

Electronic Supplementary Information (ESI)

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Title: Effect of metasilicate matrices on boron purification by Amberlite IRA 743 boron specific resin and isotope analysis by MC-ICP-MS

1. Dissolution procedure of silicates by alkali fusion approach

Silicate geological samples were dissolved by the alkali fusion procedure³¹: fine silicate powder (e.g. tourmaline, obsidian) was mixed well with K_2CO_3 with the mass ratio of 1:25 in a platinum crucible, and then the crucible was heated at 950 °C for 60 minutes in a muffle furnace. After the crucible was quenched in the air, 2 mL 2.5 M HCl was added to dissolve the sintered materials and followed by adding 3 mL of H_2O to rinse the crucible. All solution was transferred into a Teflon beaker and the transparent solution was ready for ion-exchange chromatography.

2. Ion exchange chromatography for boron purification

A three-column procedure was employed for the boron separation-purification in silicates²⁶, involving the first 2.5 mL of mixed cation-anion resin column, a ~25 μL of peristaltic pump coupled boron-specific Amberlite IRA 743 column, and the second 0.5 mL of mixed cation-anion resin column. The mixed resin consists of strongly acidic 200-400 mesh cation resin (Dowex 50W \times 8, H-Form, USA) and weak alkaline 60-100 mesh anion resin (Ion Exchanger II, HCO_3^- -Form, Germany). The individual cation and anion resins were conditioned using 3 M HCl and saturated $NaHCO_3$ to convert into the H^+ and HCO_3^- -forms. Due to the difference in size, Ion Exchanger II and Dowex 50W \times 8 can be separated from each other by sieving through 100 meshes for regeneration. The detailed procedure for boron separation/purification by the three-column ion exchange chromatography is shown in Table S1. The recovery of boron is evaluated to be 100.6 % through the whole treatment procedure.

Table S1. Boron purification procedure by the three-step ion exchange column

First column-2.5 mL of mixed resin consisting of 50 % Dowex 50W×8 cation resin and 50 % Ion Exchange II anion resin (v/v)					
Step	Procedure	Reagent	Dosage (μL)	Collect/Discard	Notes
1	Load column	Mixed resin	2500	Discard	
2	Clean	Milli-Q water	4000	Discard	
3	Load sample	Sample solution	200	Collect	
4	Elute boron	Milli-Q water	5000	Collect	Neutral solution
Second column-25 μL of Amberlite IRA 743 boron specific resin					
Step	Procedure	Reagent	Dosage (μL)	Pump speed	Collect/Discard
1	Load column	IRA-743 B-specific resin	25	20	Discard
2	Clean	Water	4000	20	Discard
3	Clean	0.1 M HCl	400	10	Discard
4	Clean	Milli-Q water	2000	10	Discard
5	Equilibrate	0.3 M NH ₃ H ₂ O	400	10	Discard
6	Rinse	Milli-Q water	2000	10	Discard
7	Load	Sample at pH ~8		0.5	Discard
8	Elute cations	Milli-Q water	8000	10	Discard
9	Elute boron	0.1 M HCl	2000	2	Collect
10	Evaporate	at 60 °C			
Third column-0.5 mL of mixed resin consisting of 50 % Dowex 50W×8 cation resin and 50 % Ion Exchange II anion resin (v/v)					
Step	Procedure	Reagent	Dosage (μL)	Collect/Discard	Notes
1	Load column	Mixed Resin	500	Discard	
2	Clean	Milli-Q water	8000	Discard	
3	Load sample	Sample solution	200	Collect	
4	Elute boron	Milli-Q water	8000	Collect	
5	Divide	Divide the solution into two aliquots for TIMS and MC-ICP-MS measurement respectively			
6	(a) Adding CsOH	B:Cs=1:2 and heat at 60°C			TIMS analysis
	(b) Adding HNO ₃	3% HNO ₃ medium			MC-ICP-MS analysis

3. Boron isotope analysis

3.1 Boron isotope analysis by PTIMS

A Triton TI (Thermo Fisher Scientific, Finnigan, Germany) thermal ionization mass spectrometer (TIMS) was used for boron isotope analyses by collecting $^{133}\text{Cs}_2^{11}\text{B}^{16}\text{O}_2^+$ (m/z 309) and $^{133}\text{Cs}_2^{10}\text{B}^{16}\text{O}_2^+$ (m/z 308) ions. Single tantalum filaments (0.75 cm × 0.076 cm × 0.0025 cm) from NIST were degassed under vacuum for 1 hour at a current of 3.0 A and then allowed to oxidize at ambient atmosphere (protected from contamination in closed boxes) for at least 24 hours prior to use.

