



Wet-dry seasonal variations of hydrochemistry and carbonate precipitation rates in a travertine-depositing canal at Baishuitai, Yunnan, SW China: Implications for the formation of biannual laminae in travertine and for climatic reconstruction

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ABSTRACT

Biannually laminated freshwater carbonate deposits (tufas and travertines) are potential sources of high-resolution terrestrial paleoclimate data. In order to understand the processes of carbonate precipitation, the formation of the biannual laminae in endogenic (thermogene) travertine, and the characteristics of the climate information recorded in them, the seasonal variations of hydrochemistry and carbonate precipitation rates in a travertine-depositing canal at Baishuitai, Yunnan, SW China were investigated. Plexiglass substrates (5 cm × 5 cm × 0.5 cm) for carbonate collection were placed in the flowing water at ten sampling sites in the canal and replaced semimonthly for one hydrological year, to determine the rates of carbonate precipitation. Water temperature, pH and specific conductivity at these sampling sites were measured daily in situ throughout the year. From these data the concentrations of Ca²⁺, HCO₃⁻, the calcite saturation index and CO₂ partial pressure were derived. The hydrochemistry and rate of carbonate precipitation at all sites displayed the same clear seasonal pattern, lower in the warm rainy season and higher in the cold dry season. The lower solute chemical concentrations and carbonate precipitation rates in the rainy season were due to the dilution of ground water concentrations by overland flow after rainfall. The endogenic travertine had much clearer biannual lamination structure than is normal in the epigenic tufa in Japan. The lamina consisted of a thin dark porous warm-rainy-season layer alternating with a thick light dense cold-dry-season layer: in contrast, a thick, dark and dense summer–autumn layer alternates with a thin, light and porous winter–spring layer in any biannual lamina found in normal epigenic tufa that is controlled mainly by the change of temperature and CO₂. The biannual lamination in the thermogene travertine was primarily controlled by changes in the dilution-dominated carbonate precipitation rate, the darker color of the warm-rainy-season layer being due to soil-derived clay and organic matter introduced by the overland flow. This study thus demonstrates that rates of carbonate precipitation and the formation of lamination in the travertine at Baishuitai were controlled chiefly by a climatic factor (rainfall), which has implications for using the fossil travertine at the site to reconstruct the climate in the past. Additionally, it shows that differences in rate-controlling mechanisms of carbonate precipitation must be considered when using epigenic tufa and endogenic travertine to reconstruct the paleoclimate and paleoenvironmental parameters (temperature + CO₂ vs. rainfall).

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1. Introduction

Travertine and tufa are chemical sedimentary deposits that are precipitated from flowing waters that become supersaturated with calcite due to degassing of CO₂ (Liu et al., 1995; Pentecost, 1995; Ford and Pedley, 1996; Liu et al., 2003; Yoshimura et al., 2004; Pentecost, 2005). They have porous textures consisting of microgranular calcite, which normally encrusts filamentous microbionts (mainly cyanobac-

teria) and, in many cases, displays biannual laminations (millimeter to centimeters in thickness) that reflect seasonal changes in water chemistry, cyanobacterial growth and hydrology of the depositional environment (Chafetz et al., 1991; Matsuoka et al., 2001; Kano et al., 2003, 2004; Andrews and Brasier, 2005; Kawai et al., 2006; Liu et al., 2006a; O'Brien et al., 2006; Kano et al., 2007; Hori et al., 2008; Kandianis et al., 2008; Kawai et al., 2009). Therefore, freshwater tufa and travertine can provide valuable paleoclimatic and paleoenvironmental information with high temporal resolution, up to seasonal, monthly or even daily in density (Hennig et al., 1983; Chafetz and Folk, 1984; Pentecost, 1995; Ford and Pedley, 1996; Andrews et al., 1997; Ihlenfeld et al., 2003; Kano et al., 2003, 2004; Andrews and Brasier, 2005; Andrews, 2006; Liu et al., 2006a; O'Brien et al., 2006;

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Kano et al., 2007; Hori et al., 2008; Takashima and Kano, 2008; Brasier et al., 2009; Lojen et al., 2009).

However, the relationship between biannual lamination and the hydrochemistry and carbonate precipitation rate must be determined before tufas or travertines can be confidently used as paleoclimatic tools. Most of the previous studies cited above have focused on the processes and seasonal patterns of annual laminations in epigenic (meteoric water or meteogene) tufa where the CO_2 is sourced from soil and atmosphere (Ford and Pedley, 1996) and have paid little attention to endogenic (thermogene) travertine where the CO_2 may derive from a range of sources including hydrolysis and oxidation of reduced carbon, decarbonation of limestone, or directly from deep crust or upper mantle (Ford and Pedley, 1996; Minissale et al., 2002; Crossey et al., 2009). The purpose of this study was to measure and analyse the seasonal variations of hydrochemistry, carbonate precipitation rates and formation of biannual laminae in a travertine-depositing canal at Baishuitai, Yunnan, SW China, and to understand the climatic implications of their deposition (Liu et al., 2003). This study improves upon work reported earlier from the Baishuitai site (Liu et al., 2006a) because that of 2006 (i) utilised only meteorological data from Shangri-La Town, which is ~ 100 km distant from and ~ 800 m higher in altitude than the study area, so that relationships between travertine lamina and meteorological measurements were indirect and speculative; (ii) used low resolution (seasonally) monitoring of the hydrochemistry and carbonate precipitation rates, insufficient to reveal details of the carbonate precipitation and the formation of biannual laminae, and (iii) had only one travertine sample, so it was not possible to answer such a question “Are the discoveries site-specific or not?”. This study offers better site-specific meteorological data, high resolution (daily or semi-monthly) monitoring of the hydrochemistry and carbonate precipitation rates, and a broader sample base. Therefore, it constitutes a continuation and intensification of the 2006 work that ensures that the findings and explanation are sound and sufficient.

