Determination of B/Ca of Natural Carbonates by HR-ICP-MS

SUPPLEMENT

Supplement 1. Calibration Standards for Metal/Ca ratio determination

Element ratios	Li/Ca µmol/mol	B/Ca µmol/mol	Na/Ca mmol/mol	Mg/Ca mmol/mol	Al/Ca mmol/mol	Mn/Ca µmol/mol	Fe/Ca mmol/mol	Zn/Ca µmol/mol	Sr/Ca mmol/mol	Cd/Ca µmol/mol	Ba/Ca µmol/mol	U/Ca nmol/mol
Standards												
Standard Solution 0	0.3	0.7	0.007	0.003	0.001	0.2	0.000	0.77	0.005	0.005	0.05	0.1
Standard Solution 1	2.2	15.5	1.970	0.199	0.020	9.9	0.010	1.80	0.478	0.025	2.00	1.0
Standard Solution 2	4.5	32.1	3.133	0.625	0.042	26.2	0.031	2.95	0.832	0.057	3.16	5.2
Standard Solution 3	6.5	62.7	4.118	1.230	0.062	51.4	0.051	4.01	1.023	0.108	4.13	15.4
Standard Solution 4	7.9	94.6	4.673	1.692	0.085	93.5	0.065	5.68	1.122	0.146	4.72	46.8
Standard Solution 5	10.5	132.7	5.693	2.271	0.114	188.1	0.084	8.59	1.317	0.193	5.69	94.4
Standard Solution 6	14.2	179.4	6.967	2.987	0.148	342.6	0.108	11.11	1.582	0.253	8.94	198.2
Standard Solution 7	18.4	228.8	8.503	4.253	0.213	529.9	0.136	17.21	1.902	0.325	12.42	367.6
Standard Solution 8	21.4	274.7	9.493	5.269	0.264	681.1	0.156	22.49	2.093	0.427	15.72	530.3

Supplement 2. B/Ca blank / contamination calculations

B/Ca ratio change for a 0.4 pg B blank during analysis:

$[Ca]_{Matrix}$: *10 ppm = 10 µg/ml*

Volume of solution per analysis = 150 µl = 0.15 ml

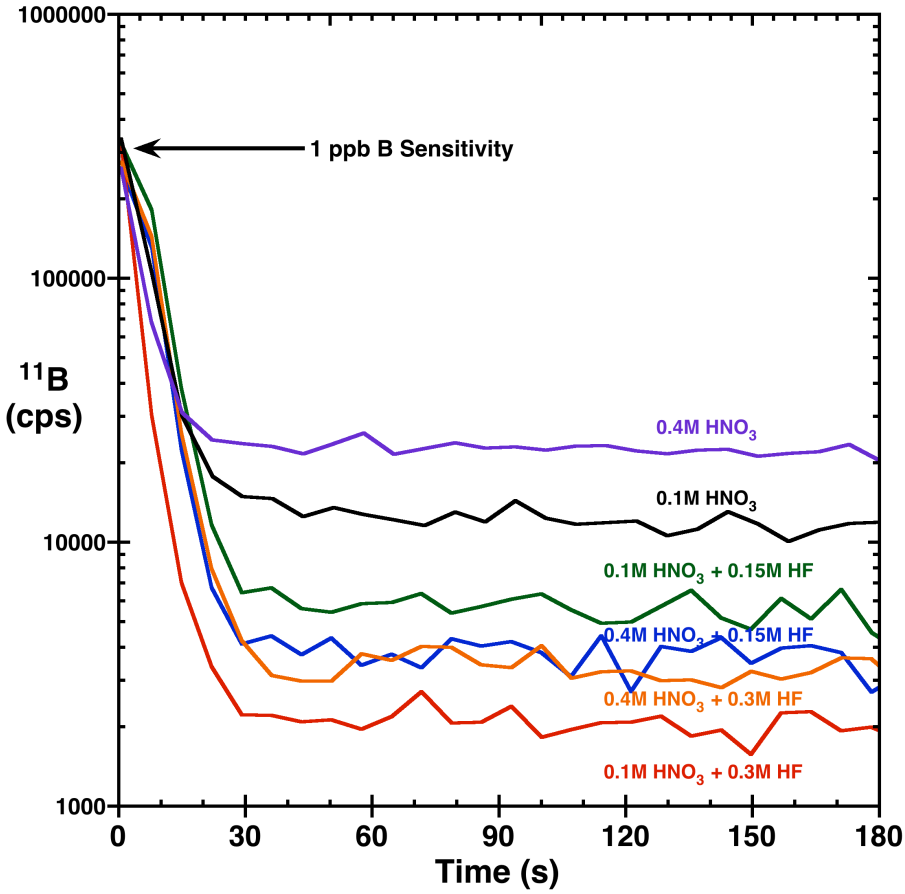
Total Ca = 10 µg/ml x 0.15 ml = 1.5 µg

Mass of B contamination = 0.4 pg

$(B/Ca)_{Contamination}$ *= 0.4 pg / 1.5 µg = 0.4 µg / 1.5 g = 10.67 µg / 40 g*

= 1 µmol / 1 mol = 1 µmol / mol

Supplement 3. Boron washout in different acid matrices

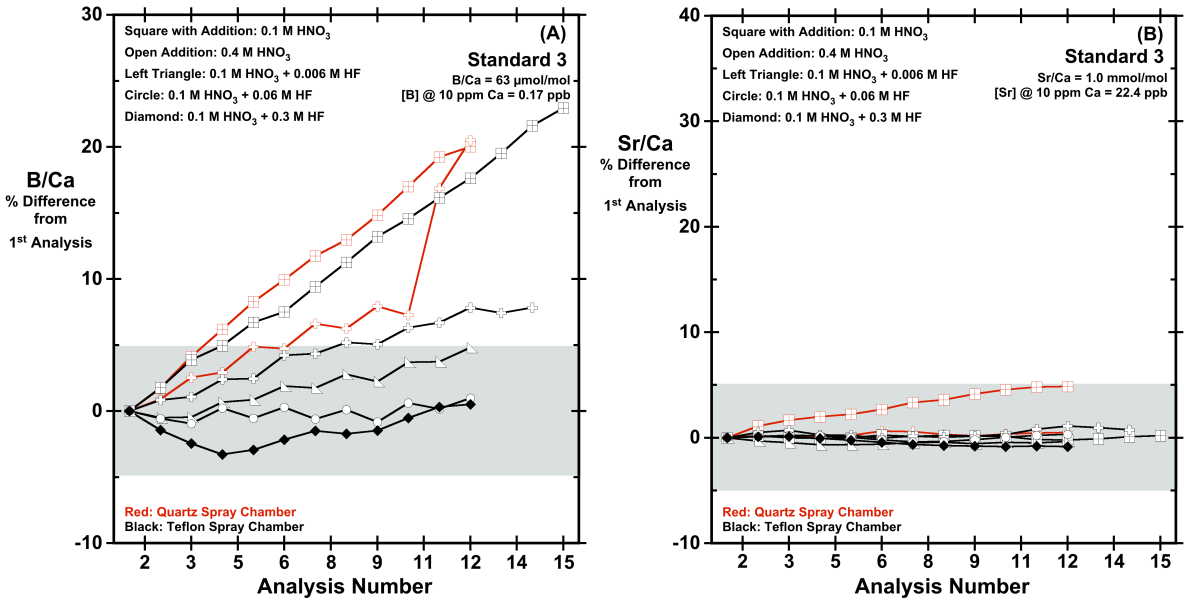


Supplement 3. Time-resolved comparison of boron washout in different molarity HNO_3 and HF acid matrices under identical instrument conditions. Boron sensitivity is plotted on a logarithmic scale to amplify the differences between the matrices. The washout curves are color coded according to their matrix acid and matrix strength. The washout patterns were generated after aspiration of a 1 ppb (ng/ml) high purity boron solution for 180s, typical sample analysis time for $\delta^{11}B$ determination, in the same matrix under investigation.

Quantitative Washout:

When the post sample/standard analysis matrix boron blanks are within ±1% of the pre analysis matrix boron blanks (uncorrected for instrumental drift) – is defined here as 'quantitative washout'.

Supplement 4 (A) and (B). Matrix dependent B/Ca and Sr/Ca washouts



Supplement 4 (A) and (B). Comparison of B/Ca and Sr/Ca memory effects in different acid matrices. Figures (A) and (B) represent back to back analyses of an intermediate concentration standard (Standard 3) bracketed by acid blanks (**Figure 1 and Supplement 1**) – the data for the Standard 3 are shown here. The figures represent percent difference between the first analysis and subsequent analyses for both B/Ca and Sr/Ca. All analyses were performed at 10 ppm $[Ca]_{Matrix}$. The B/Ca and Sr/Ca data are acid blank corrected; however, none of the data are corrected for instrument drift. The grey area in figures (A) and (B) represents ± 5% variation from the first analysis. The red symbols represent analyses performed with a quartz cyclonic spray chamber. All other analyses were performed with a Teflon® Scott type spray chamber – black symbols. The symbols are as follows: 0.1 M HNO_3 – squares with addition symbols; 0.4 M HNO_3 – open addition symbols; 0.1 M HNO_3 + 0.006 M HF – left-triangles; 0.1 M HNO_3 + 0.03 M HF – right-triangles; 0.1 M HNO_3 + 0.06 M HF – circles; 0.1 M HNO_3 + 0.12 M HF – squares; 0.1 M HNO_3 + 0.18 M HF – diamonds; 0.1 M HNO_3 + 0.24 M HF – up-triangles; and 0.1 M HNO_3 + 0.3 M HF – down-triangles.