Graphite (John-Matthew Company, 99.9999% pure) slurry was prepared by mixing the graphite with 80% ethanol/20% water (v/v). A drop of graphite slurry with a volume of ca. 1.0 μL was first loaded onto the filament. After vaporizing the slurry drop at room temperature for 30 seconds, the sample solution is added on top of the graphite. Both samples and the NIST SRM 951 standard solutions with the molar ratio of B/Cs 2:1 were loaded as described above. The detailed information related to the static double-collection method for boron isotope measurements was described in our previous investigation ²⁶, and $^{11}\text{B}/^{10}\text{B}$ ratios were obtained from measured 309/308 ratios with a correction for oxygen isotopes (^{17}O): $^{11}\text{B}/^{10}\text{B} = R_{309/308} - 0.00079$. Boron isotopic composition is reported as $\delta^{11}\text{B}$ in per mil (‰) deviation from the standard (NIST SRM 951) as follows: $\delta^{11}\text{B} \text{ ‰} = 1000[(^{11}\text{B}/^{10}\text{B}_{\text{sample}} / ^{11}\text{B}/^{10}\text{B}_{\text{standard}}) - 1]$. Stable runs ($n \geq 3$, 100 cycles in each run) were obtained with loading the standard NIST SRM 951 and natural samples containing $\sim 0.5 \mu\text{g}$ of boron on the filament when the filament current is at $\sim 1.2 \text{ A}$ (less than $\sim 650 \text{ }^\circ\text{C}$). The average ($n=10$) internal analytical precision and the external precision of the measured $^{11}\text{B}/^{10}\text{B}$ ratios of NIST 951 are $\pm 0.05 \text{ ‰}$ and 0.09 ‰ , respectively.

3.2 Boron isotope analysis by MC-ICP-MS

A Neptune Plus (Thermo Fisher Finnigan, Germany) MC-ICP-MS with an ESI PFA 50 $\mu\text{L}/\text{min}$ nebulizer in a quartz spray chamber were used in this work. The ions of $^{11}\text{B}^+$ and $^{10}\text{B}^+$ are detected using Faraday cups H3 and L3. The mass bias is corrected by a sample-standard bracketing procedure (SSB). $(^{11}\text{B}/^{10}\text{B})_{\text{true}} = (^{11}\text{B}/^{10}\text{B})_{\text{measured}} \times (M^{11}/M^{10})^\beta$, and β is a correction factor where $\beta = \ln[(^{11}\text{B}/^{10}\text{B})_{\text{standard NIST 951}} / (^{11}\text{B}/^{10}\text{B})_{\text{measured NIST 951}}] / \ln(M^{11}/M^{10})$ and $(^{11}\text{B}/^{10}\text{B})_{\text{standard NIST 951}} = 4.04362 \pm 0.00137$, the certified value by NIST. The boron content in both sample solution and NIST 951 solution was kept close to 200 ng mL^{-1} to obtain $\sim 1.2 \text{ V}$ of $^{11}\text{B}^+$ signal with the conventional H-skimmer cone. The memory effect was reduced to around $\sim 3\text{-}9 \text{ mV}$ with continuous washing with 3% HNO_3 and 1% HNO_3 and boron-free Milli-Q water in sequence for ~ 25 minutes. All reproducibilities described in this work are quoted from duplicate measurements ($n \geq 3$, 2 S.D., 95% confidence limits). The

average internal analytical precision ($n = 100$) and the external precision of the measured $^{11}\text{B}/^{10}\text{B}$ ratios of 200 ng mL^{-1} NIST 951 are $\pm 0.02 \text{ ‰}$ and 0.11 ‰ , respectively.

4. Elemental content analysis

The concentrations of B and Si were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, JY38S) with an analytical reproducibility (2σ) of $\pm 5\%$ or better.