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Analysis of Iodine Isotopes in Travertine from Baishuitai, Yunnan Province, China

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ABSTRACT: Travertine and tufa can be used as a high-resolution record for reconstructing the paleoclimate and paleoenvironment. It is not clear whether travertine is able to preserve the radionuclides for the reconstruction of modern human nuclear events. In this study, we developed and compared two sample preparation methods for the determination of ¹²⁹I and ¹²⁷I in travertine samples using direct acid dissolution and pyrolysis combustion. The analytical results of the levels of ¹²⁹I and ¹²⁷I as well as the ¹²⁹I/¹²⁷I ratios in travertine are presented here for the first time, and the hydrodynamic influence on the levels and distribution of iodine isotopes are discussed. It was found that the concentration of ¹²⁷I in travertine was low in the winter but high in the summer. This temporal variation of ¹²⁷I is likely related to the level and species of iodine in the water supply by mixing geothermal water

with rainfall, as well as the amount of iodine-containing impurity. The ¹²⁹I level clearly suggests that the Baishuitai travertine is endogenic and slightly affected by the amount of rainfall and biological impurities. The results of this study show that endogenic travertine can be used in reconstructing the influence of human nuclear activity with high resolution, and also imply that hypergenic tufa has great potential for such studies. Both archives have implications on the mechanism used for iodine incorporation into carbonate in the natural environment.



INTRODUCTION

Endogenic travertine and hypergenic tufa are calcareous deposits in freshwater and formed under a wide range of climatic conditions from cool temperature to semi-arid.¹ Travertine and tufa have a long depiction time span, and a clear microlayer structure with annual and quarterly resolution. Similar to lacustrine sediments and loess, they also act as important geological archives for the study of past climate changes because of their high resolution and sensitive record of the climate and the environment.^{2,3} In addition to the implications in paleoclimate and paleoenvironment reconstruction, it is likely that the travertine and tufa systems may record human activities, such as nuclear weapons testing, accidents and other civil nuclear uses that started in the 1950s. In turn, anthropogenic radionuclides originating from nuclear activities can potentially indicate the genetic type and deposition rate of travertine and tufa, as well as help to explain the evolution of the climate and the environment. Much data for

natural radioactive nuclides in travertine and tufa has been reported. For instance, cosmogenic radionuclides (14C and 10Be) as well as natural radionuclides (228Th, 228Ra, 234U and 238U) were obtained for dating and paleoclimate studies.^{4,5} However, no anthropogenic radioactive nuclides in travertine have vet been detected. The long-lived radioactive iodine isotope ¹²⁹I, with a half-life of 15.7 million years, is produced by nature mainly through fission of uranium in the earth, the reaction of cosmic rays with xenon in the air, and by human nuclear activity through fission of uranium and plutonium.⁶ More than 95% of ¹²⁹I in the environment is discharged by nuclear reprocessing plants.7 Globally, ¹²⁹I is transported through the earth's atmosphere and circulation of the oceanic currents.8,9 Travertine and tufa are likely intercalated with airborne and deposited iodine during their formation. Recently, iodine in marine bio-carbonaceous deposits was used as a proxy for ocean oxygenation events, ¹⁰ while iodine in terrestrial carbonate systems and its potential use is still not clear. Therefore, it is vital to investigate anthropogenic ¹²⁹I and natural stable ¹²⁷I in travertine and tufa for future human nuclear activity reconstruction and understanding the mechanism of how iodine is incorporated into carbonate deposits in the various natural environments.

A series of analytical methods for the determination of 129 I in solid samples have previously been developed $^{11-14}$ using pyrolysis combustion in combination with either solvent extraction or coprecipitation. However, the analytical procedure for 129 I in travertine samples has to be investigated due to its carbonaceous medium. Carbonate deposition should be easily digested by acid in solution. For instance, 17-20% H₃PO₄ was used to directly dissolve coral samples, then filtering the sample solution to remove the insoluble residue, and finally extracting the solid residue with CHCl₃ to purify iodine from the solution.^{15,16} Direct acid dissolution is a good choice for the analysis of carbonate samples since it is a simple method requiring less time and labor. On the other hand, because it is not known whether direct acid dissolution is suitable for freshwater-deposited travertine samples, the reliable pyrolysis combustion method was also applied.

