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Article

Determination of Boron Isotope Ratios in Tooth Enamel by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) After Matrix Separation by Ion Exchange Chromatography

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Boron isotopes in teeth has been a new proxy for dietary reconstructions and its resistance to diagenetic alteration. In this study a method using inductively coupled plasma source mass spectrometry (ICP-MS) for the measurement of boron isotope ratio in human dental enamel has been developed. Human dental enamel were digested with HNO_3-H_2O_2 in a microwave system. Boron in solution was separated from the matrix components using Amberlite IRA-743 resin. The factors that may affect precision and accuracy in isotope ratio determination by ICP-MS, including memory effects, mass bias drift, and concentration effects, were investigated to obtain optimum conditions. Then, the $^{10}B/^{11}B$ ratios in teeth were measured. The results showed that 2% of HNO_3 + 2% of $NH_3 \bullet H_2O$, selected as the diluent/rinse solution could be effective in the elimination of boron memory effect. There was no concentration effect on boron isotope ratios when the ratio of samples B concentration to standard B concentration (refers to C_{sample}/C_{std}) varied from 0.5 to 2. The result of $^{10}B/^{11}B$ ratios in tooth enamel by sex and age fluctuated over a broad range, ranged from 0.2007 to 0.2574. This method is expected to be used for boron isotope ratio analyses in archeometry, forensic identification, paleoecology, and other disciplines in the future.

Keywords: boron isotope ratios, tooth enamel, inductively coupled plasma mass spectrometry (ICP-MS), ion exchange separation

Introduction

Human teeth are valuable archives of the life history and behaviour of vertebrates. The bioapatite of the skeletal remains records in its element and isotope composition information about the diet, physiology and mobility as well as climate and environmental conditions. If this geochemical information is not biased by chemical alteration during fossilisation, it can provide valuable insights into the palaeobiology, palaeoecology, and evolution of extinct vertebrates.[1-3]

Boron is shown to be an essential element for plants early this century and there is now evidence that it is also necessary for humans. Boron is distributed throughout the human body with the highest concentration in the bones and dental enamel. It is surprising that boron was found in teeth in the range as high as 25-85 ppm. Boron was found to be significantly increased in carious teeth than non-carious teeth despite loss of minerals during cariogenesis.[4] Because food provides most of the boron ingested daily by terrestrial mammals (e.g., ca. 90% in humans), the boron isotope of bioapatite could potentially be a new paleodietary proxy.[5,6]

The determination of boron isotope ratios ($^{10}B/^{11}B$) has been carried out by a variety of methods. These include atomic absorption spectrometry,[7-9] thermal ionisation mass spectrometry (TIMS),[10-14] multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS),[15-18] glow discharge mass spectrometry (GDMS), the secondary ion mass spectrometry (SIMS),[19] laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS),[20-22] spark source mass spectrometry,[23] and inductively coupled plasma mass spectrometry (ICP-MS), etc.[24-35]

The objective of this work was to investigate the possibility of using ICP-MS for the determination of boron isotope ratios ($^{10}B/^{11}B$) in tooth enamel after pre-treatment

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by ion exchange separation. The factors that may affect precision and accuracy in isotope ratio determination by ICP-MS include memory effects, mass bias drift, and concentration effects were carried out to obtain optimum conditions. The present method is applicable to a wide field of boron isotopic research in teeth enamel for dietary reconstructions and its resistance to diagenetic alteration.

Experimental

Instrumentation

Instrumentation included a ICP-MS (Perkin Elmer-Nexion 300D, PerkinElmer Corporation, USA) with an S10 autosampler, optimized by using a standard ^{89}Y solution at a concentration of 10 ppb in 2% HNO_3, the MARS 6 microwave-assisted digestion system (CEM Microwave Technology Ltd operates, USA) and the Milli-Q ultrapure water system (Millipore Corporation, USA).

Reagents and materials

Boron isotopic reference materials: National Institute of Standards and Technology (NIST) boric acid SRM 951 (formerly NBS SRM 951 of the National Bureau of Standards, USA). A certified reference material of bone ash (SRM NIST 1400) and bone meal (SRM NIST 1486) from National Institute of Standards and Technology were also used. Milli-Q H_2O (18.2 MΩ at 25 °C) from Millipore (Elix-Millpore, USA). HNO_3 was obtained from the Beijing Institute of Chemical Reagent and purified using the SavillexTM DST-100 sub-boiling distillation system (Minnetonka, MN, USA). H_2O_2 (30 wt.% in H_2O) was from Sigma-Aldrich Co. LLC.

