formed. It is a typical karst landscape, which has been formed by calcite-supersaturated aqueous solutions, and covers about 3 km² (Zhao and others 1998). It is believed to be one of the largest travertine deposits in China, and becomes an important natural tourism resource due to its beauty and as the cradle of Donba Culture of the Naxi Minority (Fig. 1).

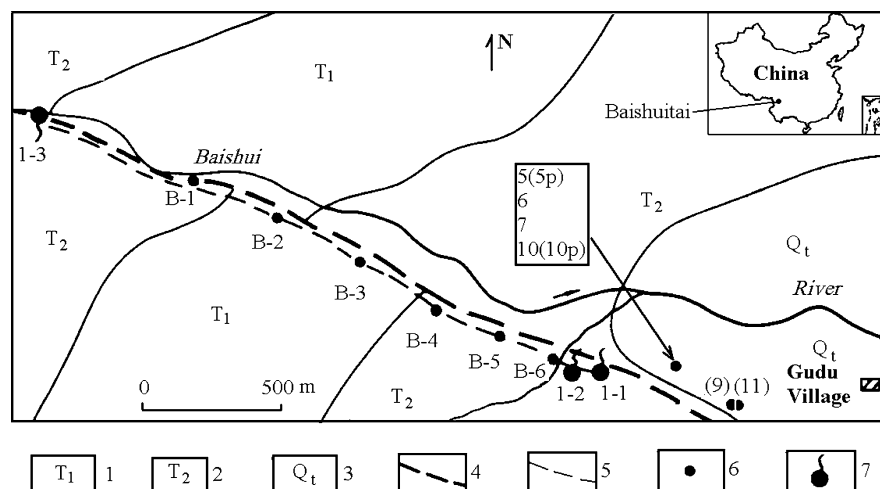


Fig. 1

Distribution of the Baishuitai springs and travertines. 1 Lower Triassic shale and sandstone; 2 Middle Triassic limestone; 3 Quaternary travertine; 4 fault; 5 canal; 6 travertine sampling spots; 7 spring

Since the Ming Dynasty (about 600 B.P.), Baishuitai has become a famous tourist and religious attraction in Yunnan Province. However, the origin of the Baishuitai travertine has not been well understood. It has been considered to be a product of a special karst ecological environment (Zhu 1992), associated with a warm and humid climate (Zhao and others 1998). There has also been speculation that the travertine may be endogenic, or related to an endogenic CO₂ source (Pentecost and Zhang 2001). These inconsistent interpretations suggest that further research is necessary to clarify the origin and forming-processes of the travertine at Baishuitai. Moreover, there is a possibility of paleoenvironmental reconstruction within this kind of travertine deposit.

Climatic, botanical and geological background at Baishuitai

Though Baishuitai lies in the subtropics, the altitudes are highly variable. There are thus four climatic zones present simultaneously, depending on the elevations on the mountain slope: a warm-temperate zone (altitude 2,200–2,500 m), a temperate zone (altitude 2,500–3,000 m), a cold-temperate zone (altitude 3,000–3,500 m) and a frigid zone (altitudes above 3,500 m). Because of these climatic variations, plants near Baishuitai also have distinct vertical zonation. The native plants in the upper course of the Baishuitai River are protected quite well, therefore the forest cover can be up to 80% or more (Zhao and others 1998). However, native plants were seriously destroyed in the lower reaches of the river, therefore the major component is the secondary shrub below an altitude of 2,600 m a.s.l.

Baishuitai is on Shisanjiao Mountain with limestone of the Triassic Beiya Formation. Due to intensive neotectonic movement (Zhao and others 1998) and rock weathering, the rock is highly fractured, and faults and fissures are well developed. This provides good conditions for rainfall infiltration and groundwater flow. However, due to the cut-off by a major northwest oriented fault, groundwater resurges at an altitude of about 2,600 m a.s.l., and forms