In this work, two sample preparation methods will be used for the purpose of developing the analytical method for ¹²⁹I in travertine samples, coupled with accelerator mass spectrometry measurements. The level and source of radioactive ¹²⁹I and stable ¹²⁷I will be investigated in the travertine samples collected from Baishuitai, Yunnan, P.R. China, to show the potential use of travertine iodine isotopes for reconstructing the history and impact of human nuclear activities, and for establishing the deposition type and rate of travertine and tufa.

EXPERIMENTAL

Instruments and reagents. The experiments were performed using the 3 MV accelerator mass spectrometer (AMS, High Voltage Engineering Europa B.V., The Netherlands) and the Agilent 8800 ICP-QQQ-MS instrument (USA) at the Xi'an AMS Center, Institute of Earth Environment, CAS. The AMS analytical system consists of a cesium sputter negative ion source with a 50-target carousel, a 35 keV low energy injector, a 3 MV tandetron and acceleration tube with magnetic and electrostatic suppression, high energy magnetic-electrostatic-magnet analyzer, and gas ionization chamber detector ¹⁷.

Two ¹²⁹I standards with ¹²⁹I/¹²⁷I atomic ratios of 1.002×10⁻¹⁰ and 9.954×10⁻¹² in a medium solution of 0.40 mol L⁻¹ NaOH and 0.02 mol L⁻¹ NaHSO₃ were prepared by mixing a stock solution of NIST 4949c (National Institute of Standards and Technology, USA) with an ¹²⁹I-free iodine solution (Woodward Company, USA). The ¹²⁷I⁻ standard solution of 1000 mg L⁻¹ was purchased from Spex CertiPrep Group (USA) for iodine calibration by ICP-MS measurement. All chemicals used in this work were analytical grade reagents, and all solutions were prepared with deionized water (18.2 MΩ cm).

Sampling. Nineteen travertine samples were collected on 5cm×5cm×0.4cm plexiglass substrates, placed in travertinedepositing pools in Baishuitai (27°30'N, 100°02'E), Yunnan Province, SW China.¹⁸ The elevation of Baishuitai is from 2380 m to 3800 m ASL. These travertine samples were formed during 2006-2007. The samples were air dried, ground to fine powder and analyzed for iodine isotopes.

Sample preparation. Travertine is a carbonate deposit and can be dissolved in acid solution. Two methods, the direct acid dissolution and high temperature pyrolysis combustion, were used to extract the iodine isotopes from the travertine samples.

1) Acid dissolution. For ¹²⁹I analysis, 5-10 g travertine sample was weighed into a centrifuge tube and moistened with deionized water. 0.1 mL of 0.5 mol L⁻¹ NaHSO₃ was added to the samples to provide a reductive condition to avoid iodine loss during dissolution. 3.0 mol L⁻¹ HNO₃ was slowly added into each sample until the travertine sample was completely dissolved. The small amount of remaining residue was removed from the solution by filtration with 0.45 µm filter fiber.