Experimental methods

Collection and treatment of permanent teeth

The permanent teeth were collected from 7 to 79 years old male and female humans who have lived in Shaanxi (NW China) for many years.[36] The healthy teeth were extracted from sample providers who do not smoke or drink. The teeth were healthy permanent teeth extracted due to impacted wisdom tooth deformity, orthodontic treatment, or other reasons. Extracted teeth with complete crowns, no caries or mottled enamel, complete enamel development, and no obvious wear or defects on the morsal surface were selected. The selected carious teeth exhibited clear cavities. The teeth were soaked in acetone solution for 24h. Then, the teeth were separated and ground following the method described in literature.[37-41]

The microwave digestion conditions used in this study for teeth digestion were adapted to those previously used for biological samples following the method of Li *et al*.[36] with some modification. Teeth samples were weighed, ground to powder using mortar and pestle, and weighed again before the digestion (depending on the tooth type and size, they ranged from 0.0090 to 0.7350 g). In this study, powdered teeth samples were pre-dissolved in 3 mL of 50% HNO_3 solution and 2 mL of 30% H_2O_2 solution using microwave digestion tank (The MARS 6 microwave-assisted digestion system, CEM Microwave Technology Ltd operates, USA). The tank was then gently shaken. Approximately 3 mL Milli-Q water was added dropwise, and the samples were digested according to procedure in Table 1.

For the certified reference material (NIST SRM 1400 and NIST SRM 1486), an amount of ca. 0.0500 g of sample was digested in microwave as described above.

Table 1. Microwave digestion programs for teeth

Program/reagents	Stage	time / min	Temperature / °C	Power / W
3 mL HNO_3 (50%), 2 ml H_2O_2 (30%)	1	5	0-120	580
	2	3	120	580
	3	5	120-180	580
	4	15	180	470
	5	20	180-0	0

Separation and enrichment of B with an ion-exchange process

The mineral phases of tooth enamel are mostly hydroxyapatite crystals of various structures and composition with incorporated trace elements. Major elements found in enamel are Ca, P, Na, Mg, and Cl. Their mean concentrations are well known, and their approximate concentrations are 37% Ca; 18% P; 0.4% Mg; 0.7% Na, and 0.28% Cl. Because of unavoidable matrix interference during the measurement of the ^{10}B and ^{11}B isotopes with ICP-MS, even after microwave digestion of the samples, it was necessary to separate B from all the other elements and matrix components still present. An ion exchange procedure using Amberlite IRA 743 was adapted and optimized for this purpose.[18,33] The detailed methods of the experiment are listed in Table 2.

$^{11}B/^{10}B$ isotope ratio measurements

$^{11}B/^{10}B$ isotope ratio was determined by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer-Nexion 300D, PerkinElmer Corporation, USA) with an S10 autosampler. The ICP-MS instrument operating parameters were established by automatically optimizing the

instrument conditions. The ICP-MS operating parameters are given in Table 3.

Table 2. Columns for B separations using Amberlite IRA 743 resin

Stage	Column Procedure	Reagent
1	Rinse	Milli-Q water (100 μL × 4)
2	Clean	2% HNO_3 (100 μL × 4)
3	Precondition column	Acetic buffer (100 μL × 4)
4	Precondition column	Milli-Q water (100 μL × 4)
5	Load sample	50 μL × 10
6	Wash	Milli-Q water (50 μL × 4)
7	Wash	Milli-Q water (100 μL × 4)
8	Elute B	2% HNO_3 (100 μL × 4)
9	Tailing check	2% HNO_3 (50 μL × 2)
10	Neutralize resin	Milli-Q water (100 μL × 4)

Table 3. Experimental conditions used for the ICP-MS measurements

Parameter	Value
Plasma mode	normal
RF forward power / W	1400
RF generator / MHz	40.68
Carrier gas flow / (L min^{-1})	1.26
Dilution gas flow / (L min^{-1})	0.4
Diameter of the sampling cone hole / mm	1.1
Diameter of the skimming cone hole / mm	0.9
Diameter of the hyper-skimmer cone / mm	1.0
Scanning mode	peak hop
Isotope ratio mode	on
Isotopes monitored	^{10}B, ^{11}B
Dwell time / ms	^{10}B = 4 ms
Sweeps / reading	1000
Reading / replicate	3
Replicates	10
Total analysis time / min	4

