Comparison of microsublimation and ion exchange chromatography for boron isolation preceding its isotopic analysis via multi-collector ICP-MS

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Supporting Information

1. Influence of remaining natural B on final $\delta^{11}B$ of isotopic reference materials

1.1 Boron isotope ratio of mixture of two sources

The final $^{11}B/^{10}B$ isotope ratio in the samples $(^{11}B/^{10}B)_{mix}$ can be considered as a mixture of two sources, the remaining natural B $(^{11}B/^{10}B)_{bl}$ and the spiked reference material AE120, AE121 or AE122 $(^{11}B/^{10}B)_{sa}$. The final isotope ratio of the mixture can be calculated as:

$$\left(\frac{^{11}B}{^{10}B}\right)_{mix} = \frac{^{11}B_{sa} + ^{11}B_{bl}}{^{10}B_{sa} + ^{10}B_{bl}} \quad \text{(Eq. S1)}$$

In this case, both $(^{11}B/^{10}B)_{bl}$ and $(^{11}B/^{10}B)_{sa}$ are known, as well as the total mass of B present in the blank and the sample. Hence, each of the four terms in the equation can be calculated. For example:

$$^{11}B_{sa} = n(B_{sa}) \times f^{11}B_{sa} \quad \text{(Eq. S2)}$$

where $n(B_{sa})$ is the number of moles of B and $f^{11}B_{sa}$ is the fraction of ^{11}B in the standard spike. Both terms in this equation can be calculated following:

$$f^{11}B_{sa} = \frac{100 \times \left(^{11}B/_{10}B\right)_{sa}}{1 + \left(^{11}B/_{10}B\right)_{sa}} \quad \text{(Eq. S3)} \qquad \text{and} \qquad n(B_{sa}) = \frac{m(B_{sa})}{MM_{sa}} \quad \text{(Eq. S4)}$$

In the latter equation, $m(B_{sa})$ is the mass of B and MM_{sa} is the molar mass of B in the spiked standard. The molar mass can be calculated using the following equation:

$$MM_{sa} = \frac{f^{11}B_{sa}}{100} \times 11.00931 + \frac{100 - f^{11}B_{sa}}{100} \times 10.01924$$

(Eq. S5)

The three other terms in equation S1 can be determined in a similar way.

1.2 Calculation of $\delta^{11}B_{mix}$ in seawater, spinach and silicate glass

Using the equations outlined above, the $\delta^{11}B_{mix}$ values were calculated in order to evaluate if the low concentrations of remaining natural B in the sample matrices could have affected the final result of the spiked standard. In literature reported $\delta^{11}B$ values for seawater, plant material and NIST 610 silicate glass were used as input parameters for the calculation of $\delta^{11}B_{mix}$. All data input and final results of $\delta^{11}B_{mix}$ in seawater samples are given in Table S1. It is clear that final $\delta^{11}B$ values equal those of the reference materials.

Table S1 - Input parameters and final $\delta^{11}B$ values in seawater matrices spiked with certified boron reference materials

Seawater						
	Microsublimation			Chromatography		
$m(B_{bl})$ (ng)	0.3			0.6		
$\delta^{11}B_{bl}$ (‰)	39.6 [S1]			39.6		
$m(B_{sa})$ (ng)	800			4000		
$\delta^{11}B_{sa}$ (‰)	-20.2	19.9	39.7	-20.2	19.9	39.7
$\delta^{11}B_{mix}$ (‰)	-20.2	19.9	39.7	-20.2	19.9	39.7

To our knowledge, no $\delta^{11}B$ data on NIST 1570 spinach powder have been published. Therefore, two outer values of the range in $\delta^{11}B$ observed in plant material were used as input parameters, *i.e.* -30 and +40 ‰ [S2]. For microsublimated samples, a maximum deviation of 0.1 ‰ can be expected due to the 26 µg/l of natural B remaining in the samples.

Table S2 - Input parameters and final $\delta^{11}B$ values in spinach matrices spiked with certified boron reference materials

Spinach powder												
	Microsublimation						Chromatography					
$m(B_{bl})$ (ng)	1.3			1.3			2.6			2.6		
$\delta^{11}B_{bl}$ (‰)	-30			40			-30			40		
$m(B_{sa})$ (ng)	800			800			4000			4000		
$\delta^{11}B_{sa}$ (‰)	-20.2	19.9	39.7	-20.2	19.9	39.7	-20.2	19.9	39.7	-20.2	19.9	39.7
$\delta^{11}B_{mix}$ (‰)	-20.2	**19.8**	**39.6**	**-20.1**	19.9	39.7	-20.2	19.9	39.7	-20.2	19.9	39.7

Finally, the lowest and highest $\delta^{11}B$ values of NIST 610 silicate glass published in literature are -8.4 and 0.0 ‰, respectively [S3, S4]. When these values, together with a mass of remaining B

calculated from the limit of detection, are used as input parameters, no significant deviation from the certified values is expected.