2. General setting of the study area

Baishuitai is located ~ 100 km south of Shangri-La Town, in Yunnan Province, in the southwest of China. The elevation ranges from 2380 m to 3800 m above sea level (asl). The area is characterized by a subtropical monsoon climate, with $>75\%$ of the annual precipitation (~ 750 mm) occurring during the rainy season from May to October, and an annual mean air temperature of 8°C (Liu et al., 2003). Although Baishuitai lies in the subtropics it has four climatic zones:

warm-temperate zone at 2200–2500 m asl, temperate at 2500–3000 m, cold-temperate at 3000–3500 m and a frigid zone above 3500 m. Because of these climatic variations, the natural vegetation at Baishuitai also has distinct vertical zonation, i.e., from evergreen shrubs at 2200–2500 m, *Pinus yunnanensis* forests at 2500–3000 m, spruce forests at 3000–3500 m, to fir forests above 3500 m.

The endogenic travertine examined in this study was being deposited in a dug canal (2.5 km in length that descends from 3000 to 2500 m asl, a difference of 500 m). It is supplied chiefly by spring S1-3 (Fig. 1, Liu et al., 2003). The width of the canal is from 60–70 cm and the depth is 8–15 cm; the flow rate in it varies between 50 and 70 l/s.

The canal headwater sources changed following a heavy flood on July 7, 2006 while the study was still in progress. Before the flood, they were a mixture of S1-3 spring water with that of Baishui River, a surface stream with lower concentrations of Ca^{2+} and HCO_3^- , and mean specific conductivity $488 \mu\text{s}/\text{cm}$ in the rainy season, and $668 \mu\text{s}/\text{cm}$ in the dry season. On July 7, 2006, the connection between the canal and Baishui River was destroyed, and from this time onwards the canal was supplied only by spring S1-3, which has higher values of specific conductivity, $[\text{HCO}_3^-]$, $[\text{Ca}^{2+}]$ and pCO_2 (Table 1). There were almost no macroscopic algal mats or biofilms in the canal, so the effect of aquatic photosynthesis can be ignored.

The discharge of spring S1-3 was perennial but varied slightly (~ 50 – 60 l/s) in response to the monsoonal rainfall distribution. The spring drains a karst catchment with the area of ~ 10 km² consisting of Middle Triassic limestone and Lower Triassic shale and sandstone. The area is covered with 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 (evergreen shrubs, fir, spruce, and pine trees). There are ~ 3 km² of fossil travertine deposits within the karst area. Modern endogenic travertine deposition occurs only along the canal and downstream of springs S1-1 and S1-2 (Liu et al., 2003, 2006a,b). Epigenic tufa deposits are absent at Baishuitai due to the cold climate caused by the high altitudes (>2500 m).

3. Methods

3.1. Installation and collection of plexiglass substrates and measurement of modern travertine precipitation rates

In order to obtain the modern travertine (carbonate) precipitation rates, plexiglass collector substrates measuring $5\text{ cm} \times 5\text{ cm} \times 0.5\text{ cm}$

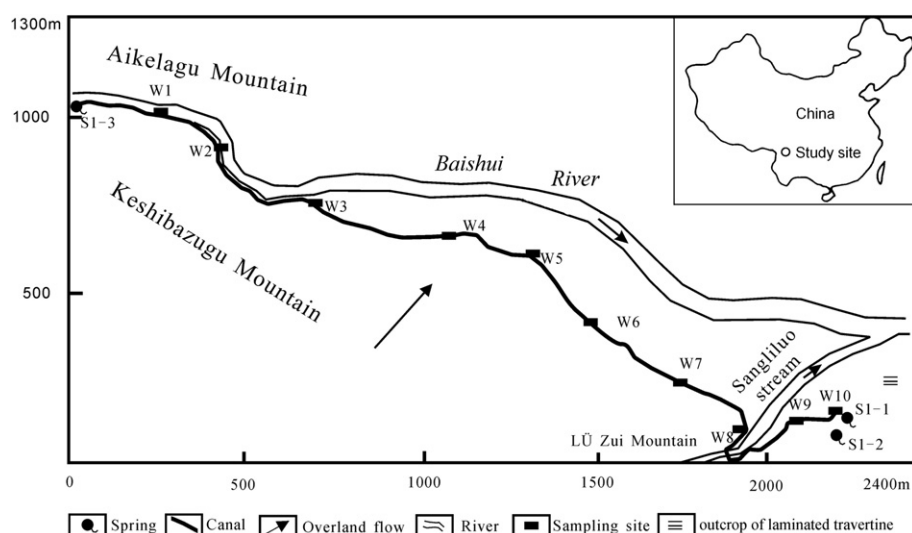


Fig. 1. Distribution of the sampling sites in the travertine-depositing canal of Baishuitai, Yunnan, SW China. Note: there is a bridge with the canal near site W8, so the canal crosses the Sangliu stream.

Table 1
Hydrochemical compositions of the Spring S1-3.

Sampling date ^a	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)	pH	Water temp. (°C)	SpC (μs/cm, 25 °C)	SI _c ^b	PCO ₂ ^c (ppmv)
Nov.4, 2006	0.41	4.24	176.71	13.21	2.59	606	11.53	7.11	7.0	852	0.35	35481
Dec.2, 2006	0.49	4.51	181.16	13.51	2.65	616	11.87	6.98	6.9	874	0.23	48978
Feb.5,2007	0.42	3.93	174.46	14.88	2.47	610	10.72	6.86	7.0	877	0.10	63096
Mar 19,2007	0.49	5.96	169.87	14.82	2.72	616	10.60	6.91	7.1	873	0.14	57544
Apr.24,2007	0.49	7.45	171.24	15.38	2.67	610	10.92	7.03	7.1	860	0.26	42658

^a Spring water samples in the warm rainy season were not taken because of the access problem.

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

^c calculated CO₂ partial pressure of water by WATSPEC (Wigley, 1977).