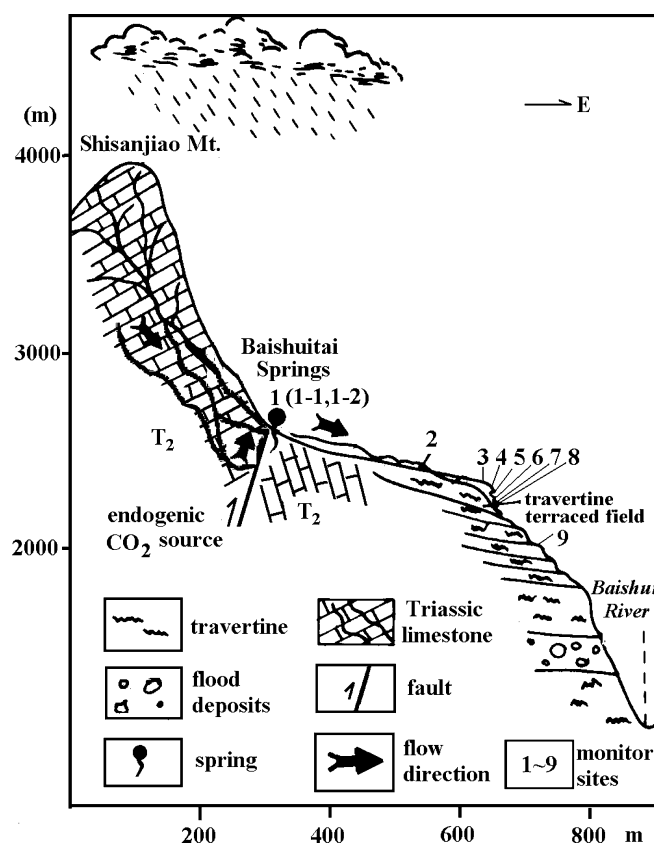


Fig. 2

Cross section showing the geological conditions for the origin and formation of the Baishuitai travertine (modified after Zhao and others 1998). Monitoring site: 1 Baishuitai spring; 2 flowing water 100 m from the spring; 3–8 travertine pool Nos. 5–10 respectively; 9-site for hydrochemical data logging, about 500 m downstream from the spring

the Baishuitai Spring. There are three main springs: spring No.1-1 to No.1-3 (Fig. 1). During the contact of spring water with the atmosphere, a large amount of CO₂ is released and calcium carbonate has been deposited, and through time this natural wonder of colored travertine scenery has formed (Figs. 1, 2).

The temperature (about 11 °C) of the springs is approximately 3° higher than the annual mean air temperature (8 °C) at the altitude where the springs flow out (Song and others 1994). This suggests that the spring water may be heated by a deep-seated geothermal source, especially considering that the high altitude recharge waters (ca. 4,000 m) are significantly colder. Further support of this is shown by the following analysis of hydrochemistry and stable carbon isotopes.

Methods

The methods include hydrochemical data logging, in situ titrating and sample analysis in the laboratory

The MultiLine P3 multi-parameter instrument (made by WTW-Wissenschaftlich-Technische-Werkstätten in Germany) automatically records temperature, pH and electrical conductivity of water *in situ*, with resolutions of 0.1 °C, 0.01 pH and 1 µs/cm, respectively. The time interval of data acquisition ranged from 15 to 60 min. By automatic recording, values of the water's physicochemical characteristics and their diurnal changes were obtained. In situ titrating was used to measure the HCO₃⁻ and Ca²⁺ of water with the Aquamerck alkalinity test and hardness test. The resolutions are 6 mmol/l and 1 mg/l, respectively. Samples of water and travertine were collected for analysis of major hydrochemical components and the compositions of stable carbon and oxygen isotopes ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, ‰, PDB) according to standard procedures in laboratory. The water samples for $\delta^{13}\text{C}$ of dissolved inorganic carbon were treated in situ with NaOH (2 N) to increase pH to above 12.00 (special attention was paid to avoiding absorption of CO₂ by the alkali from atmosphere), then with a saturated BaCl₂ solution to precipitate BaCO₃. They were then filtered and the BaCO₃ analyzed in the laboratory using a VG903 isotope mass spectrometer.

Results

Table 1 shows the hydrochemical and stable carbon isotopic compositions of the springs, and the stable carbon and oxygen isotopic compositions of travertines can be seen in Table 2.

