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3 1 **A fully automated direct injection nebulizer (d-DIHEN) for MC-ICP-MS**
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5 2 **isotope analysis: application to boron isotope ratio measurements**
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25 13 **Abstract**

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27 14 This work presents a fully automated setup for using direct injection nebulization as
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29 15 introduction system for solution measurement by MC-ICP-MS, here applied to boron isotopes
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31 16 in pure boric acid solutions and natural samples. In this setup, a direct injection nebulizer (d-
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33 17 DIHEN) is plugged into the plasma torch without any spray chamber, and an automated 6-
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35 18 port valve interfaces the nebulizer and the autosampler. The advantages of d-DIHEN for
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37 19 boron isotope ratio measurement are high sensitivity and short washout times, allowing for
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39 20 sample-standard bracketing (SSB) measurements at a higher rate than spray chambers. The
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41 21 measurement of boron isotopes by MC-ICP-MS at unprecedented sub 0.1‰ repeatability
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43 22 level (2 standard deviation = 2SD) was achieved for pure boric acid solutions. The improved
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45 23 precision is allowed by a better stability of the introduction system with continuous operation
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47 24 of the peristaltic pump (which was manually switched off between samples before
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49 25 automation), and to the possibility of multiple analyses of the same sample solution.
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51 26 However, such a good repeatability was not systematically obtained for boron isotopes SSB
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53 27 measurements of natural samples (*in fine* 2SD are between 0.02 and 0.5‰). Boron from
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55 28 natural samples has to be extracted before isotope analysis, with one to four steps depending
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57 29 on the sample type. Repeated analyses of boron independently separated up to ten times from
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59 30 the same sample lead to an external reproducibility no better than 0.2‰. Boron chemical
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31 separation from the samples prior to MC-ICP-MS analyses seems to remain the main
32 limitation to precise measurement of boron isotope ratios.

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3 334 34 **Introduction**

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7 35 One of the most powerful applications of boron isotopes in geochemistry is their potential to
8 36 record present and paleo-ocean pH in marine carbonates¹⁻⁴. For example, ocean acidification
9 37 rates of up to -0.0017 pH units per year over the last 30 years have been reported⁵. According
10 38 to the seawater pH – ¹¹B/¹⁰B relationship¹, a change of 0.01 pH unit corresponds to a change
11 39 of 0.1‰ of the ¹¹B/¹⁰B ratio of marine carbonates, which is thus the required analytical
12 40 precision to apply B isotope measurements.

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15 41 With the recent development of MC-ICP-MS (Multi-Collector Inductively Coupled Plasma
16 42 Mass Spectrometry), boron isotope ratio measurements have gained in accuracy and sample
17 43 throughput^{6,7} compared to TIMS (Thermal Ionization Mass Spectrometry) techniques^{8,9,10}.
18 44 The best reproducibility achieved for B isotope ratio measurements by MC-ICP-MS is now of
19 45 0.25‰ (2SD, standard deviation)^{11,12}. However, improved performances for B isotope
20 46 analysis by MC-ICP-MS have long been hampered by the fact that B is (1) a “sticky”
21 47 element, *i.e.* difficult to wash away from the introduction system, resulting in a strong
22 48 memory effect, and (2) a volatile element partly lost in desolvation units such as the APEX
23 49 (ESI, USA) or the Aridus (CETAC, USA) classically used to enhance sensitivity. For B and
24 50 other elements characterized by similar memory effects, or volatility, direct sample injection
25 51 is a most suitable technique¹³. This technique consists in spraying directly the sample into the
26 52 plasma without using any spray chamber. To this aim, a long quartz nebulizer is directly
27 53 inserted into the plasma torch, and the solution is actively forced into the nebulizer using a
28 54 peristaltic pump. This setup offers many advantages over traditional spray chambers or
29 55 desolvation devices. First, 100% of the sample volume is introduced into the plasma, thereby
30 56 enhancing analyte sensitivity, even without sample desolvation. Secondly, the contact surface
31 57 area between sample and introduction system is minimal, allowing for much shorter wash
32 58 times. A previous study from our group¹² has demonstrated the benefits of using a d-DIHEN¹⁴
33 59 (demountable-Direct Injection High Efficiency Nebulizer) device for B isotope analysis.
34 60 However, with this setup, the continuous presence of the operator was required. Indeed, direct
35 61 injection makes the plasma very sensitive to introduction of air bubbles, which can lead to its
36 62 extinction and possible torch melting¹². To circumvent this problem, before switching from
37 63 one solution to the next, *i.e.* every 2 to 3 min, we had to manually interrupt the peristaltic
38 64 pump that forces the sample through the nebulizer. This limitation has precluded automated
39 65 measurements of B isotopes and has seriously imparted both the sample throughput and the
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3 66 potential associated improvement in the statistical value of the analyses.
4 67 In the present paper, we describe a fully automated method for MC-ICP-MS measurement
5 68 with d-DIHEN as introduction system, using an injection valve coupled with the autosampler,
6 69 which allows for continuous operation of the peristaltic pump. We also report the resulting
7 70 significant improvements for B isotope measurements of standard solutions and natural
8 71 samples, such as seawater, calcium carbonate, river water and sediment samples.
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14 73 **2. Experimental**

