

Geochemical and isotopic characteristics of spring water and travertine in the Baishuitai area (SW China) and their implications for paleoenvironmental reconstruction

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1. Method

A method of combining *in situ* hydrochemical titrating (Photo 1) with measurement of stable carbon and oxygen isotopes was used to reveal the geochemical and isotopic characteristics in the Baishuitai travertine scenic area of SW China (Figures 1 and 2; Photos 2, 3, 4 and 5).



Photo 2 A far view of the Baishuitai travertine deposits



Photo 3 Travertine terrace fields on the right side of Baishuitai



Photo 1 In situ hydrochemical titrating at No.1 of the Baishuitai Springs

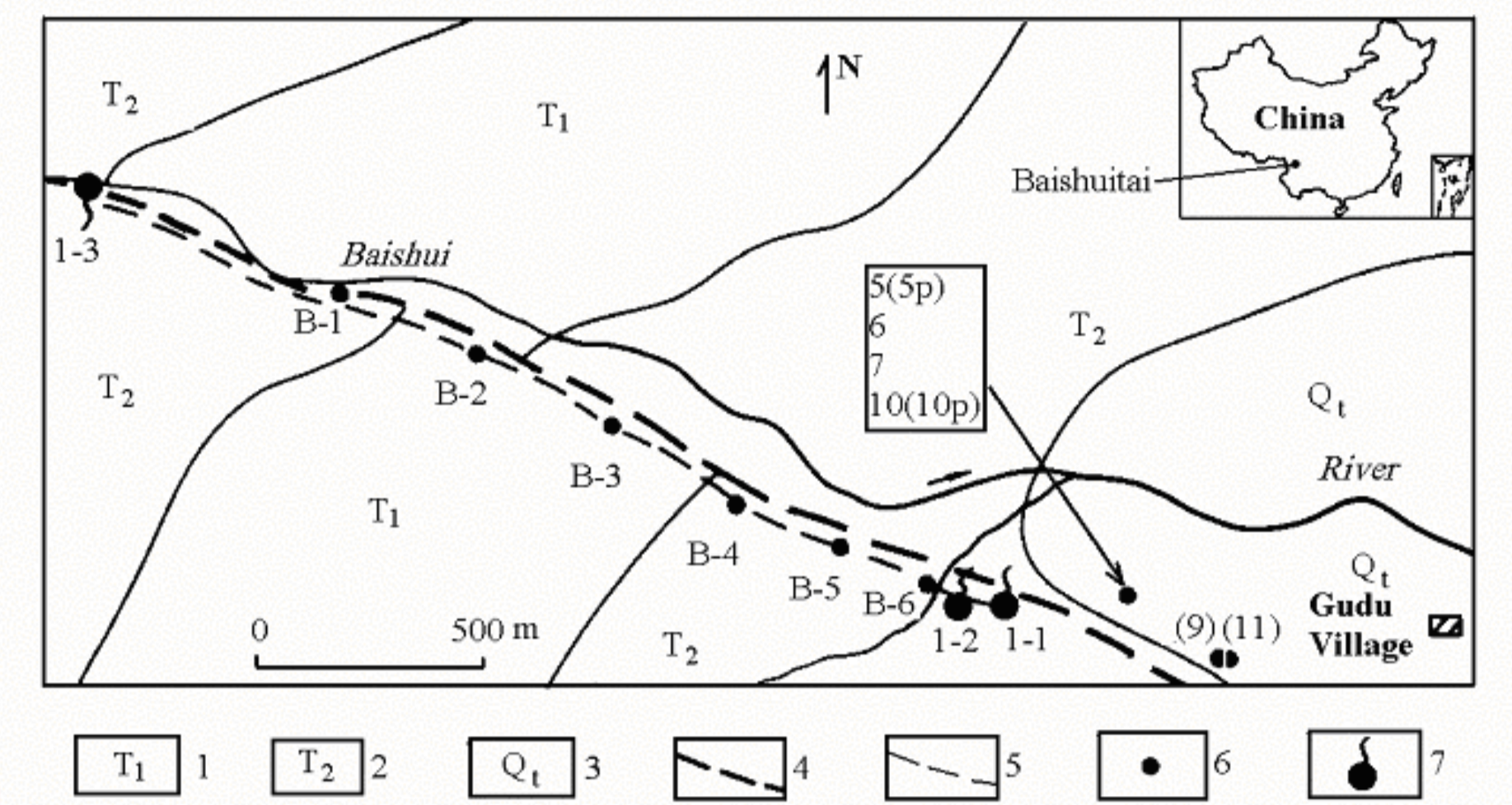


Fig. 1 Distribution of the Baishuitai springs and travertines.
1. Lower Triassic shale and sandstone, 2. Middle Triassic limestone, 3. Quaternary travertine, 4. Fault, 5. Canal, 6. Travertine sampling spots, 7. Spring

2. Major findings and discussions

2.1 The CO₂ source and relevant travertine are mainly endogenic

It was found that the travertine-forming springs have a very high concentration of calcium and bicarbonate, and accordingly very high CO₂ partial pressures (Table 1), which are not likely to be produced by biological activity in soil alone. Further analysis of the stable carbon isotopes of the springs (Table 1) 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.

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

Spr. 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
No.1-1	1.10	7.92	191.34	27.43	3.48	698.50	25.01	7.40
No.1-2	1.16	8.04	192.65	28.49	3.48	708.42	23.97	7.40
No.1-3	0.48	3.52	174.02	13.13	6.08	584.19	8.47	-

Spr. Name	Water Temp. (°C)	pH	Electrical conductivity (μs/cm)	SI ^a	Pco ₂ ^b (Pa)	δ ¹³ C _{DIC} ^c (‰, PDB)
No.1-1	10.7	6.61	990	-0.03	14400	-1.27
No.1-2	10.9	6.53	1009	-0.10	17560	-1.18
No.1-3	7.2	6.95	863	+0.16	5552	-

^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, the equilibrium reaches.

^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.