Determination of the B isotope ratio, $^{11}B/^{10}B$, by means of ICP-MS is complicated by a large mass discrimination effect (because of the relatively large mass difference between the two B isotopes) and the drift in the mass discrimination during measurement, which may lead to a concomitant drift in the measured isotope ratio. Therefore, to take into account the variations in mass bias with time, we employed the correction method using the NIST SRM 951 as standard sample.[31] The isotopic ratio of boron $(^{10}B/^{11}B)_{meas}$ was calculated by equations (1) and (2):

$$\left(^{10}B/^{11}B\right)_{meas} = \frac{^{10}B_{samp} - {}^{10}B_{blk}}{^{11}B_{samp} - {}^{11}B_{blk}} \times f \quad (1)$$

$$f = \frac{1}{2}\left(\frac{^{11}B_{std1} - {}^{11}B_{blk}}{^{10}B_{std1} - {}^{10}B_{blk}} + \frac{^{11}B_{std2} - {}^{11}B_{blk}}{^{10}B_{std2} - {}^{10}B_{blk}}\right) \times \left(^{10}B/^{11}B\right)_{cert} \quad (2)$$

Here, the signal intensities of ^{10}B and ^{11}B in the sample solution is represented as $^{10}B_{samp}$ and $^{11}B_{samp}$, the certified standard value of the $^{10}B/^{11}B$ ratio for NIST SRM 951 is represented as $(^{10}B/^{11}B)_{cert}$, and the measured value of the isotopic ratio of boron for each sample as $(^{10}B/^{11}B)_{meas}$. The signal intensities of ^{10}B and ^{11}B in the blank solution and NIST SRM 951 solution averaged over n measurements are represented in the Table 4. The measurements were repeated 10 times for each sample and the average was set as the measured value.

Table 4. The measurement procedure for boron isotope ratios

Step	Procedure	n
1	Measure signal ratio of $^{10}B/^{11}B$ of blank solution ($^{10}B_{blk}$, $^{11}B_{blk}$)	3
2	Measure $^{10}B/^{11}B$ of standard sample NIST SRM 951 ($^{10}B_{std1}$, $^{11}B_{std1}$)	10
3	Rinsing of sample introduction tube, spray chamber and nebulizer (500 s)	-
4	Measure $^{10}B/^{11}B$ of sample solution ($^{10}B_{samp}$, $^{11}B_{samp}$)	10
5	Rinsing of sample introduction tube, spray chamber and nebulizer (500 s)	-
6	Measure $^{10}B/^{11}B$ of standard sample NIST SRM 951 ($^{10}B_{std2}$, $^{11}B_{std2}$)	10

Results and Discussion

Boron memory effects

The high sensitivity of ICP-MS makes this technique suitable, reliable and rapid for boron determinations. However, measuring boron at ultratrace levels by ICP-MS often present a significant memory effect. Over the past decades, most researchers have used several methods to eliminate boron memory effect. One was direct injection nebulization (d-DIHEN),[29] and another was using different diluents/rinse solution, including water, nitric acid, Triton X-100, ammonia and mannitol in water, in nitric acid and in ammonia.[26] These attempts has been achieved satisfactory results.

Several reagents, including water and 2% of HNO_3, 2% of HNO_3 + 2% NH_3•H_2O and 2% of HNO_3 + 2% mannitol were tested and evaluated according to the memory effect, the analytical precision and the background. For each reagent, an equivalent blank and a 100 ng mL^{-1} standard solution were analyzed. The ion-time response for $^{11}B^+$ was continuously monitored. First, the signal was collected with the reagent blank for about 5 min, then the B solution with the same reagent was introduced for 5 min, and finally the reagent blank was introduced again as the flush solution for about 10 min. Table 5 and Figure 1 gives the B ion-time response (counts s^{-1}) for the selected reagents.

Table 5. Relationship between boron ion strength and changes with the cleaning time

time / s	H_2O + 2% HNO_3 / (counts s^{-1})	2% HNO_3 + 2% NH_3•H_2O / (counts s^{-1})	2% HNO_3 + 2% mannitol / (counts s^{-1})
0	15000	15000	15000
10	10000	8000	8000
20	8000	6050	6030
30	6000	5050	5010
40	5000	4080	4030
50	4000	3020	3000
60	3000	2100	2000
70	2900	2000	1950
80	2850	1950	1900
90	2800	1900	1800
100	2800	1850	1800
110	2800	1850	1805
120	2800	1850	1800
130	2800	1850	1800
140	2800	1850	1805
150	2800	1850	1800
160	2800	1850	1800
170	2800	1850	1805
180	2800	1850	1800

Figure 1 gives the B ion-time response (counts s^{-1}) for the selected reagents. The results show that 2% HNO_3 + 2% NH_3•H_2O and 2% HNO_3 + 2% mannitol exhibit similar and significant memory effects. Then 2% HNO_3 + 2% NH_3•H_2O was selected for sample analysis in this text.