Table S3 - Input parameters and final $\delta^{11}B$ values in silicate glass matrices spiked with certified boron reference materials

NIST 610 silicate glass												
	Microsublimation						Chromatography					
$m(B_{bl})$ (ng)	0.1			0.1			0.2			0.2		
$\delta^{11}B_{bl}$ (‰)	-8.4			0.0			-8.4			0.0		
$m(B_{sa})$ (ng)	800			800			4000			4000		
$\delta^{11}B_{sa}$ (‰)	-20.2	19.9	39.7	-20.2	19.9	39.7	-20.2	19.9	39.7	-20.2	19.9	39.7
$\delta^{11}B_{mix}$ (‰)	-20.2	19.9	39.7	-20.2	19.9	39.7	-20.2	19.9	39.7	-20.2	19.9	39.7

2. Mass discrimination correction

In this work, a combination of internal correction using the common analyte internal standardization (CAIS) method and external correction relying on sample-standard bracketing (SSB) was used. The isotopic reference material Li_2CO_3 IRMM-016 was spiked to all standards and samples as an internal standard. Pure NIST SRM 951 boric acid bracketing standards and 2 M HCl - doped standards were included in the MC-ICP-MS measurement sequence.

The first step in the application of CAIS internal correction, is establishing a linear relationship between the measured (uncorrected) $^{11}B/^{10}B$ and the $^{7}Li/^{6}Li$ isotope ratios in the pure and 2 M HCl doped standards, $(^{11}B/^{10}B)_{ref,meas}$ and $(^{7}Li/^{6}Li)_{ref,meas}$, respectively. An example of such a linear relationship is given in Figure S1. Hence, for each sample, the expected measured $(^{11}B/^{10}B)_{ref,meas}$ can be calculated from the observed $(^{7}Li/^{6}Li)_{ref,meas}$. The ratio of the true $(^{11}B/^{10}B)_{ref,true}$ to the calculated $(^{11}B/^{10}B)_{ref,meas}$ now gives the extent of mass discrimination and this factor is subsequently used to correct the measured $(^{11}B/^{10}B)_{sample,meas}$ into $(^{11}B/^{10}B)_{sample,corr}$. This procedure can be summarized via the following equations:

$$\left(\frac{^{11}B}{^{10}B}\right)_{sample,corr} = \left(\frac{^{11}B}{^{10}B}\right)_{sample,meas} \times \frac{\left(^{11}B/^{10}B\right)_{ref,true}}{\left(^{11}B/^{10}B\right)_{ref,meas}} \quad \text{(Eq.S6)}$$

Where:

$$\left(^{11}B/^{10}B\right)_{ref,meas} = a \times \left(\frac{^{7}Li}{^{6}Li}\right)_{ref,meas} + \quad b \quad \text{(Eq.S7)}$$

and $\left({}^{11}B/{}^{10}B\right)_{ref,true}$ is 4.0436 ± 0.0027 [S5]

Finally, in equation S7, the parameters *a* and *b* are deduced from the linear regression between $({}^{11}B/{}^{10}B)_{ref,meas}$ and $({}^{7}Li/{}^{6}Li)_{ref,meas}$ in the pure and doped standards.

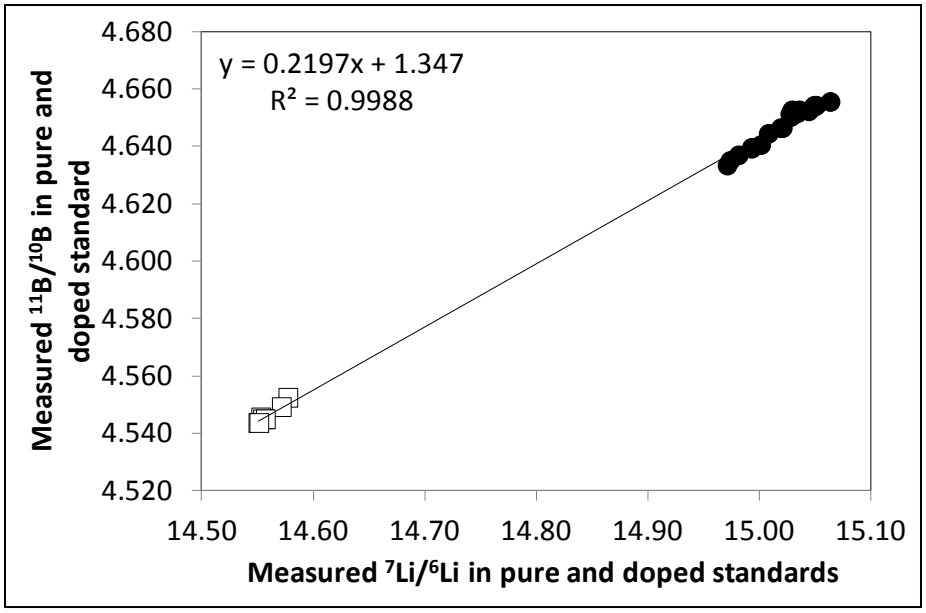

Figure S1 - Linear correlation between $({}^{11}B/{}^{10}B)_{ref,meas}$ and $({}^{7}Li/{}^{6}Li)_{ref,meas}$ observed in pure (●) and HCl doped (□) standards.