The downstream hydrochemical evolution at Baishuitai is shown in Fig. 3, and Fig. 4 shows the diurnal change in temperature, pH-value, and electrical conductivity of the Baishuitai downstream water at site No.9 in Fig. 2. The details of the results are explained in the following section.

Discussion and conclusions

Origin of the Baishuitai travertine

If the CO₂ partial pressure of spring water is higher than that of the surrounding atmosphere, CO₂ will outgas

Table 1
Hydrochemical and stable carbon isotopic compositions of the Baishuitai spring water

Spring name	K ⁺ (mg/l)	Na ⁺ (mg/l)	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	Cl ⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	SiO ₂ (mg/l)	Water temp. (°C)	PH	Electrical conductivity (µs/cm)	SI ^c	Pco ₂ ^b (Pa)	$\delta^{13}\text{C}_{\text{DIC}}$ ^c (‰, PDB)
No. 1-1	1.10	7.92	191.34	27.43	3.48	698.50	25.01	7.40	10.7	6.61	990	-0.03	14,400	-1.27
No. 1-2	1.16	8.04	192.65	28.49	3.48	708.42	23.97	7.40	10.9	6.53	1009	-0.10	17,560	-1.18
No. 1-3	0.48	3.52	174.02	13.13	6.08	584.19	8.47	-	7.2	6.95	863	+0.16	5,552	-

^aCalcite saturation index in water (SI=log₁₀IAP/K, where IAP is ionic activity product and K is the calcite equilibrium constant). If SI>0, supersaturation occurs and travertine will deposit; if SI<0, water is aggressive to calcite; and if SI=0, equilibrium is reached

^bCalculated CO₂ partial pressure of water by SOLMINEQ88 (Kharaka and others 1988)

^cDIC is the dissolved inorganic carbon in water and its value is approximate to [HCO₃⁻] at pH>6.50

Table 2
Stable carbon and oxygen isotopic compositions of the Baishuitai travertine

Sample no.	Type of samples	TIMS ages (years) ^a	$\delta^{13}\text{C}$ (PDB, ‰)	$\delta^{18}\text{O}$ (PDB, ‰)
(9)-1~(9)-41	Old travertines ^b	2,530~2,570	2.18~4.12 (mean 3.15)	-14.65~-15.85 (mean -15.32)
(11)-1~(11)-41	Older travertine ^c	1,970~2,010	2.7~5.61 (mean 3.58)	-13.92~-15.41 (mean -14.48)
5p	Active travertine in pool ^d	≤ 1	3.82	-12.88
5	Active travertine at dam ^d	≤ 1	3.62	-12.85
6	Active travertine at dam ^d	≤ 1	3.64	-13.28
7	Active travertine at dam ^d	≤ 1	3.85	-12.66
10	Active travertine at dam ^d	≤ 1	4.98	-12.86
10p	Active travertine in pool ^d	≤ 1	5.67	-13.04
B-1	Active travertine on tree branch ^e	≤ 1	3.71	-12.18
B-2	Active travertine on tree branch ^e	≤ 1	3.88	-12.35
B-3	Active travertine on tree branch ^e	≤ 1	4.79	-11.96
B-4	Active travertine on tree branch ^e	≤ 1	5.01	-12.00
B-5	Active travertine on tree branch ^e	≤ 1	5.41	-11.71
B-6	Active travertine on tree branch ^e	≤ 1	6.04	-11.38

^aThe dating was done by Dr. Cheng Hai in University of Minnesota, USA

^{b,c}The 41 samples were collected at the travertine sampling spots Nos. 9 and 11 in Fig. 1

^dSamples Nos. 5(5p), 6, 7, and 10(10p) correspond to monitoring sites Nos. 3, 4, 5 and 8, respectively, in Fig. 2

^eThe samples were formed in a canal constructed in November of 1999, transmitting the Baishuitai Spring (No. 1-3 in Fig. 1) water saturated with calcite to prevent the old travertine from weathering (Fig. 1)

from the water, which can lead to calcite supersaturation and deposition (Herman and Lorah 1987; Dreybrodt and others 1992; Liu and others 1995, 1997; Liu and Yuan 2000; Pentecost and Zhang 2001; Song and others 1994; Zhao and others 1998). That is, research on travertine origin must deal with the analysis of the source of carbon, water and calcium of the three components. Considering the background of the climate, botany and geology at Baishuitai, it is inferred that the Baishuitai spring water originates from the infiltration of rainfall, the calcium in the water is related to dissolution of Triassic limestone, and CO_2 (which dissolves limestone) comes from either the biological CO_2 in soil or the endogenic CO_2 , or a mixture of both. In the following, the source of the CO_2 will be clarified further through analysis of hydrochemical and stable carbon isotopic data.