(with an aggregate surface area of 60 cm² each) were mounted in the flowing water, at ten sites (W1 to W10) along the canal (Fig. 1, Liu et al., 1995). The substrates were replaced every fifteen days. The amount of travertine deposited on them was determined by measuring the weight increase of the plexiglass substrates. Before immersion and after collection each plexiglass substrate was dried at 50 °C for a period of 24 h and weighed. The carbonate precipitation rate (R) was calculated by:

$$R = (W_{ts} - W_s) / A * T$$

where W_{ts} and W_s are the weight of the plexiglass substrates after and before each experimental run respectively, A is the overall surface area of the substrate (60 cm²) and T is the exposure time for carbonate to precipitate on the plexiglass substrate for each run (~15 days).

3.2. Measurement of the water chemistry

Water temperature, pH and specific conductivity at each sampling site were measured in-situ daily with a hand-held water quality data logger, Model WTW 350i, with resolution of 0.01 pH, 0.1 °C and 1 μs/cm, respectively. Probes were calibrated prior to use with pH 7 and pH 10 buffers.

Values of [HCO₃⁻] and [Ca²⁺] were calculated by the linear relationship between them and specific conductivity (SpC) obtained by Liu et al. (2006b): [Ca²⁺] = 0.24 × SpC - 5.58 and [HCO₃⁻] = 0.72 × SpC - 7.813.

To measure the chemistry more accurately, water samples at the sampling sites were collected by syringes with 0.45 μm Minisart® filters and analyzed in the laboratory semi-monthly for the hydrological year, April 2006–April 2007. The water sample containers were thoroughly cleaned in the laboratory and then rinsed in the canal water and, wherever possible, sealed while still under water to avoid any contact with the atmosphere. The analytical methods used were standard titration for HCO₃⁻, atomic absorption for K⁺ and Na⁺, titration with EDTA for Ca²⁺, Mg²⁺ and SO₄²⁻, and Mohr titration for Cl⁻ (Liu et al., 2007).

3.3. Rainfall recording

The rainfall was recorded every 15 min with a CTD300 rain gauge at spring S1-1; measurements are within 4% in error (Liu et al., 2007). The data were stored on a Greenspan CTD300 multi-channel data logger installed at the spring.

3.4. Estimating CO₂ partial pressure and the calcite saturation index from water temperature, pH and specific conductivity

The full hydrochemical data sets, including recorded temperature and pH, calculated concentrations of Ca²⁺ and HCO₃⁻, and monthly mean concentrations of K⁺, Na⁺, Mg²⁺, Cl⁻ and SO₄²⁻, were processed with the program WATSPEC (Wigley, 1977), which calculates

CO₂ partial pressure (pCO₂) and calcite saturation index (SI_c) for each record (Liu et al., 2006b). pCO₂ was obtained from:

$$pCO_2 = \frac{(HCO_3^-)(H^+)}{K_H K_1} \quad (1)$$

where K_H and K_1 are the temperature-dependent Henry's Law and first dissociation constants for CO₂ gas in water, respectively.

SI_c was calculated from:

$$SI_c = \log \left(\frac{(Ca^{2+})(CO_3^{2-})}{K_c} \right) \quad (2)$$

where activities are denoted by brackets, and K_c is the temperature-dependent equilibrium constant for calcite dissociation. If SI_c > 0, water is supersaturated with respect to calcite, and calcite could deposit; if SI_c < 0, water is aggressive to calcite, and calcite dissolution could happen; and if SI_c = 0, the equilibrium is reached.

4. Results and explanations

4.1. General hydrochemical compositions of the Baishuitai Spring S1-3

Table 1 gives the general hydrochemical composition of Baishuitai Spring S1-3, which feeds the canal. Ca²⁺ was the major cation, with molarity percentage of >85%, and HCO₃⁻ the major anion (molarity percentage >95%). Thus, the hydrochemical type was HCO₃-Ca, which reflects the control of the middle Triassic limestone bedrock in the spring catchment area (Liu et al., 2003). The spring had high concentrations of Ca²⁺ and HCO₃⁻, and high pressures of CO₂, which was endogenic in origin according to Liu et al. (2003). According to Sun (2008), the springs at Baishuitai show no seasonal variations in hydrochemistry that are due to the endogenic origin of CO₂. The low spring temperature of ~7 °C is mainly due to the high altitudes (>3500 m) of the recharge area of the spring.

4.2. Seasonal variations of canal water chemistry

Fig. 2 shows the hydrochemical variations at sampling sites W4 and W7 between April 25, 2006 and April 20, 2007 (see Appendix A for the data). It can be seen that all chemical properties at both sites display seasonal changes. For example, at W4, during the period, May 16–31, 2006, as the warm rainy season was commencing SpC decreased from 707 μs/cm to 418 μs/cm, [HCO₃⁻] from 501 mg/l to 293 mg/l, [Ca²⁺] from 164 mg/l to 94 mg/l, and pCO₂ from 1977 ppmv to 1140 ppmv. As the rainfall amount increased gradually, there was synchronous decrease in SpC, [HCO₃⁻], [Ca²⁺] and pCO₂, caused chiefly by the dilution effect of overland flow during the rains. Following some reduction in the rains, June 1–30, a general increasing trend can be seen in these geochemical properties (Fig. 3) due to the decrease of the dilution effect. However, SpC, [HCO₃⁻], [Ca²⁺] and pCO₂ increased