After correction using the CAIS method, external correction, relying on SSB, is applied according to equation S8.

$$\left(\frac{{}^{11}B}{{}^{10}B}\right)_{corr,final} = \left(\frac{\left({}^{11}B/{}^{10}B\right)_{sample,corr}}{\frac{\left({}^{11}B/{}^{10}B\right)_{std-1,corr} + \left({}^{11}B/{}^{10}B\right)_{std+1,corr}}{2}}\right) \times \left(\frac{{}^{11}B}{{}^{10}B}\right)_{ref,true}$$

(Eq.S8)

3. Boron concentration in procedural blanks after microsublimation and ion exchange chromatography

Boron concentrations in procedural blanks were determined after four-fold dilution in 0.29 M HF. Determined concentration in each replicate, although typically < LOD, is shown in Table S4.

Table S4 – B concentration in procedural blank samples after microsublimation and ion exchange chromatography

	Microsublimation			**Chromatography**		
	A	B	C	A	B	C
Ca^{2+} solution	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08
Seawater	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08
Spinach	< 0.08	< 0.08	0.44	0.50	0.40	0.60
Silicate glass	< 0.08	< 0.08	< 0.08	0.60	0.40	< 0.08

4. Investigation of correlation between $\delta^{11}B$ offset and B recovery in individual samples

Figure S2 plots $\delta^{11}B$ offset against the B recovery for each individual sample. The offset is defined as the difference between the experimentally determined $\delta^{11}B$ value and the corresponding reference value. The horizontal lines represent the 0.6 ‰ expanded uncertainty as indicated on the certificate of ERM AE 120, 121 and 122 $\delta^{11}B$ reference materials. From the figure, it is clear that within each sample set, no correlation between offset and recovery can be found.

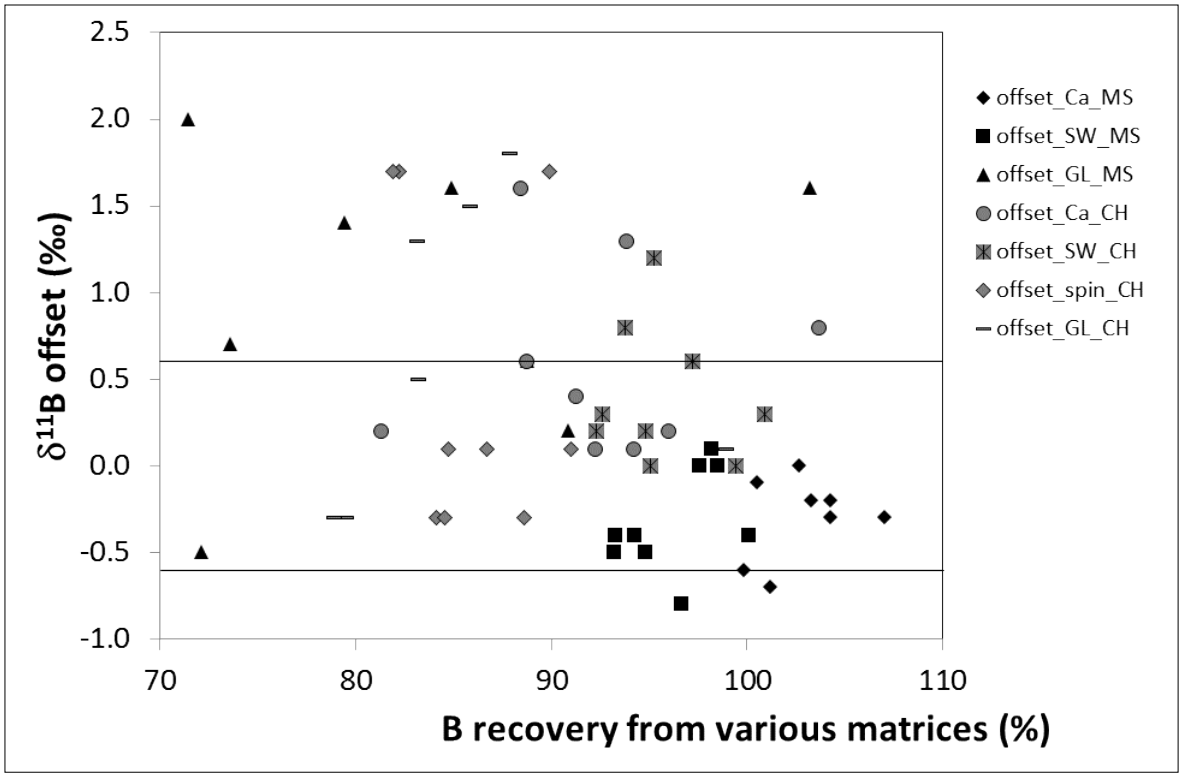

Figure S2 - Scatterplot of $\delta^{11}B$ offset vs. B recovery in individual samples

4. Reference

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[S4] Jochum, K.P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D.E., Stracke, A., Birbaum, K., Frick, D.A., Günther, D., Enzweiler, J., *Geostand Geoanal Res*, 2011, **35**(4), 397-429.

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