2) Pyrolysis combustion. The detailed procedure for the separation of iodine from solid samples using combustion has been reported elsewhere.^{11,12,18} In brief, 5-10 g travertine samples were weighed into quartz boats, and 5 kBq of ¹²⁵I was spiked into each sample for monitoring the chemical yield. Iodine in the samples was separated from the matrix by combustion at 800°C in a four-tube pyrolyzer furnace and following the protocol in Table 1. Iodine was released in the form of molecular I₂ and trapped in 35 mL trap solution (0.4 mol L⁻¹ NaOH and 0.02 mol L⁻¹ NaHSO₃). 0.3 g of the trap solution was reserved for the determination of ¹²⁷I. 1.0 g of the solution was taken into a tube for ¹²⁵I measurement using a NaI gamma counter (Model FJ2021, Xi'an Nuclear Instrument Factory, P.R. China) to determine the

Step	Temperature of Zone 1 (°C)	Duration (min)	Temperature of Zone 3 (°C)	Injecting gas and ratio (v:v)	Flow rate (L min ⁻¹)
1	Room temp-250	20	Auto	N ₂ : O ₂ =1:1	0.2
2	250	10	Auto	N ₂ : O ₂ =1:1	0.2
3	250-400	30	Auto	N ₂ : O ₂ =1:1	0.2
4	400	20	Auto	N ₂ : O ₂ =1:1	0.2
5	400-800	40	800	O_2	0.2
6	800	60	800	O_2	0.2

Table 1. Temperature Protocol for Pyrolysis Combustion of Travertine (Modified from Luo et al.¹⁹)

Table 2. Optimized Operating Parameters of the ICP-INIS and AIVIS Systems at the AT an AIVIS Center	Table 2.	Optimized	Operating	Parameters	of the ICP-	MS and A	AMS Sy	stems at the	Xi'an A	MS Center ¹⁴
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ICP-MS	8800 series (Agilent)	AMS	3 MV (HVEE)
RF power	1480 W	Energy of Cs-sputter negative ion	35 keV
		source	
Sampling depth	4.0 mm	Bouncer frequency	100 Hz
Plasma gas	15 L min ⁻¹	Injection time of ion	Mass 129: 9 ms;
			Mass 127: 100 µs
Auxiliary gas	0.8 L min ⁻¹	Stripper gas	Ar
Carrier gas	0.9 L min ⁻¹	Acceleration voltage	2.5 MeV
Nebulizer	MicroMist	Charge state of iodine	+5
Data acquisition mode	Full quantitative data collection	Mass resolution M/ΔM for ¹²⁹ I	820
Analysed isotopes	¹²⁷ I, ¹³³ Cs	Stripping yield of I ⁵⁺	3.6-3.8 %
Analysis mode	Single quadrupole, no collision/reaction	Iodine ion current in the Faraday	0-100 nA for AgI-AgCl
	gas	cup	coprecipitation targets
Dwell time	0.1 s	Energy resolution $E/\Delta E$ of the	750
		cylindrical electrostatic analyzer	
Repeat of measurements	3	Mass resolution $M/\Delta M$ of the 30°	175
		deflection magnet	
CeO/Ce	< 2.0 %	Measurement time per cycle	5 min per sample
Ce ²⁺ /Ce	< 3.0 %	Cycle number	6 cycles
Spray chamber temperature	2.0 °C		

iodine chemical yield during combustion. The remaining solution was used for purification of iodine and preparation of ¹²⁹I targets. The blank samples were prepared using the same procedures without addition of travertine samples.

Purification of ¹²⁹**I.** The acid dissolution and trap solutions were adjusted to pH< 2 with 3.0 mol L⁻¹ HNO₃. 1 mL of 0.5 M NaHSO₃ was added for reduction of iodate to iodide, and 0.1 g of 2.0032 mg g⁻¹ ¹²⁹I-free ¹²⁷I solution (Woodward Company, USA) was added as iodine carrier. After thorough mixing, 1 mL of 0.5 mol L⁻¹ AgNO₃ was directly added to the solution to precipitate iodine as coprecipitate of AgI-AgCl-Ag₂SO₃-Ag₂SO₄. The formed precipitate was separated from the supernatant by centrifugation at 3000 rpm for 3 min. The precipitate was sequentially washed with 3.0 mol L⁻¹ HNO₃ to remove Ag₂SO₃ and Ag₂SO₄, washed with deionized water and 5-20% ammonium hydroxide to remove excessive AgCl to a final amount of 2-3 mg of precipitate and finally, rinsed with deionized water.