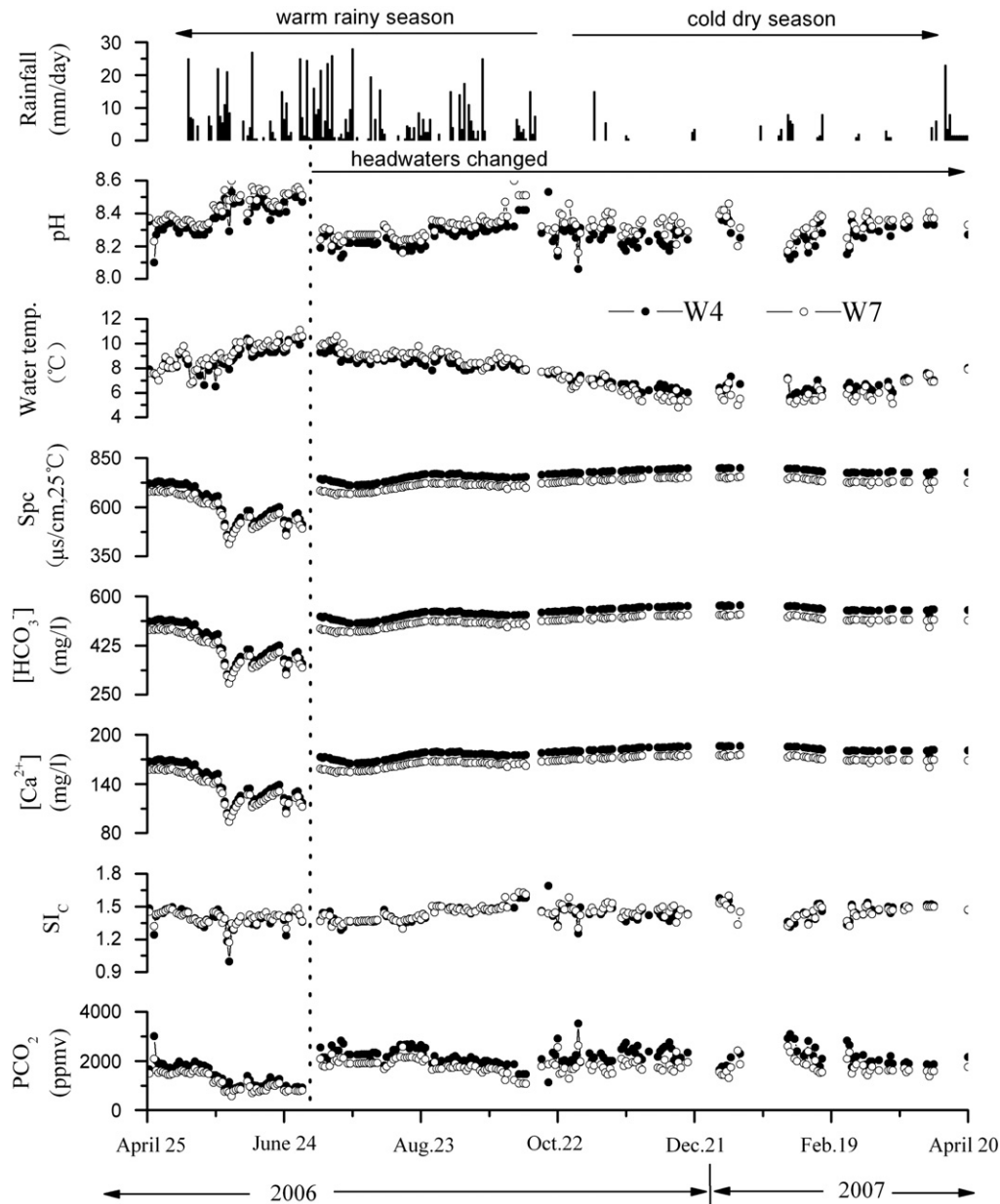


Fig. 2. Hydrochemical variations at sample sites W4 and W7 along the Baishuitai travertine-depositing canal during the hydrological year. Note: water temp., pH and SpC are logged temperature, pH and specific conductivity of water respectively by the data logger; $[\text{HCO}_3^-]$ and $[\text{Ca}^{2+}]$ are the concentrations of bicarbonate and calcium respectively calculated by their linear relationship with specific conductivity; SI_c and pCO_2 are the saturation index of calcite and CO_2 partial pressure of water computed by running the WATSPEC program (Wigley, 1977).

abruptly after July 7, 2006 because of the change (avulsion) of the headwaters of the canal as noted above.

Fig. 2 shows that the canal water temperature also had very clear seasonal variations, ranging from 5.6 to 10.5 °C. It was high in the warm rainy season and low in the cold dry season, reflecting the ambient air temperature. Values of pCO_2 , SpC and concentrations of Ca^{2+} and HCO_3^- in the warm rainy season were lower. However, this was not caused by any temperature-induced carbonate precipitation but reflects the effect of dilution by Baishui river water and overland flow in the rainy season, because the carbonate precipitation rate was also lower in this season due to dilution, as shown below.

After canal repairs on July 7, the source waters feeding the canal changed from both Spring S1-3 and Baishui River to Spring S1-3 only. From this time onwards, the dilution effects became much weaker because there was only overland flow diluting the ground water. For example, at site No.4, there was a jump of conductivity (SpC) from 511

to 743 $\mu\text{s}/\text{cm}$ just after the headwaters changed on July 7, showing about 45% decrease in intensity of dilution. Apart from the very clear seasonal change in water temperature, which was controlled mainly by the ambient air temperature as stated above, Fig. 2 shows much weaker seasonal changes in SpC, Ca^{2+} and HCO_3^- concentrations after July 7, reflecting the weakened dilution.

4.3. Seasonal variations in the carbonate precipitation rates on the plexiglass substrates

To simplify the explanation, we use sampling sites W4 and W7 as examples of the travertine deposition at upstream and downstream sites in the canal, respectively. Fig. 4 shows the carbonate precipitation rates on the substrates, the coeval rainfall amounts and average water temperatures, $[\text{Ca}^{2+}]$ and SI_c at the two sampling sites over the sample hydrologic year. It is seen that four distinct periods can be defined: (1) a

