Seasonal Variations of Hydrochemistry and Carbonate Precipitation Rate in a Travertine-Depositing Canal at Baishuitai, Yunnan, SW China: Implications for the Formation of Biannual Laminae in Travertine and Climatic Reconstruction

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1 Introduction

Travertine or tufa is a chemical sedimentary deposit that is precipitated from spring-fed stream water supersaturated with calcite due to CO2-degassing (Liu et al. 1995; Pentecost 1995; Ford and Pedley 1996). These deposits have biannual laminations which could provide valuable paleoclimatic and paleoenvironmental information with high resolution (Liu et al. 2006; Kano et al. 2007; Brasier et al. 2009; Lojen et al. 2009).

However, the relationship between hydrochemistry and carbonate precipitation rate must be determined before tufas or travertine can be confidently used as paleoclimatic tools. The purpose of this study is to examine seasonal variations of hydrochemistry, carbonate precipitation rates and formation of biannual lamination in a travertine-depositing canal at Baishuitai, Yunnan, SW China, and to understand the processes and seasonal pattern of biannual lamination in travertine and the climatic implications of these laminae of the endogenic travertine (Liu et al. 2003, 2006).

2 General Settings of the Study Area

Baishuitai is located in ~ 100 km south of the Shangri-La Town, Yunnan Province, SW China. The elevation ranges from 2380 m to 3800 m ASL. The area is charac-

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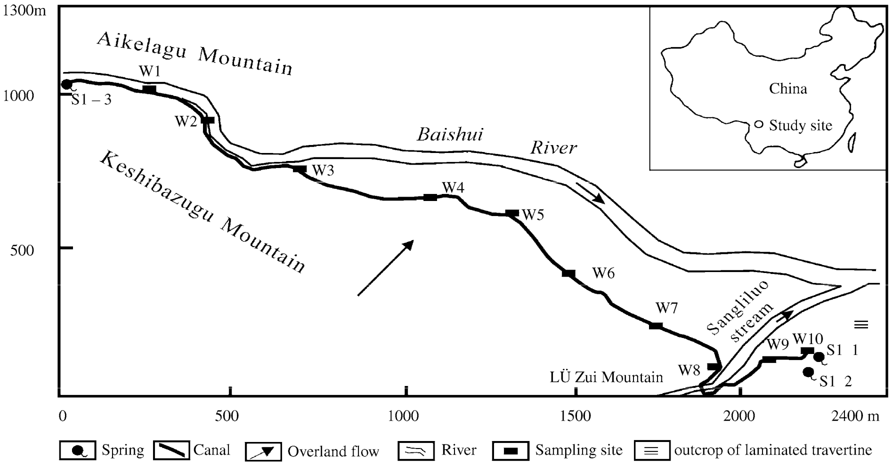

Fig. 1 Distribution of the sampling sites in the travertine-depositing canal of Baishuitai, Yunnan, SW China

terized by a subtropical monsoon climate, with $>75\%$ of the annual precipitation (~ 750 mm) occurring during the rainy season from May to October and annual mean air temperature of 8 °C (Liu et al. 2003).

The endogenic travertine for this study is deposited in a canal which was supplied mainly by the spring S1-3 (Fig. 1). The canal headwaters were changed after a heavy flood on July 7, 2006. They were supplied by both the spring S1-3 and the surface river-Baishui River (with lower concentration of Ca^{2+} and HCO_3^-) before July 7, 2006. However, on July 7, 2006, the connecting path between the canal and Baishui River was destroyed by the flood, and from this time on the canal was only supplied by the spring S1-3, which had high values of specific conductivity, [Ca^{2+}], [HCO_3^-] and pCO_2 (Liu et al. 2003).

3 Methods

In order to obtain modern travertine precipitation rates, the plexiglass substrates (5 cm × 5 cm × 0.5 cm) for depositing travertine were placed in the flowing water. The substrates were substituted semimonthly and the travertine deposited on the substrates were collected and weighted to obtain the carbonate precipitation rates.

Water temperature, pH and specific conductivity of water at each sampling site were measured in-situ daily with hand-held water quality data logger (WTW 350i), with resolutions of 0.01 pH, 0.1 °C and 1 μs/cm, respectively. In situ titrating was used to measure the [Ca^{2+}] and [HCO_3^-] of water semimonthly with Aquamerck Alkalinity Test and Hardness Test.