15 74 **2.1 Instrumentation**

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19 75 Boron isotope ratio measurements were carried out at the Institut de Physique du Globe de
20 76 Paris on a MC-ICP-MS Neptune (Thermo Scientific, USA). This instrument is equipped with
21 77 9 Faraday collectors (10^{11} ohms amplifier resistors): 4 low-mass (L1 to L4) and 4 high-mass
22 78 (H1 to H4) collectors, on each side of a fixed center cup. Collectors can be moved according
23 79 to the mass array of the isotopes to be measured. For B isotope analyses, Faraday cups L3 and
24 80 H3 recorded ^{10}B and ^{11}B signals, respectively. The d-DIHEN nebulizer (Analab, France) was
25 81 inserted into the plasma torch in place of a regular quartz injector. Solutions were pumped
26 82 into the nebulizer using a 12-rod peristaltic pump (SPETEC, Germany) rotating at 15 rpm,
27 83 resulting in an uptake rate of $50 \mu\text{L min}^{-1}$. With 100% sample volume being injected into the
28 84 plasma, this introduction system generates “extra-wet plasma” conditions. MC-ICP-MS
29 85 operating parameters are given in Table 1. Measurements were automatized using a FAST 6-
30 86 port valve (ESI, USA), connected to a SC-autosampler (ESI, USA) and controlled by the ESI
31 87 SC-autosampler software.
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44 88 **2.2 Chemistry materials, standards and reagents**

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46 89 All stock solutions of standards and reagents were preserved in PTFE and PP bottles. Nitric
47 90 acid was purified by sub-boiling distillation in a DST-1000 unit (Savillex, USA). Ammonia
48 91 was purified by distillation at room temperature. Ultra-pure water was produced by a Milli-Q
49 92 unit (resistivity higher than $18\text{M}\Omega\cdot\text{cm}$, Millipore, USA). Boron standard solutions were
50 93 prepared from the international standard reference material (SRM) boric acid salt SRM 951
51 94 (NIST, USA) ($^{11}\text{B}/^{10}\text{B} = 4.04362 \pm 0.00137$)¹⁵. Traditionally, $^{11}\text{B}/^{10}\text{B}$ ratios for natural
52 95 samples, or $(^{11}\text{B}/^{10}\text{B})_{\text{sample}}$ are expressed as $\delta^{11}\text{B}$ in per mil unit (‰), the deviation relative to
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3 96 the SRM 951 boron standard :

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5 97 $\delta^{11}\text{B} = ((^{11}\text{B}/^{10}\text{B})_{\text{sample}} / (^{11}\text{B}/^{10}\text{B})_{\text{SRM951}} - 1) \times 1000$

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7 98 ^{10}B -enriched standard solutions were prepared by mixing weighed amounts of SRM 951 and
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9 99 952 B solutions (NIST, USA)^{12,15}. One of these solution, named SE43, and the international
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11 100 seawater reference material NASS-5 (National Research Council of Canada) were used as in-
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13 101 house B isotope reference solutions¹². Two ion exchange resins were used for the chemical
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15 102 extraction of B from natural samples: anionic resin Amberlite IRA-743 (Dow, USA) with
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17 103 very high partition coefficient for B at pH 8-10, and the cationic resin AG 50W-X8 (BioRad).
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19 104 Alkaline fusions were performed with high purity- K_2CO_3 (Puratronic, Alfa Aesar), using a
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21 105 1/7 sample/flux ratio. All chemistry work was carried out in a clean air (HEPA H13)
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23 106 laboratory room with positive pressure.