Preparation of ¹²⁹I standards. Two ¹²⁹I working solutions were prepared by mixing the prepared ¹²⁹I standard solutions with NaCl solution in a chlorine-to-iodine mass ratio of 5:1. From each standard, 0.5 mL of working solution was taken into a 15 mL centrifuge tube, and 0.1 mL of 0.1M NaHSO₃, 0.2 mL of 1M HNO₃, and 10 mL of deionized water were added. Then, 0.1 mL

of 1.0 mol L^{-1} AgNO₃ was added to coprecipitate iodine as AgI-AgCl. After centrifugation, the precipitate was sequentially washed with 3.0 mol L^{-1} HNO₃ and deionized water.

Determination of ¹²⁷I using ICP-MS. The sample solution by dissolution with nitric acid or 0.3 g of the trap solution from the pyrolysis combustion method was diluted to 30 g with 1% NH₃·H₂O. The concentration of ¹²⁷I was determined using inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ-MS, Agilent 8800, USA). Cs⁺ was used as the internal standard, and 1% NH₃·H₂O was used as the washing solution for the samples. The detection limit of iodine in the solutions was 0.02 μ g L⁻¹.

Determination of ¹²⁹I using AMS. The separated AgI-AgCl precipitates were dried in an oven at 60-70 °C, ground to fine powder, then mixed with 5 times the mass of niobium powder (325-mesh, Alfa Aesar, Ward Hill, MA), which was finally pressed into a copper holder with a pneumatic press (Zhenjiang Aode Presser Instruments Ltd). The ¹²⁹I/¹²⁷I ratios in the prepared targets were measured by AMS using the 3MV Tandem AMS system (HVEE) at the Xi'an AMS center. The I⁵⁺ ions, sputtered from the cesium ion source, were chosen for measurement, where ¹²⁷I⁵⁺ was measured as the charges (current) using a Faraday cup, and ¹²⁹I was measured using a gas ionization detector. All samples

were measured for 6 cycles, using 5 min per sample for each cycle. The optimal parameters of the ICP-MS and AMS systems are shown in detail in Table $2.^{14}$

RESULTS AND DISCUSSION

Method comparison for iodine analysis in travertine samples. It has been reported that carbonate deposits, such as coral, are easily digested with acid for analysis of ¹²⁹I.^{15,16} Considering time and labor consumption, direct acid dissolution has great advantages. Similar to coral, the travertine samples easily reacted with nitric acid and produced CO2. Although the chemical yield of this method could reach up to 95%, a large amount of foam was formed during acid dissolution. The digested solution was light yellow to yellow color, indicative of the presence of organic matter and possible detritus in travertine. This can be explained by the presence of aerosols, eolian dust and biological forces of bush, grass, moss, algae, etc., which act as major components, supporting the framework and binder during deposition of calcite.²⁰ It was observed that the travertine sample BST-12, collected from the headrace (Channel 2), which contained undecomposed brush leaf residue. In contrast, the sample from the pools contained much less plant residue. Due to the presence of organic matter, travertine is difficult to completely dissolve with nitric acid. Thus, further digestion of organic matter using hydrogen peroxide or potassium persulfate has to be carried out to mineralize the iodine isotopes. Otherwise, for 129I preparation, no AgI precipitate can be formed in spite of addition of 1 mg iodine carrier and a sufficient amount of AgNO3 solution. In this case, the direct acid dissolution method does not suitably apply to analyze the travertine samples unless the decomposition step is used, which would be time- and labor-consuming. Since all species of