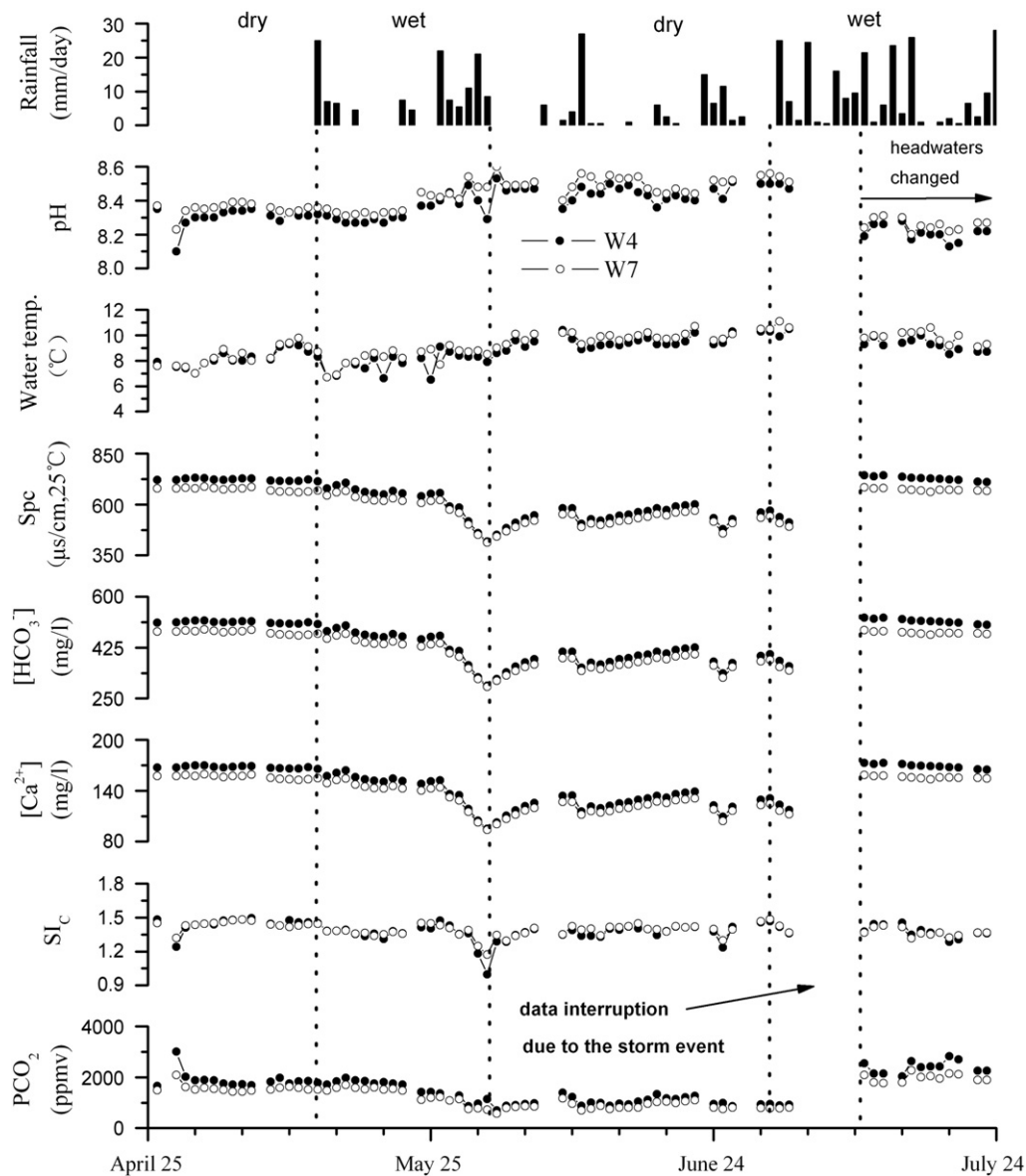


Fig. 3. Hydrochemical variations at sample sites W4 and W7 along the Baishuitai travertine-depositing canal from April 25 to July 24, 2006. Note: water temp., pH and SpC are logged temperature, pH and specific conductivity of water respectively by the data logger; $[\text{HCO}_3^-]$ and $[\text{Ca}^{2+}]$ are the concentrations of bicarbonate and calcium respectively calculated by their linear relationship with specific conductivity; SI_c and pCO_2 are the saturation index of calcite and CO_2 partial pressure of water computed by running the WATSPIC program (Wigley, 1977).

period of increasing dilution and (2) of decreasing dilution in the warm rainy season, followed by (3) a period of decreasing temperature and (4) of increasing temperature in the cold dry season (Fig. 4).

In the warm rainy season, carbonate precipitation rates on the plexiglass substrates at the two sites all show the control of rainfall, i.e., decreasing as dilution increases, and increasing again as the dilution falls off (Fig. 4). The decrease of the carbonate precipitation rates was related to the decrease of $[\text{Ca}^{2+}]$ and SI_c in the canal water caused by dilution by overland flow after rainfall, as discussed in Section 4.2 (refer to Fig. 2).

In contrast, in the cold dry season, carbonate precipitation rates at the two sites all show control by temperature, i.e., decreasing in the period of declining temperature, and increasing again as the temperature rises, though the differences in precipitation rate were not very large in the cold season (Fig. 4). The reason for the temperature control is two-fold. First, temperature controlled the rate constant of calcite precipitation (Dreybrodt, 1988; Liu and Dreybrodt, 1997). For example, where ε (diffusion boundary layer thickness) = 0.01 cm, δ (water depth) = 10 cm, and $\text{pCO}_2 = 1000$ ppmv, conditions which are similar to this case study, α (the rate constant) increases from 2.15 to 3.28 cm/s

when water temperature increases from 5 to 10 °C (Liu and Dreybrodt, 1997). Temperature also controls the release of CO_2 from water. It is generally accepted that higher temperatures produce more CO_2 release from water, which drives more calcite deposition.

It will be noted that the change of headwaters after July 7 increased the carbonate precipitation rate due to the higher concentrations of $[\text{Ca}^{2+}]$ and $[\text{HCO}_3^-]$ in the canal water (Figs. 2 and 4). This is possibly the reason why the carbonate precipitation rate in the 15-day late July experimental run did not decrease further but increased a little although the highest rainfall was recorded during that run and lowered the SI_c value (Fig. 4).