The spring water has very high concentration of calcium and bicarbonate (Table 1). They are 200 and 700 mg/l, or 5 and 11.5 mmol/l, respectively, and the corresponding CO_2 partial pressure is more than 14,400 Pa. (Note: The water of spring No.1-3 was diluted by snow-melting water nearby, and so not considered here). According to observations in China (Liu and Yuan 2000), even in the warm and humid tropical and sub-tropical zones, the partial pressure of biological CO_2 in soil is no more than 10,000 Pa, and the concentration of calcium and bicarbonate are typically less than 150 and 450 mg/l, respectively. Pentecost and Zhang (2001) also found that concentrations of dissolved inorganic carbon that comes from limestone dissolution caused by biological CO_2 rarely

exceeds 10 mmol/l (usually 2-5 mmol/l). Therefore, the hydrochemical features of the Baishuitai springs cannot be explained by biological activity in soil alone (Zhao and others 1998), and also, 8 °C is too cold for significant biogenic CO_2 production. A more important role by endogenic CO_2 is likely.

According to Deines and others (1974), if an isotopic exchange equilibrium condition has been met, one has a relationship as follows:

$$\delta^{13}\text{C}_{\text{HCO}_3} - \delta^{13}\text{C}_{\text{CO}_2} = -4.54 + 1.099 \times 10^6 / T^2$$

where T is absolute temperature in K.

At Baishuitai, from the data by this study the temperature of spring water is 10.8 °C (or absolute temperature $T=283.95$ K) and the composition of the stable carbon isotopes of bicarbonate ion ($\delta^{13}\text{C}_{\text{HCO}_3}$) is -1.23‰ (the average value in Table 1). Therefore, with the relationship above, the composition of stable carbon isotope of CO_2 in spring water can be obtained. The value is $\delta^{13}\text{C}_{\text{CO}_2}=-10.32\text{‰}$. This is the stable carbon isotopic composition of the CO_2 for the origin of the Baishuitai travertine. It is obvious that the value is different from that of pure biological origin CO_2 in soil ($\delta^{13}\text{C}_{\text{soil CO}_2} \approx -25\text{‰}$; Galimov 1966), but much closer to that of endogenic CO_2 gas on Yunnan-Sichuan-Tibet plateau (Liu and others 1993, 1995, 1997, 2000). More recently, the $\delta^{13}\text{C}$ value for the endogenic CO_2 gas from a hot spring (31.4 °C) near Baishuitai (about 4 km away) has been obtained. It is -7.87‰ . From this it can be determined that the proportions come from the endogenic CO_2 and biological CO_2 sources, respectively at Baishuitai.