23 107 **2.3 MC-ICP-MS measurements**

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25 108 Before analysis, sample and standard solutions were generally diluted to 200 ppb with 0.05 M
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27 109 HNO_3 , the introduction medium for the MC-ICP-MS. Analyses were made in low-resolution
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29 110 mode (M/ Δ M about 400). The method started with an uptake of 1 min followed by a 30 s-
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31 111 baseline in “defocus” mode (extraction lens cut off), and by 15 cycles of 8 s integration for
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33 112 ^{10}B and ^{11}B signals. A wash time of 3 min resulted in a residual ^{11}B signal of only 1% of the
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35 113 intensity measured for the 200 ppb B standard solution. For solutions at 100 ppb B or higher,
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37 114 residual background was not corrected for (see 3.3), but was still monitored. The ^{11}B peak
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39 115 was centered every 25 measurements. Over two years, the sensitivity varied between 4 and 10
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41 116 V on ^{11}B for 200 ppb B standard solutions introduced at $50 \mu\text{L min}^{-1}$. Mass bias was corrected
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43 117 by standard-sample bracketing (SSB), following a specific sequence. Each sample was
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45 118 measured three times in a row, allowing for statistical analysis of five $\delta^{11}\text{B}$ values (Fig. 1;
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47 119 three $\delta^{11}\text{B}$ values from the three samples bracketed by the standards and two $\delta^{11}\text{B}$ values from
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49 120 the two standards bracketed by the samples¹⁶). The average and 2SD (2 standard deviation)
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51 121 for these five values are called hereafter “ $\delta^{11}\text{B}_{\text{smpl}}$ ” and repeatability, respectively. By contrast,
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53 122 the reproducibility of a sample is defined as the 2SD from many $\delta^{11}\text{B}_{\text{smpl}}$ values generally
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55 123 measured during different MC-ICP-MS sessions.

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55 125 **2.4 Connecting the SC-FAST system and the d-DIHEN to the MC-ICP-MS**

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57 126 The FAST device is commonly used to decrease wash times during ICP-MS analysis. With
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3 127 this apparatus, the sample is introduced into the nebulizer through an injection loop, allowing
4 128 washout of the autosampler probe and tubings while the sample is being analyzed. The
5 129 interest of using the FAST valve resides in (1) its very small dead volumes (0.4 μm -bore
6 130 holes for the low-flow version of the valve) and (2) its software, designed to operate in
7 131 conjunction with both the SC-autosampler and MC-ICP-MS Neptune software.

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11 132 The d-DIHEN / FAST / autosampler assembly is represented in Figure 2. The autosampler
12 133 and the d-DIHEN are connected to ports 4 and 5 of the FAST valve; port 1 discharges into a
13 134 waste bottle via the peristaltic pump; port 6 receives a carrier solution (HNO_3 0.05 M). Ports
14 135 2 and 3 are simply connected as a small loop. In the present setup, the FAST valve
15 136 introduction loop was not used. The autosampler wash station was fed by a 2 L bottle of
16 137 HNO_3 0.05 M.

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22 138 The experimental setup was optimized to limit solution volumes in the introduction system,
23 139 and all the tubings used for the different connections towards the d-DIHEN were PTFE- or
24 140 Tygon-made, with an inner diameter (id) of 0.19 mm. The autosampler probe tubing id was
25 141 0.25 mm. The outlet to the waste bottle had an id of 0.51 mm. All the connections and Tygon
26 142 tubing were systematically checked before plasma ignition to avoid any air bubble in the
27 143 circuit and to ensure a stable flow of solution towards the injector. The Tygon tubings were
28 144 changed every 3 to 5 days.