5. Discussion

5.1. Rainfall and temperature controls of seasonal variations in carbonate precipitation rates

Chemical processes associated with tufa/travertine deposition have been comprehensively reviewed, as noted above (Dreybrodt, 1988;

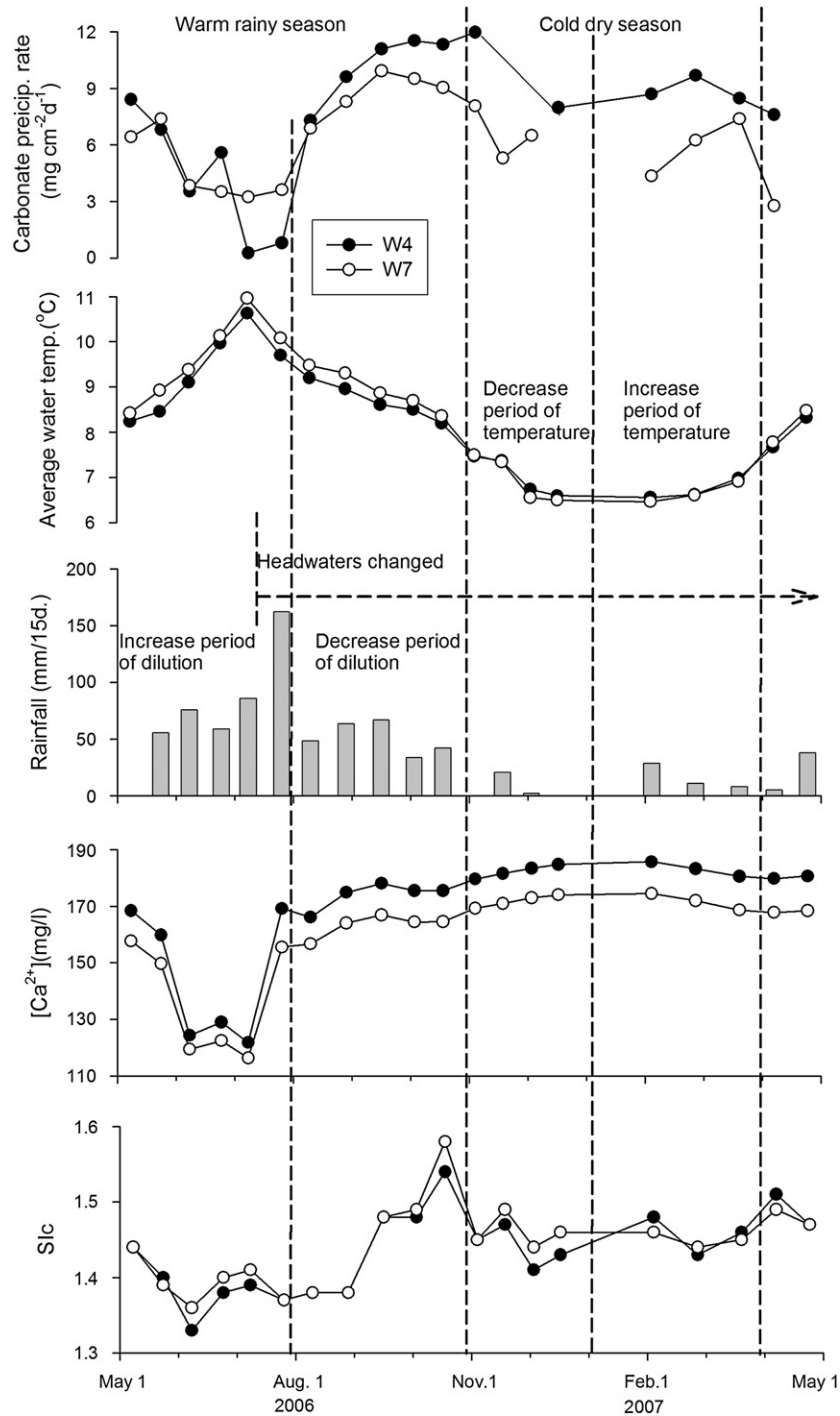


Fig. 4. Seasonal variation in carbonate precipitation rates on the plexiglass substrates at sampling sites W4 and W7 of Baishuitai and its relation with rainfall, water temperature, $[Ca^{2+}]$ and Slc. Note: the water temperature, $[Ca^{2+}]$ and Slc and rainfall are the average and the total in each experimental run.

Pentecost, 1995; Ford and Pedley 1996; Pentecost, 2005). It has been suggested that the most fundamental requirement for carbonate precipitation is supersaturated water with high concentrations of $[Ca^{2+}]$ and $[HCO_3^-]$ plus high flow turbulence (Dreybrodt, 1988; Liu et al., 1995). The depositional system at Baishuitai conforms to these requirements (Liu et al., 2003). On the other hand, temperature and rainfall can influence carbonate precipitation by impacting various physicochemical processes, such as in/outgassing of CO_2 as we have shown above.

To further examine their effects, Figs. 5 and 6 show the relationship between carbonate precipitation rate and rainfall and temperature respectively at sampling site W4 before and after the source waters changed on July 7, 2006.

It can be seen that there was a negative correlation between the carbonate precipitation rate and the rainfall amount, but that the slope of the line and correlation coefficient before July 7 are higher than those after July 7, showing the reduced dilution effect after the headwaters changed (Fig. 5). This is reasonable because only overland flow contributed to dilution after July 7, while both Baishui River and the overland flow contributed before that date.

There is also a negative correlation between the carbonate precipitation rate and water temperature although this was very weak after July 7 (Fig. 6). Such correlation was unexpected because the carbonate precipitation rate should increase with increasing temperature (Dreybrodt, 1988). The reason for the negative correlation is

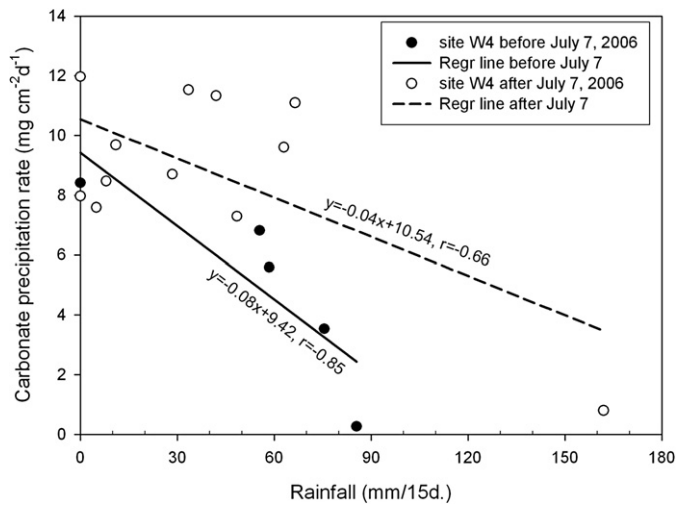


Fig. 5. Relationship between the carbonate precipitation rate and the coeval rainfall at the sampling sites W4 before and after the headwaters changed on July 7, 2006.