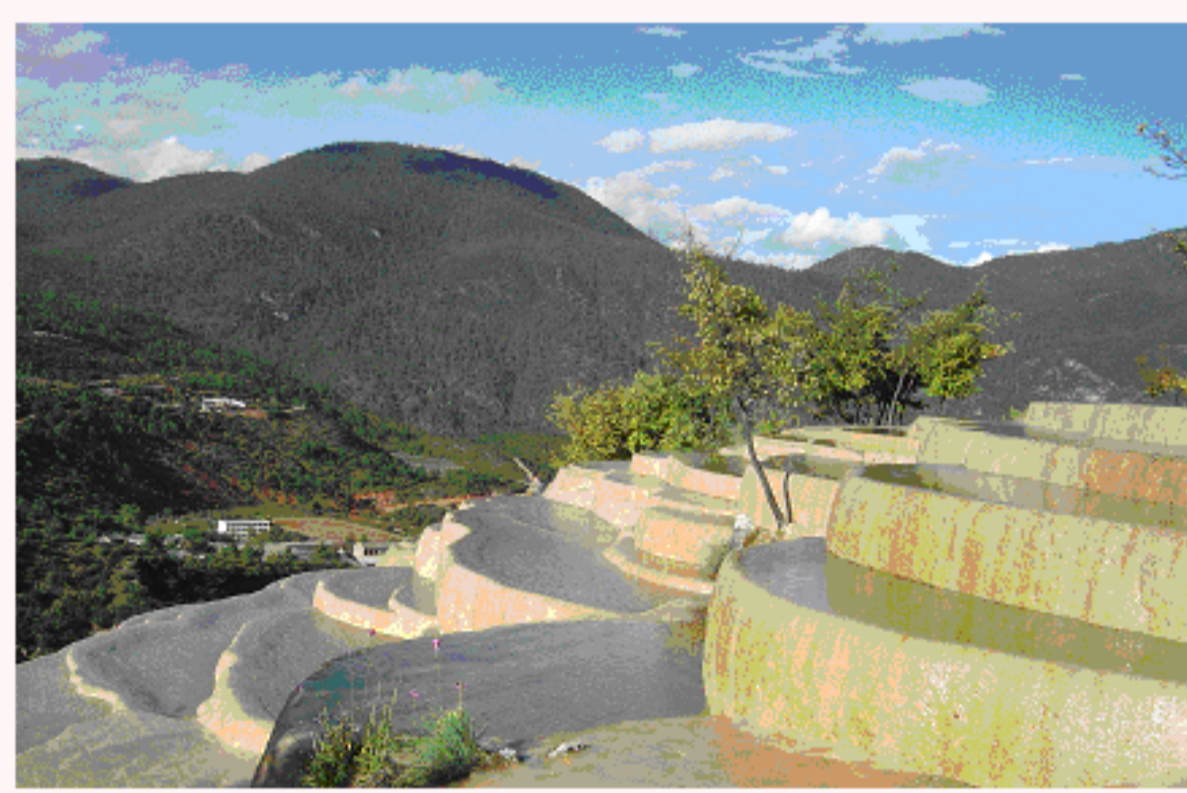


Photo 4 Travertine terrace fields on the left side of Baishuitai



Photo 5 The annual laminated structure of Travertine at Baishuitai

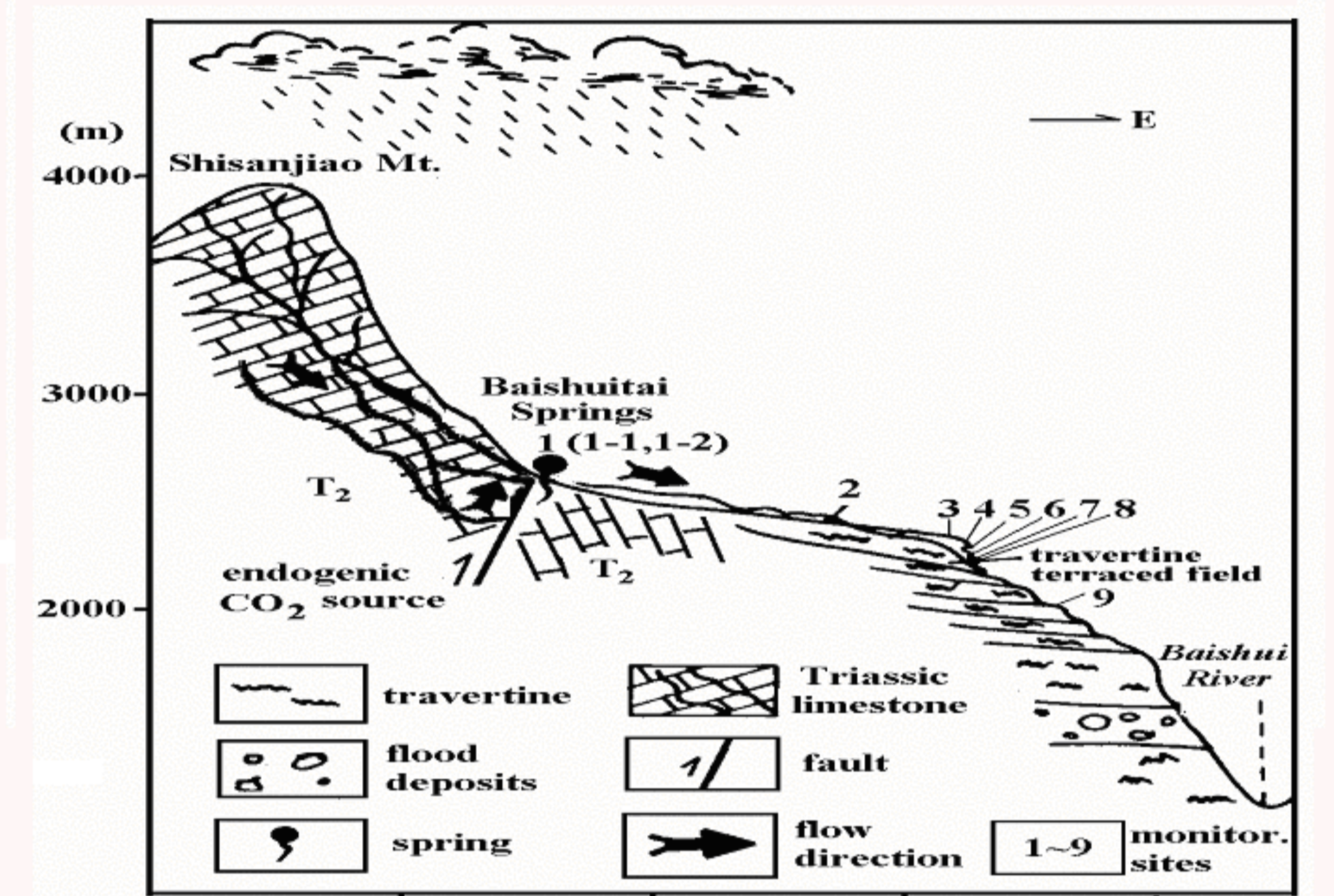


Fig. 2 Cross section showing the geological conditions for the origin and formation of the Baishuitai travertine (modified after Zhao and others 1998).
Sites: 1-Baishuitai spring, 2-flowing water 100m from the spring, 3 to 8-travertine pool No.5 to No.10 respectively

2.2 Spatial evolution of hydrochemistry and enrichment in ¹³C of travertine during CO₂-degassing

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 (Figure 3). The preferential release of ¹²CO₂ to the atmosphere results in a progressive increase of travertine δ¹³C downstream (Table 2).

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

Sample No.	Type of Samples	TIMS Ages (years) ^a	δ ¹³ C (PDB,‰)	δ ¹⁸ O (PDB,‰)
(9)-1~(9)-41	Old travertines ^a	2530~2570	2.18~4.12 (mean 3.15)	-14.65~-15.85 (mean -15.32)
