

Accurate and Precise Determination of Boron Isotope Ratio by QQQ-ICP-MS: Application to natural waters and carbonates

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We present a new method for accurate and precise ($\pm 0.4\%$) boron isotope ratio determination by single collector QQQ-ICP-MS (Agilent™8900). The key advantages of our $\delta^{11}\text{B}$ determination method are pico-gram levels of boron blanks, rapidity of sample preparation and analysis, a low mass requirement of 1.25 ng per analysis, and a relatively high tolerance for matrix mismatch. We utilized a mixture of HF and HNO_3 as ICP-MS sample matrix for rapid washout of boron and high sensitivity. Our long-term instrumental accuracy and precession of $\delta^{11}\text{B}$ determination, quantified through repeat analyses of established secondary boron standards are identical to published results(Figure.1): AE-121 = $19.69 \pm 0.26\%$ (2σ , n=40); AE-120 = $-20.18 \pm 0.23\%$ (2σ , n=16); and AE-122 = $39.60 \pm 0.36\%$ (2σ , n=8). This is the first reported boron isotope determination technique on QQQ-ICP-MS and our accuracy and precession is comparable to / better than published single collector methods.

An improved micro-distillation method for boron purification from carbonate and seawater matrices, characterized by low procedural blanks ($4 \pm 3\text{pg}$, n=9) and quantitative boron recovery ($98.7 \pm 5.5\%$), is also reported. The average seawater boron isotopic composition ($\delta^{11}\text{B}_{\text{SW}}$) of $39.63 \pm 0.40\%$ (2σ , n=51) (Figure.2A) determined on micro-distilled samples is analytically indistinguishable from published values. Additionally, the $\delta^{11}\text{B}_{\text{SW}}$ of $39.68 \pm 0.40\%$ (2σ , n=11) determined on $0.5\mu\text{l}$ seawater (2 ng-B) aliquot is identical to the $\delta^{11}\text{B}_{\text{SW}}$ of $39.67 \pm 0.42\%$ (2σ , n=18) determined on $30\mu\text{l}$ seawater aliquot (120 ng-B). However, we report a systematic offset between $\delta^{11}\text{B}_{\text{SW}}$ micro-distilled in HCl matrix ($35.43 \pm 2.34\%$, 2σ , n=17) compared to nitric acid matrix ($39.63 \pm 0.40\%$, 2σ , n=51). The long-term precision of $\delta^{11}\text{B}$ determination of carbonate samples ($\delta^{11}\text{B}_{\text{Coral}}$), determined through repeat analysis of our in-house coral standard, is $24.44 \pm 0.44\%$ (2σ , n=83)(Figure.2B). The $\delta^{11}\text{B}_{\text{Coral}}$ of the smallest sample ($\sim 2\text{ mg coral} / 15\text{-}40\text{ ng-B}$) analyzed ($24.36 \pm 0.55\%$, 2σ , n=7) identical to that of the largest mass of sample ($\sim 20\text{ mg coral} / 100\text{-}150\text{ ng-B}$) analysed ($24.49 \pm 0.34\%$, 2σ , n=19). Our external precision of $\pm 0.38\%$ (2σ), determined on seven replicates of *Orbulina Universa* samples ($18.59 \pm 0.38\%$, 2σ) from ODP Site 664 in the Atlantic Ocean, would enable pH reconstruction at a resolution (ΔpH) of 0.035 unit. This method can be utilized for applications requiring precession of $\geq 0.4\%$ irrespective of boron mass availability.