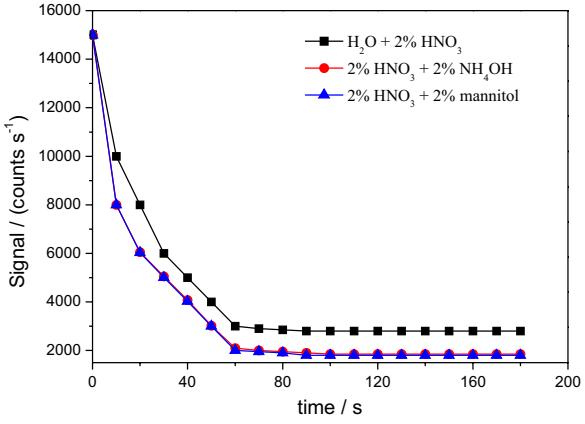

Figure 1. Comparison of background values with various washing solutions.

Effects of B concentration on the measured B isotope ratios

The term concentration effects used here refers to the phenomenon that mass fractionation during plasma source mass spectrometry varies with changes in concentration of sample solutions compared to the standard solution under a given set of working conditions. This phenomenon may be regarded as a special case of matrix effects. So, it was important to maintain the similar concentration of B in sample and standard solution.

To investigate the feasibility of concentration effect, a series of measurements have been carried out using NIST SRM 951 B solutions with B concentrations varying from 0.05 to 1.5 ppm (refers to C_{sample}) *vs.* the same NIST SRM 951 B solution at a fixed concentration of 0.5 ppm (refers to C_{std}). The measured B isotope ratios of the "sample" varing with C_{sample}/C_{std} was plotted in Figure 2. These variations cannot be explained by molecular interferences, but must result from instrumental mass fractionation. This implies that the instrumental fractionation of B isotopes varies according to the B concentration introduced into the mass spectrometer, at least for the given set of working conditions. It can be seen from Figure 2, when C_{sample}/C_{std} varied from 0.5 to 2, and there was no effect on boron isotope ratios.

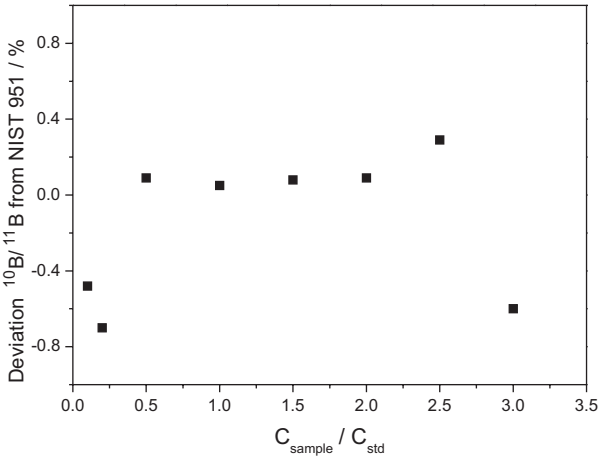

Figure 2. The effect of B concentration on B isotope ratio measurements under different mass bias correct modes (the standard content is 0.5 ppm).

Reproducibility of the measurement

To test the analytical precision and accuracy of the methods above, the boron isotope ratios of NIST SRM 951 were measured in 220 days. The results are illustrated in Figure 3. The reproducibility of all the measurements shown in Figure 3 fell below 0.2% RSD, indicating the long-term reproducibility of measurement.

Determination of $^{10}B/^{11}B$ ratios in tooth enamel

Using the above described experimental procedures, the B isotopes in the enamel of the extracted teeth were chemically separated and measured. The result of $^{10}B/^{11}B$ ratios in tooth enamel by sex and age were shown in Table 6 and Figure 4.