Table 3. ¹²⁷I Concentrations (µg g⁻¹) in Baishuitai Travertine Samples

iodine are ionized in the plasma of the ICP-MS, the presence of organic substance in the solution might not strongly affect the measurement of ¹²⁷I in the sample solution. Table 3 compares the analytical results of ¹²⁷I concentrations using the two methods and shows that the ¹²⁷I concentrations by acid dissolution are in good agreement with pyrolysis combustion. Even though insignificant, the ¹²⁷I values by acid dissolution were still slightly higher than those with the pyrolysis method, which is likely related to the carbon enhancement effects of organic matter.²¹

Similar to the preparation of soil, sediments, aerosols and vegetation samples,^{11,13,14,22} pyrolysis combustion under 800°C could completely release iodine from the travertine samples in the form of molecular I2 under the atmosphere of oxygen and nitrogen. Iodine is then trapped in the alkaline NaOH solution to produce inorganic iodide and iodate ions. The chemical yield of iodine for travertine samples ranged from 65.2% to 86.1%, showing a comparable iodine recovery to other sample types normally within the range of 70%-95% (Table 4).^{11,13,14,22} In addition, there was no significant difference among the pool and channel travertine samples, indicating that the presence of organic matter does not affect the recovery of iodine during pyrolysis combustion. However, the ignition loss varied significantly between the pool and channel samples. Mass loss of travertine samples (BST-7,8,9 and 10) from the pools was from 42.8% to 47.7%, which is rather close to the ignition loss of pure CaCO3 of 44%, suggesting that the impurities in the pool travertine samples, such as plant residue or dust, are minor components. However, the abnormally high ignition loss of 72.4% for BST-12 could be attributed to a high content of wood chips and undecomposed leaves, because the surrounding environment of this sample site consists of dense woods.^{2,18} Compared to direct acid dissolution, pyrolysis combustion is much more suitable for the analysis of iodine

No	Sample code	Sampling site	Sampling date	Deposition duration (days)	Water supply	Acid dissolution (µg g ⁻¹)	Pyrolysis combustion (µg g ⁻¹)	Ratio of acid dissolution to pyrolysis
1	BST-6	Pool 1	2007.4.23	365		0.91 ± 0.01		
2	BST-7	Pool 2	2007.4.23	365	Spring 3	1.12 ± 0.01	1.02 ± 0.01	1.10
3	BST-8	Pool 5	2007.4.23	Winter		1.47 ± 0.02	1.33 ± 0.03	1.11
4	BST-9	Pool 6	2007.4.23	365	Summar 1 and 2	3.95 ± 0.05	3.23 ± 0.04	1.22
5	BST-10	Pool 7	2007.4.23	365	Springs 1 and 2	3.54 ± 0.04	3.46 ± 0.06	1.02
6	BST-12	Channel 2	2007.4.23	365	Spring 3	0.88 ± 0.01	0.86 ± 0.01	1.02
7	BST-13	Pool 2	2006.9.16	15		0.67 ± 0.01	/	/
8	BST-14	Pool 2	2006.10.2	15		0.69 ± 0.01	/	/
9	BST-15	Pool 2	2006.11.17	15		0.80 ± 0.01	/	/
11	BST-2	Pool 2	2007.2.3	15	Spring 3	0.47 ± 0.01	/	/
10	BST-1	Pool 2	2007.2.19	15		0.46 ± 0.01	/	/
12	BST-4	Pool 2	2007.8.9	15		0.58 ± 0.01	/	/
13	BST-5	Pool 2	2007.9.15	15		0.64 ± 0.01	/	/
14	BST-16	Pool 9	2006.8.9	15		0.43 ± 0.01	/	/
15	BST-17	Pool 9	2006.8.27	15		0.43 ± 0.01	/	/
16	BST-18	Pool 9	2006.9.15	15	Summar 1 and 2	0.45 ± 0.01	/	/
17	BST-11	Pool 9	2006.10.2	15	Springs 1 and 2	0.47 ± 0.01	/	/
18	BST-19	Pool 9	2006.10.16	15		0.43 ± 0.01	/	/
19	BST-20	Pool 9	2006.11.3	15		0.48 ± 0.01	/	/