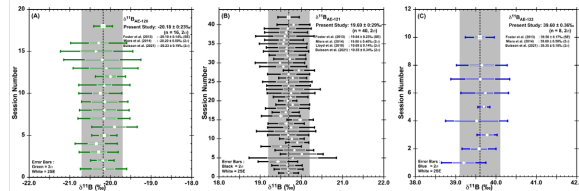


Figure 1: The long-term instrumental accuracy and precession of ^{10}B measurement for AE-120 (Panel A: green symbols), AE-121 (Panel B: black symbols), AE-122 (Panel C: blue symbols). The mean average of ^{10}B (X-axis) are plotted according to source number(Axis). The ^{10}B measurements were done across multiple instrumental sessions spread over a period of 12 months. Individual data points in each panel represent the average of an analytical session ($2 \leq n \leq 20$). Different symbols are for ^{10}B determination at different concentration of boron, viz. the right-angled triangle: 2.0 ng B, the left-angled triangle: 2.7 ng B, right triangle: 3.0 ng B, left triangle: 3.5 ng B, down triangle: 4.0 ng B, up triangle: 4.5 ng B, diamond: 5.0 ng B, circle: 6.0 ng B, square: 7.0 ng B and open plus symbol: 8 ng B. The long-term average of open black square with cross (Panel A: AE-120) ($19.69 \pm 0.26\%$), (Panel B: AE-121) ($19.69 \pm 0.26\%$), (Panel C: AE-122) ($39.60 \pm 0.36\%$). The color and white error bars represent the 2σ and 5σ error (based on 2σ uncertainty) respectively. The dashed lines represent the reported values of AE-120 (19.69%) in Panel A, AE-121 (19.69%) in Panel B, and AE-122 (39.60%) in Panel C. The grey bar in each panel represents the $\pm 0.4\%$ window of accuracy.

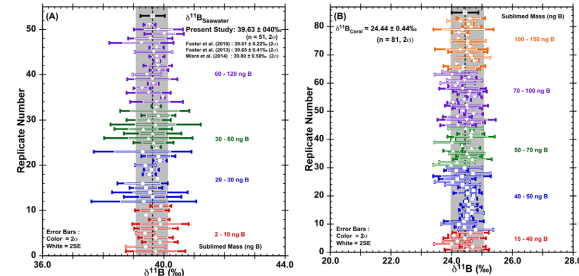


Figure 2: (A) The long-term accuracy and precession of ^{10}B determination of 51 different micro-distilled seawater samples (A) carbonate samples based on over boron coral standard (B). Panel A: Being micro-distilled a variable amount of boron, ranging in mass from 2 ng to 120 ng was processed. The different symbols are based on mass of boron micro-distilled and diameter: $2 - 10\text{ ng}$: blue square; $20 - 30\text{ ng}$: green square; $30 - 60\text{ ng}$: red triangle; $60 - 120\text{ ng}$: orange triangle. The long-term average value of $\delta^{11}\text{B}_{\text{seawater}}$ is $39.63 \pm 0.40\%$ (2σ , n=51). The dashed line represents the reported value of seawater (39.63%) and the grey bar represents $\pm 0.4\%$ window of accuracy. Panel B: A set of 83 different pieces of a homogenized modern coral sample were chemically cleaned, micro-distilled, and analyzed for ^{10}B . The total mass of boron micro-distilled per aliquot ranges from 15 ng to 150 ng . Different symbols are based on mass of boron micro-distilled and diameter: $15 - 45\text{ ng}$: blue square; $45 - 50\text{ ng}$: green square; $50 - 75\text{ ng}$: purple square; $75 - 100\text{ ng}$: orange square; $100 - 150\text{ ng}$: red triangle. The data is a subset of accuracy error of distilled boron mass. The average (black open square with error bar) of 83 measurements is $24.44 \pm 0.44\%$ (2σ , n=83). The color and white error bars represent the 2σ and 5σ error (based on 2σ analytical uncertainty) respectively. The dashed line represents the average value of $\delta^{11}\text{B}_{\text{Coral}}$ (24.44%) and the grey bar represents $\pm 0.4\%$ window of accuracy. In both the panels, each data point represents the average $\delta^{11}\text{B}_{\text{seawater}}$ for each distillation. The ^{10}B (X-axis) is plotted against sample number (Y-axis). Each data point represents the average of triplicate/replicate mass systematic determination. The data is sorted in order of increasing mass of boron micro-distilled. The color and white error bars represent the 2σ and 5σ error (based on 2σ analytical uncertainty) respectively.