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34 145 The FAST valve has two positions or settings (Fig 2): 1/ in LOAD position the carrier
35 146 solution is introduced into the d-DIHEN while the solution from the autosampler (either
36 147 sample, standard or wash) is pumped towards the FAST valve and the waste bottle; 2/ in
37 148 INJECT position the solution previously loaded from the autosampler is introduced into the d-
38 149 DIHEN, while the carrier solution rinses the valve and is delivered to the waste bottle.
39 150 Appropriate timing between the FAST valve rotation and the peristaltic pump uptake, as well
40 151 as stability of the uptake rate through time, precludes the introduction of air through the
41 152 autosampler probe during solution change. At an uptake rate of $50 \mu\text{L}\cdot\text{min}^{-1}$, using the
42 153 standard autosampler probe and tubes length (50 cm from the sample vial to the FAST valve),
43 154 15 s are necessary for the solution to reach the FAST valve. To ensure that the air bubble
44 155 pumped into the tubings during solution change has passed the valve, the FAST valve is
45 156 switched from LOAD to INJECT after another 3 s. The FAST valve program, used in the SC-
46 157 autosampler software, is given in Table 2.

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56 158 The d-DIHEN injector was tuned before being placed into the plasma torch, in order to obtain
57 159 a stable, non-pulsated, and dense spray featuring fine droplets¹². Argon flow settings for
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3 160 plasma ignition are slightly different from those classically used with spray chambers or
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5 161 desolvation systems (lower for sample gas ($0.2 \text{ L}\cdot\text{min}^{-1}$) and higher for auxiliary gas (1.2 to
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7 162 $1.6 \text{ L}\cdot\text{min}^{-1}$). After one hour of plasma stabilization, instrument settings (gas flows, torch
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9 163 position, lenses voltage) were optimized using a 200 ppb B solution, for sensitivity, stability
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11 164 and peak shape. With the instrumental settings optimized for B, the NdO^+/Nd^+ level was as
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13 165 high as 30%. The BO^+/B^+ oxide level, however, never exceeded 2%. The stability of the
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15 166 instrumental mass bias was checked systematically before sample analyses by bracketing a
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17 167 solution of pure boric acid SRM 951 at a concentration of 200 ppb over itself, and considered
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19 168 suitable when variations between two consecutive standards were lower than 0.1%. Accuracy
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21 169 and precision were assessed measuring two in-house reference solutions (NASS-5 and SE43)
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23 170 and 3 pure boric acid solutions of known isotopic ratio (see 3.1).

24 171 **2.5 Boron chemical separation from natural samples**

25 172 Boron was separated from natural samples to avoid matrix effects that bias isotopic ratio
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27 173 measurements. Different separation procedures were used according to the nature of the
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29 174 samples. The ion-exchange resin commonly used for B separation is Amberlite IRA-743, and
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31 175 our procedure was adapted from Lemarchand et al.¹⁰. Boron is best retained onto this resin at
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33 176 pH 8-10, and is eluted with HNO_3 0.5 M and 0.1 M successively¹⁷. Solutions were adjusted to
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35 177 pH 9 before loading onto the Amberlite columns. River water samples were directly loaded
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37 178 on 50 μL columns; seawater on 10 μL columns. Carbonate samples were dissolved in HNO_3
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39 179 0.5 M, while rock, soil and sediment samples were digested by K_2CO_3 alkaline fusion. Most
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41 180 cations were removed from these sample solutions using cation exchange resin AG W50-X8.
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43 181 Carbonate samples were then loaded on 10 μL Amberlite columns. Rock, soil and sediment
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45 182 samples were passed on a 50 μL Amberlite column and then B was purified through a 10 μL
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47 183 Amberlite column.
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50 185 **3. Results and discussion**

51 186 The result we mostly expected from this fully automated system was to be able to run MC-
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53 187 ICP-MS isotope ratio measurements with the d-DIHEN overnight without any human
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55 188 intervention. This goal was successfully achieved, as it is now possible to measure around 30
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57 189 samples per day (or 90 if they are only measured once instead of thrice). In addition,
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59 190 automation led to an improvement of the quality of our measurements.
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191 3.1 Improved $\delta^{11}\text{B}$ measurements of pure acid boric solutions

192 Internal standard errors ($\text{SE} = \text{SD}/n^{1/2}$, with n the number of $^{11}\text{B}/^{10}\text{B}$ integration cycles, $n=15$)
193 on the $^{11}\text{B}/^{10}\text{B}$ ratio measurements were typically between 0.01 and 0.04‰, similar to internal
194 errors measured before automation¹².