No	Sample	Sampling		Ignition loss	Chemical yield of	¹²⁹ I	¹²⁹ I/ ¹²⁷ I atomic ratio
	code	site	water supply	(%)	iodine (%)	$(\times 10^5 \text{ atoms g}^{-1})$	(×10 ⁻¹²)
1	BST-7	Pool 2	Service 2	42.8	75.0	/	/
2	BST-8	Pool 5	Spring 5	42.9	65.2	3.29 ± 0.47	52.3 ± 7.6
3	BST-9	Pool 6		43.4	86.1	0.84 ± 0.13	5.50 ± 0.85
4	BST-10	Pool 7	Spring 1 and 2	47.7	71.9	1.12 ± 0.19	6.84 ± 1.16
5	BST-12	Channel 2	Spring 3	72.4	78.6	0.99 ± 0.16	24.4 ± 3.9

Table 4. ¹²⁹I Concentrations in Travertine Samples and Ignition Loss and Chemical Yield of Iodine Using Pyrolysis Combustion

isotopes in various types of travertine.

¹²⁷I in travertine. The concentrations of ¹²⁷I in the travertine samples from Baishuitai were variable from 0.43 to 3.95 μ g g⁻¹ (Table 3), which is comparable to other carbonate deposits. For instance, ¹²⁷I in coral samples from the Pacific Ocean and South China Sea fell in the range of 3.24-6.65 μ g g⁻¹ with an average value of 4.5 μ g g^{-1,23} Whereas, in stalagmite samples from the Xianglong Cave, Shaanxi Province, China, the ¹²⁷I concentrations were found to be as low as 0.30-0.88 μ g g⁻¹ (unpublished data). Seasonal variations of ¹²⁷I in travertine from Pool 2 showed high levels in summer-autumn and low levels in the winter. There was no significant change in ¹²⁷I concentration in summer-autumn for Pools 2 and 9 (Fig. 1). Whereas the one-year deposited travertine samples contained ¹²⁷I as high as 3.95 μ g g⁻¹, close to marine coral deposits.²³ These results indicate a complex incorporation process of iodine into the various carbonate deposits during their formation.

There are three water supplies, Springs 1, 2 and 3. Springs 1 and 2 are close to each other, with only 5 m distance, and supply water to Pools 6, 7 and 9 through a short channel of less than 500 m. Spring 3 supplies water to Pools 1 and 2 by a channel about 3 km long. The average ¹²⁷I concentration of 0.79 µg g⁻¹ in travertine samples from Spring 3, including Pools 1, 2 and Channel 2, was about two times higher than that of 0.38 µg g⁻¹ from Springs 1 and 2, except the abnormally high values in Pools 6 and 7 of 3.95 and 3.54 µg g⁻¹, respectively. These results suggest that the differences in ¹²⁷I concentration of the supply water might be the major factor affecting the amount of iodine in travertine. Therefore, ¹²⁷I contents in these spring waters are necessary to understand iodine co-deposition process with calcite. On the other hand, Lu et al. 26 suggest that iodate, not iodide, is the ionic species incorporated into the carbonate structure, likely substituting for the CO32- ion. Iodine speciation in the iodine-containing springs might be another reason to control the iodine level in travertine. While the abnormally high values in the one-year deposited travertine from Pools 6 and 7 might be related to the incorporation of abundant growth of iodine-rich algae and vegetation available in early and middle summer, which might be enriched with ¹²⁷I. Therefore, further investigation is necessary for understanding the mechanism of iodine intercalated into travertine samples.