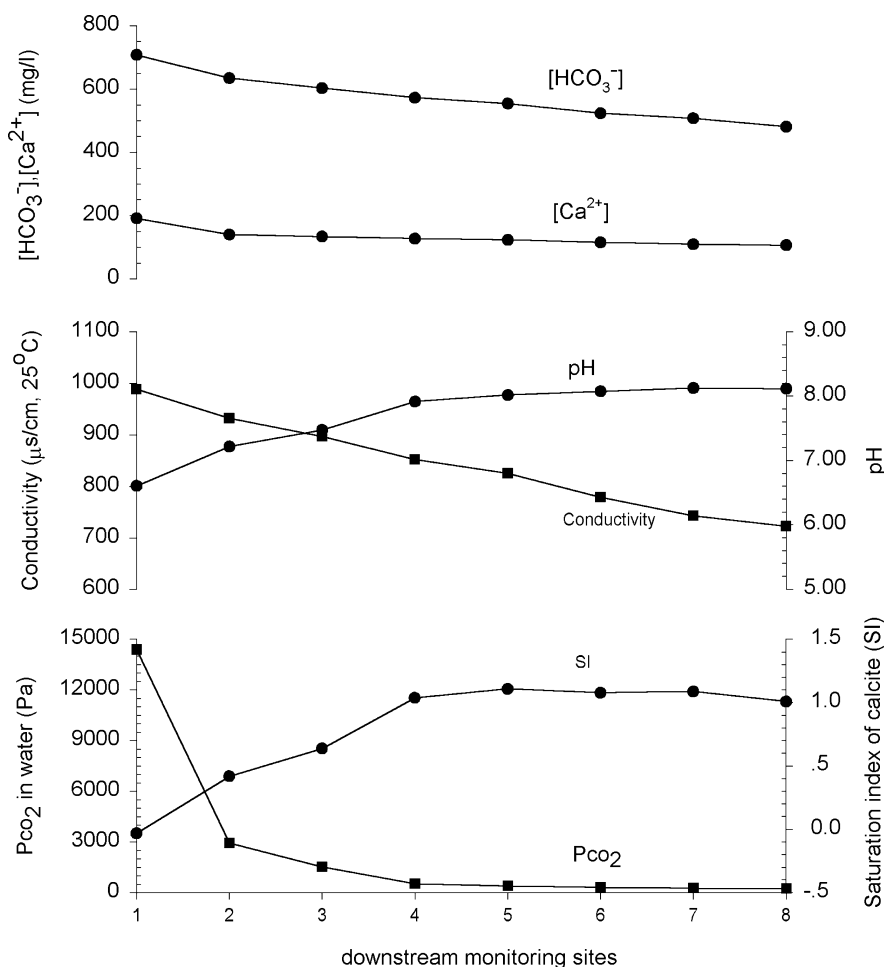


Fig. 3 Downstream hydrochemical evolution at Baishuitai. Note that $[\text{HCO}_3^-]$, $[\text{Ca}^{2+}]$, pH and conductivity are those measured in situ, and SI and P_{CO_2} are obtained by running the SOLMINEQ88 software. Monitoring sites of 1–8 are indicated in Fig. 2

If the CO_2 from the endogenic CO_2 source is considered as x percent of the total CO_2 content in Baishuitai springs, then the biological CO_2 contributes $(100-x)$ percent. Therefore, according to mass conservation of isotope, one has:

$$x\delta^{13}\text{C}_{\text{soil CO}_2} + (100 - x)\delta^{13}\text{C}_{\text{endogenic CO}_2} = 100\delta^{13}\text{C}_{\text{CO}_2}$$

Therefore, $x \approx 14$, i.e., 14% of the total CO_2 content in Baishuitai springs comes from soil CO_2 , and the other (86%) is endogenic, possibly related to a mixture of metamorphic and mantle CO_2 sources (Liu and others 1993, 1995, 1997, 2000). The existence of the endogenic CO_2 source explains why the Baishuitai spring water has such high concentrations of CO_2 , $[\text{HCO}_3^-]$ and $[\text{Ca}^{2+}]$; and, the latter provides abundant material source for travertine deposition.

Formation process of the Baishuitai travertine

The spring water at Baishuitai is near equilibrium with respect to calcite, and slightly undersaturated with respect to calcite (saturation index < 0 , Table 1). This would seem to be unfavorable to travertine formation. However, as the spring water emerges, a large amount of CO_2 is released from the water to the atmosphere due to the much higher CO_2 partial pressure of water than that of atmosphere (less than 40 Pa). After about 500 m downstream, the CO_2 partial pressure of water decreased from 14,400 Pa to