(11)-1~(11)-41	Older travertine ^b	1970~2010	2.7~5.61 (mean 3.58)	-13.92~-15.41 (mean -14.48)
5p	Active travertine in pool ^c	≤1	3.82	-12.88
5	"	≤1	3.62	-12.85
6	"	≤1	3.64	-13.28
7	"	≤1	3.85	-12.66
10	"	≤1	4.98	-12.86
10p	Active travertine in pool ^c	≤1	5.67	-13.04
B-1	Active travertine on tree branch ^d	≤1	3.71	-12.18
B-2	"	≤1	3.88	-12.35
B-3	"	≤1	4.79	-11.96
B-4	"	≤1	5.01	-12.00
B-5	"	≤1	5.41	-11.71
B-6	"	≤1	6.04	-11.38

^aThe 41 samples were collected at the travertine sampling sites No.9 and No.11 in Figure 1, respectively.

^cSamples No. 5(5p), 6, 7, and 10(10p) are corresponding to monitoring sites No.3, 4, 5 and 8 in Figure 2 respectively.

^dThe samples were formed in a canal constructed in June of 1998, transmitting the Baishuitai Spring (No.1-3 in Figure 1) water saturated with calcite, to prevent the old travertine from weathering (Figure 1).

^{*}The dating was done by Dr. Cheng Hai in University of Minnesota, USA.