4 Results and Explanations

4.1 Seasonal Variations of Canal Water Chemistry

Figure 2 shows the hydrochemical variations at sampling sites W4 and W7 from April 25, 2006 to April 20, 2007. All the chemical properties of both W4 and W7 show seasonal changes. [HCO_3^-], [Ca^{2+}], specific conductivity (spc) and pCO_2 de-

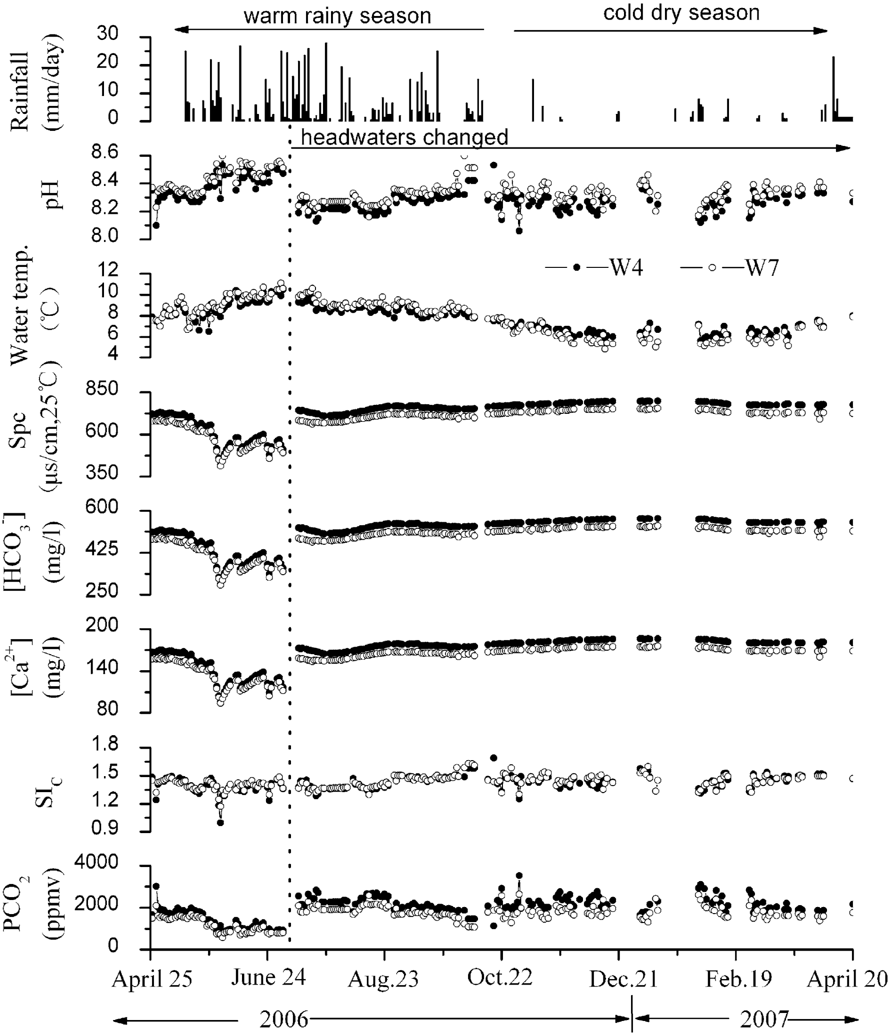

Fig. 2 Hydrochemical variations at sample sites W4 and W7 along the Baishuitai travertine-depositing canal during the hydrological year

creased gradually in the rainy period from May 13, 2006 to May 31, 2006 (Fig. 3). The period belonged to beginning of the warm rainy season at Baishuitai and the rainfall amount increased gradually, so the synchronous decrease in spc, [HCO_3^-], [Ca^{2+}] and pCO_2 were mainly caused by the dilution effect of overland flow in the rainy season.

Figure 2 shows that the canal water temperature also had very clear seasonal variations. Temperatures were high in the warm rainy season and low in the cold dry season. However, the lower values of pCO_2, spc and concentrations of Ca^{2+} and HCO_3^- in the warm rainy season were not caused by the temperature-induced carbonate precipitation, but reflected the effect of dilution by the Baishui River water and the overland flow in the warm rainy season, because the carbonate precipitation rate was low in the warm rainy season due to the dilution effect as showed later.