195 To assess the short-term stability of the automated setup and data treatment, a SRM 951
196 solution at a concentration of 200 ppb was bracketed 11 times over itself during a 25 hours
197 session, with the same method as for the samples (*i.e.* including wash). The repeatability of
198 each of these 11 $\delta^{11}\text{B}_{\text{std}}$ (average over 5 calculated $\delta^{11}\text{B}$ values, Fig. 1) was between 0.01 and
199 0.13‰ (2SD) and the reproducibility over the 11 determined $\delta^{11}\text{B}_{\text{std}}$ was 0.01‰ (2SD). The
200 reproducibility obtained on the individual $\delta^{11}\text{B}_{\text{std}}$ values (0.10‰, 2SD, $n=55$) can be
201 compared to a similar run we reported for a SRM 951 solution measured overnight, before
202 automation of the d-DIHEN introduction method¹², reaching a reproducibility (2SD) of
203 0.25‰. Importantly, this run had been done with continuous operation of the peristaltic pump
204 as well, but without washes between each measurement. Therefore, in this case the operation
205 of the peristaltic pump is not the reason for the better reproducibility. The main difference
206 with the present measurement is rather that here, the introduction setup was rinsed by
207 introducing HNO_3 0.05 N between each SRM 951 solution. In the pre-automation run¹², we
208 had observed that small air bubbles were forming on the walls of the capillary transporting the
209 sample solution to the injector. With time, these bubbles coalesced and were eventually
210 introduced in the plasma if the capillary remained in the same solution for too long. In the
211 present automated measurement, the coalescence of air bubbles was precluded by repeated
212 changes of the pumped solution (wash periods between each sample measurement), which
213 “cleans” the capillary walls when a new solution is introduced. Another reason for this better
214 reproducibility with the automated setup is that the Neptune MC-ICP-MS moved to a new
215 building, with a better air conditioning system, and a laminar flow hood was installed above
216 the sample introduction and torch parts of the instrument, enhancing the stability of the air
217 temperature and avoiding drafts.

218 The long-term stability of our setup was evaluated by repeated measurement of pure boric
219 acid solution over two years. Measurements of boric acid solution SE43 yielded a $\delta^{11}\text{B}$ value
220 of $-43.24 \pm 0.19\text{‰}$ (2SD, 45 independent $\delta^{11}\text{B}_{\text{SE43}}$ values), in good agreement with the value
221 determined prior to automation¹² ($-43.15 \pm 0.25\text{‰}$), and slightly better long-term
222 reproducibility (Fig 3a). Three other solutions made out of boric acid reference materials
223 AE120, AE121 and AE122¹⁸ were measured in good agreement with the certified values

224 (Tab. 3), with reproducibility over 5 months of 0.09 to 0.25‰ (4 independent determinations
225 of $\delta^{11}\text{B}_{\text{AE12X}}$).

226 With a reproducibility of 0.1‰, $\delta^{11}\text{B}$ measurements of pure boric acid solutions with the fully
227 automated d-DIHEN are thus very stable at a day scale but over months or years become less
228 stable. At this level of precision, several factors become crucial to improve stability, such as
229 preservation of the solutions (contamination from ambient laboratory atmosphere¹¹ or
230 adsorption onto vial walls) or MC-ICP-MS setup (plasma, torch, cones, slits) from one
231 session to the next. All these possible reasons for small variations of the measured values of
232 $\delta^{11}\text{B}$ have to be investigated in the future. Thanks to our fully automated setup that increases
233 the sample throughput, we are now able to measure a sample several times in a row, thus
234 improving the statistical value of our isotopic determinations. The $\delta^{11}\text{B}$ repeatability obtained
235 on pure B solutions, better than 0.1‰, is the best ever achieved for B isotope analyses and
236 demonstrates the interest of automated d-DIHEN sequences for precise B isotope analyses.