300 Pa, pH increased from 6.61 to 8.10, and the calcite saturation index increased from near zero in the spring to more than 1.0. Correspondingly, calcium carbonate, the travertine's major component, is deposited. With the deposition of travertine along the stream bed, the concentration of Ca^{2+} and HCO_3^- of water decreases from 200 and 700 mg/l to 110 and 480 mg/l, respectively (Fig. 3). The changes above are also reflected in the stable carbon isotopic composition of travertine. As shown in Table 2, from active travertine pool No.5 to No.10 (with the height difference of about 8 m and horizontal distance about 6 m), the $\delta^{13}\text{C}$ increases from 3.62 to 4.98‰. The increase of $\delta^{13}\text{C}$ of travertine is due to CO_2 degassing, which preferentially releases $^{12}\text{CO}_2$, with the resultant travertine becoming enriched as one moves downstream. This phenomenon was also found in active travertine on tree branches in a canal constructed in November 1999. As seen in Table 2, from the active travertine on tree branch No.B-1 to No. B-6 (separated by about 2 km, Fig. 1), $\delta^{13}\text{C}$ increased from 3.71 to 6.04‰. Moreover, after groundwater emerged, the water changed from a closed system to open to the atmosphere. Thus, its hydrochemistry and isotope characteristics experience not only spatial change, but also remarkable temporal change. Figure 4 shows the diurnal variations in pH, conductivity and temperature recorded at site No.9, about 500 m downstream of the springs (Fig. 2). All parameters show

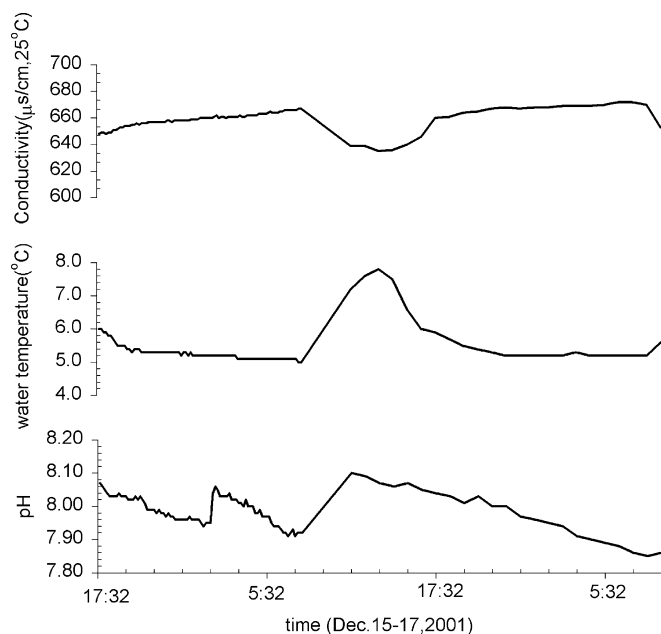


Fig. 4

Diurnal Change in temperature, pH and electrical conductivity of downstream flowing water at the monitoring site No.9 in Fig. 2

distinct diurnal changes. The decrease in temperature at night is obvious and expected. However, this is likely to affect the degassing rate of CO_2 , which should be lower at night because its solubility increases. Consequently, the pH drops, which theoretically should decrease calcite supersaturation levels and therefore calcite precipitation. This, in turn, should lead to an increase in the concentrations of calcium and bicarbonate ions in solution, and thus the conductivity of the water. At daytime, the contrary situation occurs, i.e. temperature and pH increase, and conductivity drops. It can be inferred from this finding that travertine deposition takes place mainly at daytime, particularly under sunny conditions.

Variations in water temperature recorded by Baishuitai travertines

According to ages (Table 2), the sampled Baishuitai travertines can be divided into three categories as follows:

1. the old travertine, including 41 samples with ages of 2,530–2,570 years:
2. the older travertine, including also 41 samples with ages of 1,970–2,010 years:
3. active travertine, i.e., the others except categories (1) and (2) in Table 2.

It can be seen from Table 2 that there is remarkable difference in stable oxygen isotopic composition among the three categories of travertines: the old travertine has the lowest $\delta^{18}\text{O}$ (mean, -15.32‰), the active travertine has the highest $\delta^{18}\text{O}$ (mean, -12.39‰), and the older travertine is in the middle (mean, -14.48‰). This indicates that the travertine-forming water temperature decreased with time. From the difference in stable isotopic composition of the travertines, variations in water temperature can be estimated.