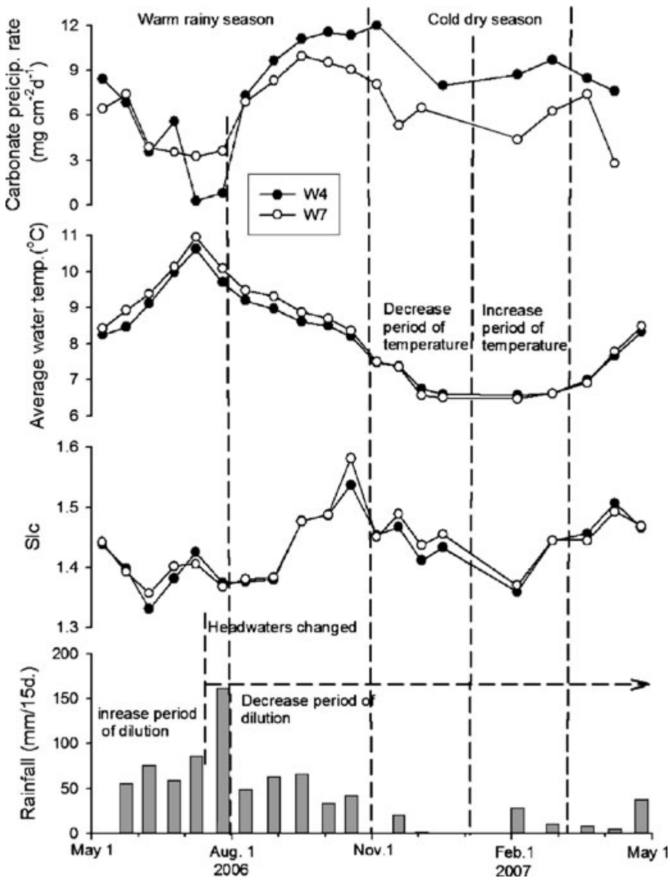

Fig. 3 The seasonal variation in carbonate precipitation rates on the plexiglass substrates at sampling sites W4 and W7 of Baishuitai and its relation with rainfall and water temperature

4.2 Seasonal Variations in the Carbonate Precipitation Rates and Formation of the Biannual Laminae in Travertine

Figure 3 shows the carbonate precipitation rates on the plexiglass substrates, the coeval rainfall amount and the coeval average water temperature at the two sampling sites against the time series. It is seen that four time periods can be defined: (1) the increase period of dilution and (2) the decrease period of dilution in warm rainy season, and (3) the decrease period of temperature and (4) the increase period of temperature in cold dry season.

In the warm rainy season, carbonate precipitation rates at the two sites all showed control of rainfall, i.e., decreased in the increase period of dilution, and increased in the decrease period of dilution (Fig. 3). The decrease of the carbonate precipitation rates was related to the decrease of [HCO_3^-] and [Ca^{2+}] in canal water caused by the dilution effect of the overland flow after rainfall as discussed in Sect. 4.1 (Fig. 2).

However, in cold dry season, carbonate precipitation rates at the two sites all showed control of temperature, i.e., decreased in the decrease period of temperature, and increased in the increase period of temperature (Fig. 3).

In order to understand the seasonal timing of the layering in the endogenic travertine at Baishuitai, plexiglass substrates were placed in the flowing waters at the sampling site W9 for one year from April 23, 2006 to April 23, 2007. Figure 4 shows the travertine collected at the sampling site W9. It is seen that the travertine exhibits one annual lamina (couplet) consists of a thin dark porous layer and a thick light dense layer.

The travertine grew from April 23, 2006, and stopped on April 23, 2007. Therefore, the thin dark porous layer (6mm thick) should form in the warm rainy season when the carbonate precipitation rate was decreased by the dilution effect of over-

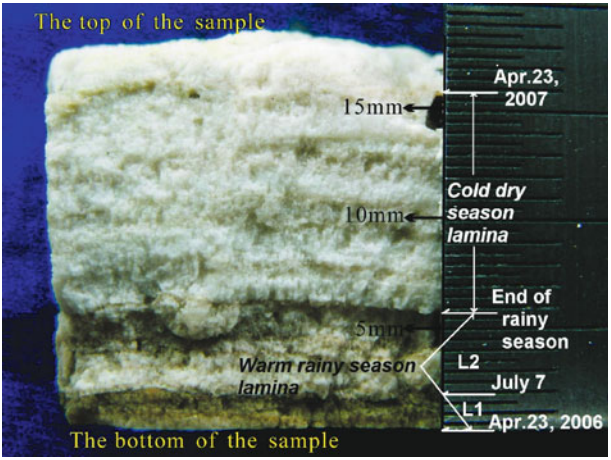

Fig. 4 The modern biannual laminated travertine deposited on the plexiglass substrate at the sampling site W9 from April 23, 2006 to April 23, 2007 in the Baishuitai canal

land flow as stated before, and the thick light dense layer (10 mm thick) formed in the cold dry season when the carbonate precipitation rate is higher because of the lack of dilution effect. The dark-color of the warm-rainy-reason lamina was possibly related to the soil-derived clay and organic matter introduced by the overland flow in the warm rainy season. On the other hand, there was no or little contamination of the clay and organic matter in dry season. Therefore, the cold-dry-season lamina is relatively pure and appears lighter (white) color.

5 Conclusions

By examining the seasonal variations in hydrochemistry and carbonate precipitation rates in a travertine-depositing canal at Baishuitai, Yunnan, SW China, it was found that the hydrochemistry and carbonate precipitation rates in the travertine-depositing canal show clear seasonal patterns, which were similarly low in warm rainy seasons and high in cold dry seasons. The lower hydrochemical compositions and thus lower carbonate precipitation rates in warm and rainy seasons are mainly related to the dilution effect of the overland flow after rainfall, showing the control of rainfall on the hydrochemistry and thus the carbonate precipitation rate.

It was also found that the endogenic travertine had much clearer biannual lamination structure. The biannual lamination in the travertine was primarily controlled by changes in the dilution-dominated rate of carbonate precipitation, and its darker brown color of laminae was possibly related to the soil-derived clay and organic matter introduced by the 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).

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