possibly that dilution effects counteract and dominate temperature effects. Therefore, in order to show the temperature effect on the carbonate precipitation rate, one has to check the case without a strong dilution effect. Fig. 7 shows the relationship between carbonate precipitation rates and temperature at sampling site W4 in both the rainy season after the headwaters changed on July 7, 2006, and in the ensuing dry season. It is clearly seen that there was a positive correlation between carbonate precipitation rate and temperature in dry season, evidencing the temperature control. However, there was an even stronger negative correlation between carbonate precipitation and water temperature in the rainy season after the headwaters changed, due to the dilution effect of rainfall overwhelming any temperature effect.

The controlling mechanism of variations in hydrochemistry and carbonate precipitation rates at Baishuitai is different from that found by Kano et al. (2003) and Kawai et al. (2006), who examined epigenic tufas in SW Japan. The concentration of dissolved CaCO_3 in tufa-depositing streams in Japanese studies, 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. Therefore, the seasonal

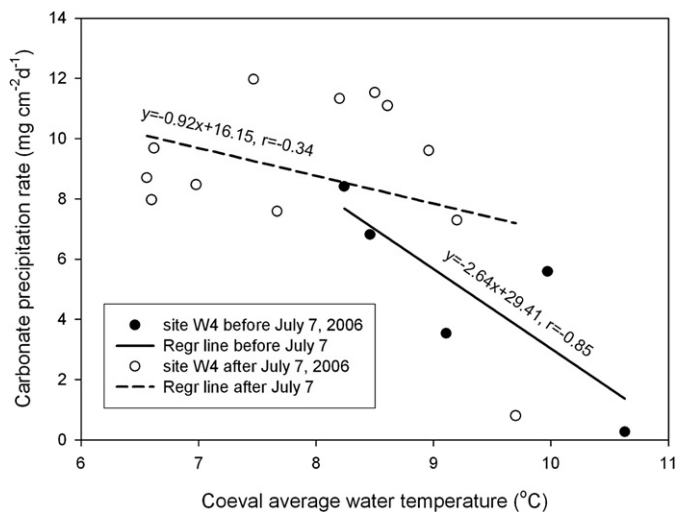


Fig. 6. Relationship between the carbonate precipitation rate and the coeval average water temperature at the sampling sites W4 before and after the headwaters changed on July 7, 2006.

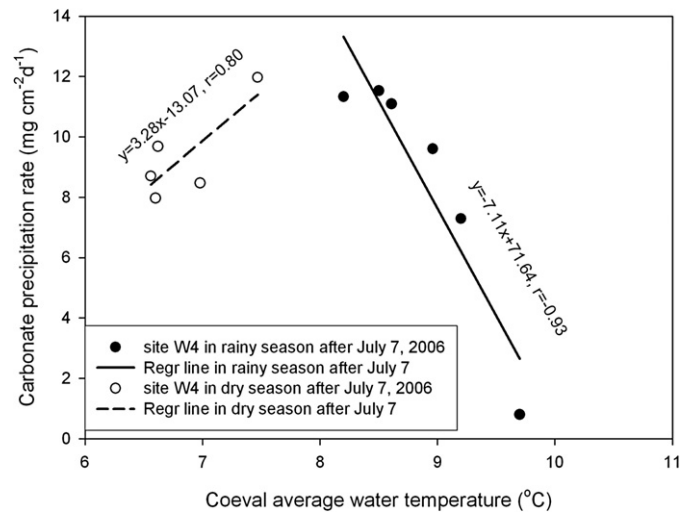


Fig. 7. Relationship between the carbonate precipitation rate and the coeval average water temperature at the sampling sites W4 in both the rainy season after the headwaters changed on July 7, 2006, and in the ensuing dry season.

precipitation rate was high in summer–autumn and low in winter–spring. However, the CO_2 from endogenic (thermogene) travertine is sourced from a range of situations, including hydrolysis and oxidation of reduced carbon, decarbonation of limestone or directly from the upper mantle (Ford and Pedley, 1996; Minissale et al., 2002; Crossey et al., 2009). Therefore, the source water in endogenic karst system is rich in free CO_2 , Ca^{2+} and HCO_3^- (Liu et al., 1995, 2003). Due to the higher concentrations of free CO_2 , Ca^{2+} and HCO_3^- in endogenic systems than in epigenic systems, seasonal dilution by rainfall can become one of major factors controlling changes of carbonate precipitation rates in an endogenic CO_2 -sourced system. Baishuitai is just such a case of endogenic karst (Liu et al., 2003). Therefore, the difference in the controlling mechanisms of carbonate precipitation rates must be considered when using epigenic tufa and endogenic travertine to reconstruct paleoclimate and paleoenvironment records (temperature + CO_2 vs. rainfall).

5.2. Formation of the biannual laminae in travertine and their climatic implications

At Baishuitai, laminated travertines were found both in the canal (Liu et al., 2006a) and near springs S1-1 and S1-2 (Figs. 8, 1). The endogenic travertine has much clearer lamination structure than the epigenic tufa found in Japan (Kano et al., 2003; Kawai et al., 2009). However, the laminae in the travertine consisted of alternating thin dark porous layers and thick light dense layers, which is the reverse of what the Japanese researchers have previously reported (Matsuoka et al., 2001; Kano et al., 2003, 2004, 2007; Kawai et al., 2009). For instance, the tufa of Shirokawa, SW Japan, was made up of densely calcified summer–autumn laminae and lightly calcified winter–spring laminae. This aspect of seasonal lamination was inferred to be related to changes in the rate of carbonate precipitation (Kano et al., 2003) as stated above. Kano et al. (2003) thought that the increased precipitation rate in summer–autumn stimulated thick calcite encrustation on cyanobacterial filaments to produce the dense textures, which was supported by the lowered organic/inorganic carbon-production ratio in summer–autumn. However, Kano et al. (2003) also noted that a reversed pattern could result from local and climatic circumstances.