Table 6. The $^{10}B/^{11}B$ ratios in tooth enamel by sex and age

Tooth enamel by sex and age	7-11 years	12-19 years	20-39 years	40-59 years	60-79 years
Healthy teeth (male)	0.2437	0.2149	0.2297	0.2511	0.2574
Healthy teeth (female)	0.2019	0.2517	0.2557	0.2439	0.2322
Carious teeth (male)	0.2539	0.2195	0.2148	0.2222	0.2007
Carious teeth (female)	0.2459	0.2548	0.2394	0.2189	0.2346

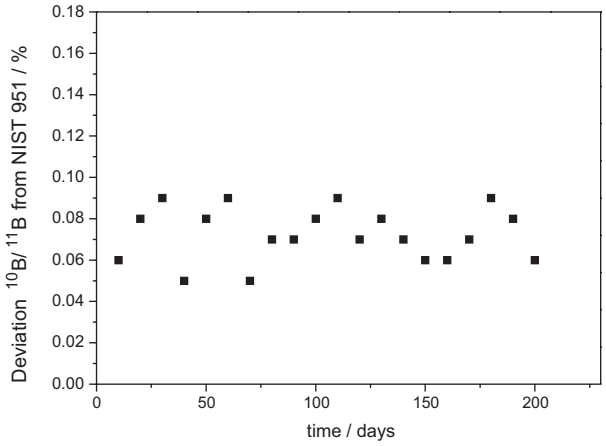

Figure 3. Repeatability of $^{10}B/^{11}B$ isotope ratios measurements of NIST SRM 951.

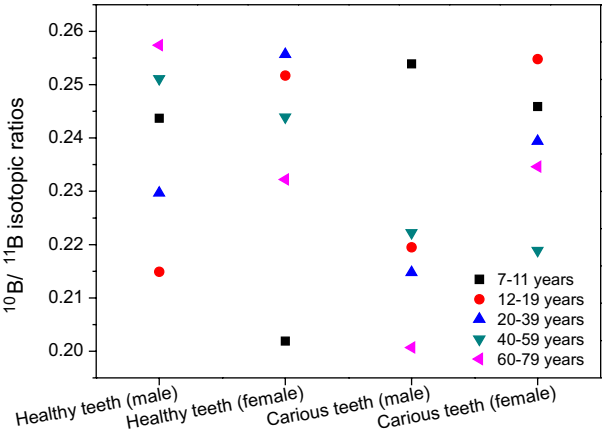

Figure 4. $^{10}B/^{11}B$ isotope ratios in the tooth samples (each group has one sample).

The data in Figure 4 indicate that the $^{10}B/^{11}B$ ratio in the enamel of the healthy teeth and carious teeth by sex and age fluctuated over a broad range, ranged from 0.2007 to 0.2574. Boron has two naturally occurring isotopes, ^{10}B (19.9%) and ^{11}B (80.1%). A relatively large mass difference (10%) between the two isotopes and high volatility results in significant boron isotopic variation from –70‰ to +75‰ in natural materials; thus, boron isotopes have numerous applications in geochemistry, isotope hydrology, oceanography, environmental sciences, cosmology, and nuclear technology.[13] The $^{10}B/^{11}B$ ratio in the enamel of the teeth could potentially be a new paleodietary proxy, but two important questions must first be answered: (*i*) what is recorded in the $^{10}B/^{11}B$ of teeth? (e.g., diet, trophic level, influence of the local vegetation or geology); and (*ii*) do the original $^{10}B/^{11}B$ values of teeth remain unaltered by the fossilization processes? In order to answer these two questions, the $^{10}B/^{11}B$ of teeth has been compared with other stable isotope proxies used in ecology, analyzed on the same specimens, to determine the influence of diet ($\delta^{13}C$),[42,43] water sources ($\delta^{18}O$),[42,43] trophic levels ($\delta^{15}N$, $\delta^{44}/^{42}Ca$),[44-46] as well as with geological and vegetation maps ($^{87}Sr/^{86}Sr$),[36,47,48] should be investigated the influence of the local bedrock and plant matter contributions, respectively.

The Sr isotope composition (i.e., $^{87}Sr/^{86}Sr$ ratio) of the healthy teeth and carious teeth at the same region in Shaanxi (NW of China) was measured by Li *et al.*[36] Their results demonstrate that $^{87}Sr/^{86}Sr$ does not appear to be affected by the caries formation, age or sex. The $^{87}Sr/^{86}Sr$ ratio in the enamel of the healthy and carious teeth of individuals of varying ages and genders ranged between 0.710935 and 0.711037, which falls into the range of the $^{87}Sr/^{86}Sr$ found in the local, naturally occurring water, soils and rocks.

Conclusions

We present here a method to measure $^{10}B/^{11}B$ ratios in tooth enamel by ICP-MS after pre-treatment by ion exchange separation. The $^{10}B/^{11}B$ ratio in the enamel of the healthy teeth and carious teeth fluctuated over a broad range, ranged from 0.2007 to 0.2574. It is anticipated that this technique offers the potential for using B isotope ratios to trace the geochemical cycling of B in scientific archaeology, forensic identification, paleoecology, and other disciplines.

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