O'Neil and others (1969) found that if there is an oxygen isotopic exchange equilibrium between calcite precipitation and water, the following relationship prevails:

$$1000 \ln \alpha_{\text{calcite-water}} = 2.78 \times 10^6 / T^2 - 2.89$$

$$\text{where } 1000 \ln \alpha_{\text{calcite-water}} \approx \delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}$$

According to Song and others (1994), $\delta^{18}\text{O}_{\text{water}}$ is -44.15‰ (PDB). Suppose this value does not change during the process of travertine deposition, the travertine-forming water temperatures can be calculated by using the formula above. They are 23, 19 and 10 °C for the old travertine, the older travertine and the active travertine, respectively. (The consistency between the calculated and actual present temperature proves that the oxygen isotopic exchange equilibrium assumption for the calculation is reasonable.) This may reflect, on one hand, the effect of strong neotectonic uplift of the area (up to 900 m in 200 ka; Zhao and others 1998), and on the other hand the decreasing effect of geothermal source on water temperature. However, the influence of the uplift during recent 2,500 years should be very small due to the short time compared to 200 ka. Therefore, the major decrease in water temperature was attributed to less intensive geothermal activity in the area during the last 2,500 years.

The problems in paleoenvironmental reconstruction with endogene travertine

Problems in ^{14}C dating of endogene travertine

The principle of ^{14}C dating of travertine is as follows: Before the deposition of travertine, ^{14}C in water is active in the natural exchange cycle, i.e., the content of ^{14}C in water is the same as that in exchangeable carbon reservoir. With the beginning of deposition, travertine no longer has exchange with this reservoir (e.g. the atmosphere and water). Because there is no replenishment of ^{14}C , the original radio ^{14}C decreases by a decay law, and timing begins. The formula for dating is:

$$t = -8033 \ln(A_{\text{SN}}/A_{\text{ON}})$$

where A_{ON} and A_{SN} are specific radioactivities of ^{14}C in the exchangeable reservoir and sample t years after the end of exchange, respectively (Stuiver and Polach 1977).

Therefore, a prerequisite for ^{14}C dating is that there is radio ^{14}C in the measured sample.

However, for endogene travertine, such as the travertine at Baishuitai, there is almost no ^{14}C , because the dissolution of old carbonate rock (with no ^{14}C in it) was mainly driven by endogenic source CO_2 , which also has no ^{14}C . This is considered to be "dead carbon" (Chen and others 1988). Thus, it is impossible to determine the real age of such travertine with the ^{14}C dating method. If there is ^{14}C in the travertine, the ^{14}C is from the exchange with atmosphere or/and biosphere after deposition. Thus, the age of travertine determined by this kind of ^{14}C is questionable

(Chen and others 1988). For example, for the old travertine mentioned above, the ^{14}C age of 18,000 to 18,800 years was determined, which is much higher than those (2,530–2,570 years) by TIMS dating method (Table 2). Valero-Garces and others (1999) also noted that the dilution effect by large quantities of ^{14}C -free CO_2 hinders accurate ^{14}C chronology of the lake records based on lacustrine organic matter and aquatic plants. This situation shows the necessity and importance of clarifying whether the travertine is endogenic or meteorogenic (associated with atmospheric and soil CO_2 ; Pentecost 1995) before ^{14}C dating. For endogene travertine, TIMS-Uranium dating may be a better choice than radiocarbon dating (Yong and Benson 1988; Hall and Henderson 2001).

Problems in paleo-vegetation reconstruction with stable carbon isotopes of endogene travertine

Biological effects, variations in carbon source inputs, and variations in the exchange rate with atmospheric CO_2 are commonly considered to be the main controls on the carbon isotope values of travertine. However, the geochemical evidence presented above favors physical process CO_2 -degassing as an important control on ^{13}C enrichment. This finding, coupled with the discussion on the origin of the Baishuitai travertine, indicates that the endogenic CO_2 source at Baishuitai, and the physical fractionation may have a greater significance than commonly accepted to explain travertine carbon isotope records. Similar results were also obtained by Melezhik and Fallick (2001). This situation shows that one has to be careful in paleo-vegetation reconstruction when using $\delta^{13}\text{C}$ data of the endogene carbonate deposits.

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