237 3.2 Improved $\delta^{11}\text{B}$ measurements of natural samples

238 The $\delta^{11}\text{B}_{\text{Smp}}$ of seawater, carbonate and river water samples
239 was generally below 0.1‰ (2SD, black crosses in Fig 4, data in Electronic Supplementary
240 Informations - ESI, Tab. S1), but reached in some cases much higher values, up to 0.5‰. In
241 most cases, this worse repeatability was attributed to residual matrix despite B separation or
242 resin fragments, affecting the instrumental mass bias¹². Doping experiments were conducted
243 to assess these matrix effects. SRM 951 solutions at 200 ppb were doped with Na, Ca, Fe,
244 SiO_2 and mannitol (used here as an analogue to organic matter) at 10, 100 and 1000 ppb and
245 the $^{11}\text{B}/^{10}\text{B}$ ratio of these solutions was measured and bracketed by a pure SRM 951 solution
246 (Fig. 5). Matrix effects are observed for Na, Ca and Fe at 1000 ppb, with $\delta^{11}\text{B}_{\text{Smp}}$ values up to
247 +0.4‰. No significant matrix effect was observed for Na, Ca, and Fe at concentrations of 100
248 ppb or lower, nor for mannitol or silica. Different tuning of the plasma and torch (auxiliary
249 gas, axial position and plasma power) may influence the amplitude of these matrix effects.
250 Preliminary tests indicate that working at 1000W instead of 1200W would reduce matrix
251 effects on sodium by a factor of up to 2.

252 For measurements of carbonates, seawaters, or river waters and sediments, we also observed
253 that $^{11}\text{B}/^{10}\text{B}$ ratio of the bracketing SRM 951 solution was less stable than for pure boric acid
254 measurements, and typically drifted by up to 0.8‰ per hour (blue squares in Fig 4a, b and c).
255 Again, this drift is most likely due to the injection into the plasma of potential matrix residues

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3 256 (from B chemical separation) affecting long-term stability of the instrumental mass bias.
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5 257 We conclude that introduction of solutions with various residual matrix (*e.g.* none for SRM
6 258 951, Ca for carbonates, Na for seawater) should lead to varying instrumental mass bias
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8 259 between different solutions. Moreover, it can be hypothesized that these residual matrix also
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10 260 have a “memory effect”, such that for example the residual matrix introduced with a sample
11 261 also affects the next pure B solution. In this case, the instrumental mass bias prevailing during
12 262 sample introduction will be fairly comparable to the mass bias during introduction of the next
13 263 standard solution, but not to the mass bias during introduction of the previous standard
14 264 solution. Therefore, we expect that the first time such a sample is measured within a series of
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16 265 three consecutive measurements, it will yield a $\delta^{11}\text{B}_{\text{smp}}$ value different from those measured
17 266 afterwards. Our scheme, consisting in repeating the standard-sample bracketing three times in
18 267 a row (Fig. 1) enables us to investigate these effects and to detect and exclude outlier $\delta^{11}\text{B}$
19 268 values. To that purpose, whenever 2SD calculated from the five $\delta^{11}\text{B}_{\text{smp}}$ values, or
20 269 repeatability, was worse than the optimum 0.1‰ obtained on pure B solutions (paragraph
21 270 3.1), the data was more closely examined (see also data table S1):

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28 271 - **Standards:** for each of the four standard solutions in our SSB sequence, a $\delta^{11}\text{B}_{\text{std}}$ value is
29 272 calculated using the $^{11}\text{B}/^{10}\text{B}$ ratios of the immediately preceding and following standard
30 273 solutions as bracketing values (small red dots in Fig. 1 and 4). If $\delta^{11}\text{B}_{\text{std}} > 0.1\text{‰}$ or $\delta^{11}\text{B}_{\text{std}} < -$
31 274 0.1‰, this measurement was considered to be affected by matrix effects and was excluded.
32 275 The next $\delta^{11}\text{B}_{\text{smp}}$ in the series (respectively previous) was calculated with the next
33 276 (respectively previous) $^{11}\text{B}/^{10}\text{B}$ standard ratio. As hypothesized above, outliers were mainly
34 277 observed for the second standard of the bracketing sequence, right after the first introduction
35 278 of a sample potentially containing residual matrix.