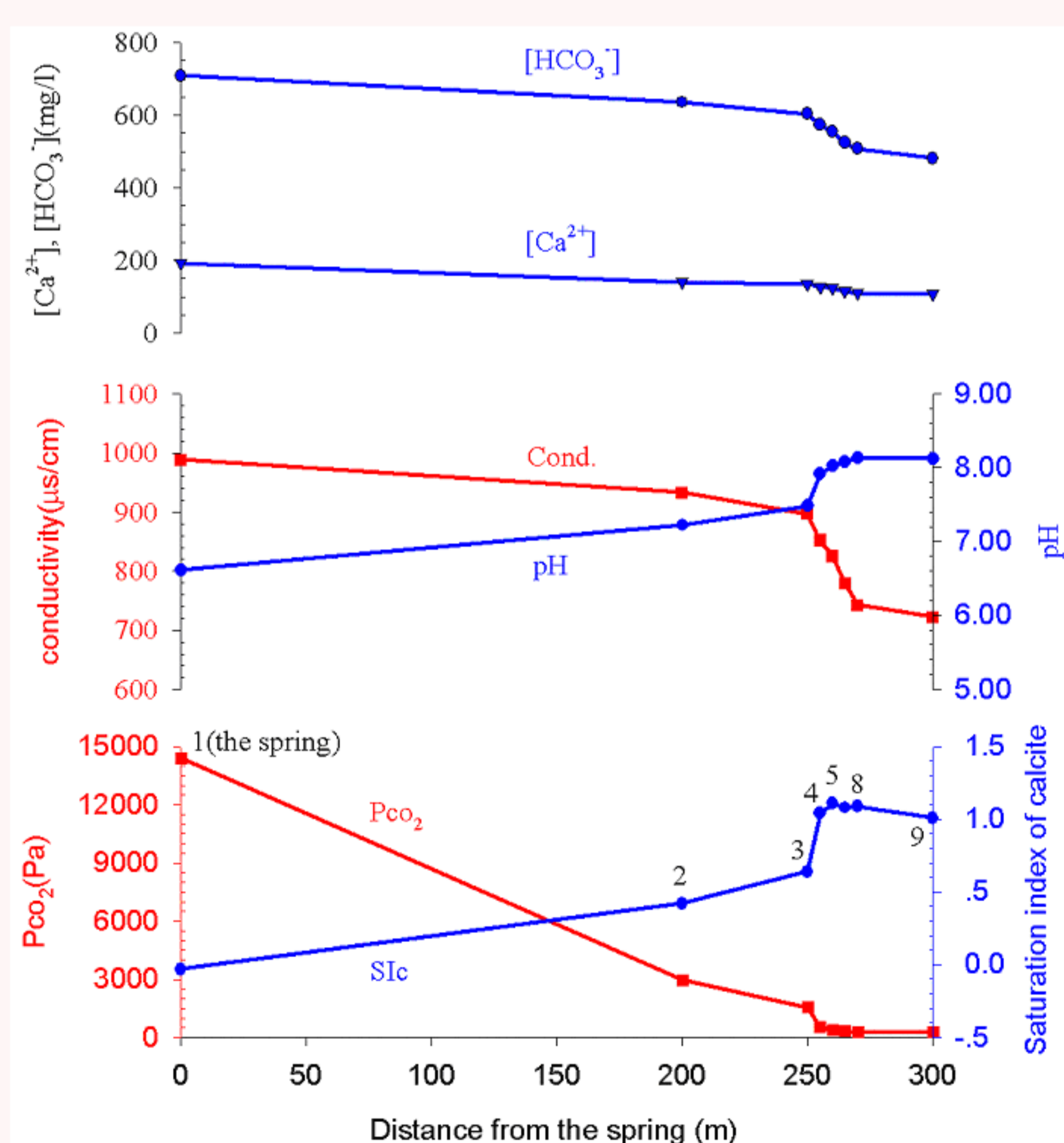


Fig. 3 Downstream hydrochemical evolution at Baishuitai.
Note: 1. [HCO₃]⁻, [Ca²⁺], pH and conductivity are those measured *in situ*, and SI and Pco₂ are obtained by running the SOLMINEQ88 software. 2. Monitoring sites of 1 to 8 are indicated in Figure 2.

2.3 ¹³C decrease in travertine-forming water temperature in the past 2500 years

According to differences in stable oxygen isotopic compositions of the travertine formed in different episodes at Baishuitai, it was found that the change in travertine-forming water temperatures 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.

2.4 The problems involved in paleoenvironmental reconstruction with endogene travertine

They are the impacts of "dead carbon" (including those in both limestone and CO₂ gas) in radiocarbon dating (so, uranium-series dating method is recommended!) 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 δ¹³C data of the endogene carbonate deposits (applying also to endogene speleothems in active tectonic areas).