In order to understand the seasonal timing of the layering in the endogenic travertine at Baishuitai, some plexiglass substrates were placed in the flowing waters at sampling sites W3, W7 and W9 for one year from Apr. 23, 2006 to Apr. 23, 2007. It was found that all



Fig. 8. Section of the sampled travertine near the spring S1-1. Visible is the alternation of thin dark porous warm-rainy-season layers and thick light dense cold-dry-season layers. A couplet comprising a thin and a thick layer represents one annual cycle.

travertines deposited on the substrates displayed clear seasonal layering patterns. As an example, Fig. 9 shows the travertine collected at site W9. It is seen that it exhibits laminated textures similar to those seen in Fig. 8, i.e., one annual lamina (couplet) consists of a thin dark porous layer and a thicker light dense layer. The travertine growth began on April 23, 2006, and ceased on April 23, 2007. Therefore, the thin dark porous layer (6 mm thick) would have formed in the warm rainy season when the carbonate precipitation rate was decreased by the dilution effect of overland flow as shown above, and the thick light dense layer (10 mm thick) formed in the cold dry season when the

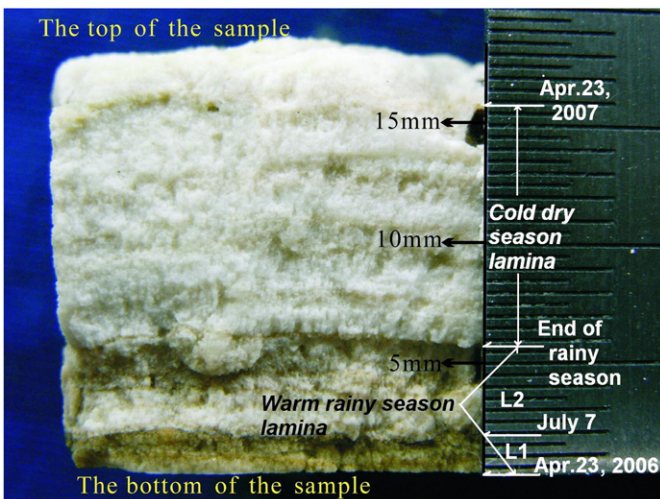


Fig. 9. Modern biannual laminated travertine deposited on the plexiglass substrate at the sampling site W9 from April 23, 2006 to April 23, 2007 in the Baishuitai canal.

carbonate precipitation rate was higher because of the lack of dilution effect (Fig. 9). It is interesting to note that due to the change in the source waters on July 7, 2006, two distinct sub-layers (L1 and L2) were formed in the warm rainy season (Fig. 9). Sub-layer L1 formed from April 23 to July 7, 2006, and sub-layer L2 between July 7 and the end of the warm rainy season of 2006. Because the intensity of dilution before July 7 was higher than after, the carbonate precipitation rate in the L1 of ~0.8 mm/month was lower than that in L2 (~1.0 mm/month). The darker color of L1 than L2 also indicates stronger soil loss induced by the stronger dilution effect before the headwaters changes on July 7. These examples clearly show the difference in the seasonal timing of layering between the endogenic travertine at Baishuitai and the epigenic tufa in Japan. The latter typically accretes a thick dark dense layer in summer–autumn and a thin light porous layer in winter–spring. This difference comes from the difference in the rate-determining process of carbonate precipitation as explained in Section 5.1 (dilution effect vs. CO₂ + temperature effect). The darker color of the warm-rainy-season lamina was related to soil-derived clay and organic matter introduced by overland flow, which is evidenced by organic matter content 2 to 4 times higher in the darker layer than the lighter layer (9.82–16.49 ppm vs. 4.22–4.76 ppm). There was no or little contamination with clay or organic matter in the dry season and therefore, the lamina is relatively pure and appears lighter (white) color. This seasonal color change of the travertine at Baishuitai has been observed directly by us in the field. In Fig. 10 it is seen that the color of the travertine in the rainy season was dark brown, and in Fig. 11 that it was white in the dry season.

6. Conclusions

By examining seasonal variations in hydrochemistry and carbonate precipitation rates in a travertine-depositing canal at Baishuitai, Yunnan, SW China, over the course of one hydrological year it was found that both display clear seasonal patterns, which were similarly low in warm rainy seasons and high in cold dry seasons. The lower solute chemical concentrations and thus lower carbonate precipitation rates in warm and rainy seasons are mainly related to the dilution effects of overland flow following rainfall.

It was also found that the Baishuitai endogenic travertine had much clearer biannual lamination structure than typical epigenic tufa. However, the biannual lamina in the travertine consisted of a thin dark porous warm-rainy-season layer and a thick light dense cold-dry-season layer, in contrast to the thick dark dense summer–autumn layer and thin light porous winter–spring layer reported in normal epigenic tufa where deposition is controlled mainly by the temperature and CO₂



Fig. 10. The color of travertine at Baishuitai on October 29, 2008 (in warm rainy season) was yellow due to the soil-derived clay and organic matter introduced by the overland flow in the warm rainy season.



Fig. 11. The color of travertine at Baishuitai on February 21, 2007 (in cold dry season) is white.

change. The biannual lamination in the travertine was primarily controlled by changes in the dilution-dominated rate of carbonate precipitation, and the darker brown color of laminae was related to the soil-derived clay and organic matter introduced by overland flow in the warm rainy season. This study demonstrates that carbonate precipitation rates and the formation of lamination in the travertine at Baishuitai were mainly controlled by climate (e.g., rainfall), which has implications for using the fossil travertine at the site to reconstruct rainfall history in the past. Additionally, this study shows that the difference in controlling mechanisms of carbonate precipitation rate must be considered when using epigenetic tufa and endogenic travertine to reconstruct paleoclimate and paleoenvironmental parameters (temperature + CO₂ vs. rainfall).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemgeo.2010.02.027.

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