¹²⁹I in travertine. To the authors' best knowledge, no ¹²⁹I data have previously been reported for travertine. Table 4 shows the ¹²⁹I concentrations and ¹²⁹I/¹²⁷I atomic ratios in the Baishuitai travertine samples within the range of $(0.84-3.29) \times 10^5$ atoms g⁻¹



Fig. 1 Temporal variation of ¹²⁷I in travertine samples from Pools 2 and 9.

and $(5.50-52.3) \times 10^{-12}$, respectively. The results were comparable to the pre-nuclear level of 1.5×10^{-12} for 129 I/¹²⁷I atomic ratio. Since the 1950s, the 129 I/¹²⁷I ratios have increased up to 10^{-10} , and even up to 10^{-6} due to the influence of modern human nuclear activities. And the data in this work indicate that these travertine samples were slightly affected by human nuclear activities, particularly at the two sampling sites of Pool 5 and Channel 2.^{22, 25}

Baishuitai travertine is endogenic due to carbonate precipitation with intense CO₂ degassing during transportation of its parent water supply.²⁶ The water in Baishuitai originates from deep geothermal water, which implies that ¹²⁹I in the water supply should be as low as 1.5×10^{-12} . But the results higher than the prenuclear ratios suggest that ¹²⁹I in these travertine samples collected during 2006 and 2007 was not from the water supply, but from modern nuclear activities. Previous studies of sediments from the Taal Lake, the Philippines, and Jiaozhou Bay, China, have shown that ¹²⁹I released by European nuclear reprocessing plants is the major source of ¹²⁹I in Southeast China via long-distance air transportation by westerly and East Asian monsoons.^{22, 27} Therefore, travertine ¹²⁹I might be due to atmospheric deposition during carbonate formation.

There are two possible pathways of atmospheric ¹²⁹I incorporating into travertine, by wet and dry deposition and from vegetation. Travertine is deposited in open air conditions in karst areas. ¹²⁹I concentration and ¹²⁹I/¹²⁷I ratios in Pool 5 were three times higher than those in Pools 6 and 7 and Channel 2. According to the sampling site, ²⁶ Pool 5 was fed by Spring 3 through a 3 km long channel, which indicates that the water can fully exchange

with air in particular because of the great recharge capacity of rainfall, and also is strongly affected by absorbing biological impurities (i.e., plant residues and algae). Although the water in Channel 2 is also fed by Spring 3, it is less affected due to it being a short distance from the vent to the sampling site. An increase in the ¹²⁹I/¹²⁷I ratios in travertine from Channel 2 to Pool 5 could confirm that this water current would introduce more ¹²⁹I into travertine. Therefore, the ¹²⁹I levels in the endogenic travertine may depend on the amount of rainfall that ultimately mixes with that area's water supply.

CONCLUSIONS

This study presents the ¹²⁹I and ¹²⁷I levels in travertine samples found at Baishuitai, Yunnan, China. Two sample preparation methods for the analysis of iodine isotopes were compared. The results show that the ¹²⁷I concentrations of both the direct acid dissolution and the pyrolysis combustion methods are in good agreement. For ¹²⁹I analysis, the pyrolysis combustion method is more suitable for the preparation of travertine due to the presence of organic matter.

Based on the limited data provided in this work, it can be stated that both iodine isotopes in the travertine samples have shown temporal and spatial variation. Considering the formation of endogenic travertine and the geological setting, the change of ¹²⁷I and ¹²⁹I concentration could be linked to the iodine level in the local water supply and the influence of the biological content. The mechanism for incorporation of iodine into carbonate deposition is preliminarily discussed and might be attributed to the coprecipitation of iodate with carbonate and iodine-containing impurities (i.e., algae and plant residue) mixed with calcite.

Since modern nuclear-derived ¹²⁹I is very limited in endogenic travertine samples, hypergenic tufa might be a better archive for reconstructing historic records of past human nuclear activities. Due to the importance of the iodine/calcium ratio in studying oceanic anoxic events, water-travertine systems also provide a natural environment, instead of controlled laboratory experiments, to understand the mechanism of iodine incorporation into carbonate.

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The authors declare no competing financial interest.

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