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42 279 - **Samples:** the five $\delta^{11}\text{B}_{\text{smp}}$ values were examined in a similar manner. If one deviated
43 280 further than $\pm 0.1\text{‰}$ than $\delta^{11}\text{B}_{\text{smp}}$, it was excluded. When these outliers (up to two out of five)
44 281 were excluded, average $\delta^{11}\text{B}$ were re-calculated with the remaining values.

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47 282 - **Stability:** the stability of the three successive bracketing measurements of one sample was
48 283 also estimated. We calculated three $\delta^{11}\text{B}_{\text{stab}}$ values from the four $(^{11}\text{B}/^{10}\text{B})_{\text{std}}$ ($=R_{\text{std}}$) and from
49 284 the three $(^{11}\text{B}/^{10}\text{B})_{\text{sample}}$ ($=R_{\text{smp}}$) as follow:

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$$\delta^{11}\text{B}_{\text{stab1}} = \{2R_{\text{std2}}/(R_{\text{std1}}+R_{\text{std3}})-1\} \times 1000 \text{ (standard over itself)}$$

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54 286
$$\delta^{11}\text{B}_{\text{stab2}} = \{2R_{\text{std3}}/(R_{\text{std2}}+R_{\text{std4}})-1\} \times 1000 \text{ (standard over itself)}$$

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56 287
$$\delta^{11}\text{B}_{\text{stab3}} = \{2R_{\text{smp2}}/(R_{\text{smp1}}+R_{\text{smp3}})-1\} \times 1000 \text{ (sample over itself)}$$

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58 288 The average of these three $\delta^{11}\text{B}_{\text{stab}}$ values is reported in Figures 1 and 4 (large black open
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3 289 circles), with the associated 2SD: the largest these average and error values, the worst the
4 290 2SD repeatability of the sample (black crosses).

5 291 In some cases, no specific pattern was observed for the distribution of the five $\delta^{11}\text{B}_{\text{smpl}}$ values,
6 292 and thus no value could be excluded. The measurement was then duplicated. If the duplicate's
7 293 repeatability was still high, another chemical separation had to be performed, when possible.

8 294 The long-term measurement of the seawater NASS-5 over two years gave a $\delta^{11}\text{B}$ average
9 295 value of $39.87 \pm 0.25\text{‰}$ (2SD, 58 independent $\delta^{11}\text{B}_{\text{NASS5}}$ determinations, Fig 3b), consistent
10 296 with those previously determined without automation ($39.89 \pm 0.25\text{‰}$)¹², with a similar long-
11 297 term reproducibility. The fact that a similar long-term reproducibility was obtained for NASS-
12 298 5 seawater with and without automation, despite the better performances observed for pure
13 299 boric acid solutions, is imputable to: i/ residual matrix effects despite the B chemical
14 300 separation and the statistical treatment described above; ii/ poor reproducibility of B chemical
15 301 separations; iii/ ageing of the solutions measured over time spans of several months; iv/
16 302 fluctuating instrumental and procedure blanks (3.3).

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18 304 With two years experience of measuring $\delta^{11}\text{B}$ in natural samples with this automatized
19 305 procedure, no general relationship appears between the type of natural sample and the
20 306 repeatability of $\delta^{11}\text{B}$ measurement. Usually, a run consists of a succession of different type of
21 307 natural samples. To understand the influence of the sample's nature measured through the
22 308 course of a run, we show in Figure 4 three runs of purified natural samples of only one type,
23 309 seawater (Fig. 4.a), carbonate (Fig. 4.b) or river water samples (Fig. 4.c) over more than 16
24 310 hours. For each of the runs shown in Figure 4, we present the time evolution of the $^{11}\text{B}/^{10}\text{B}$
25 311 ratio measured for the bracketing standard solution. To evaluate the stability of the measured
26 312 standard ratios, we perform a "standard-standard bracketing" where each standard $\delta^{11}\text{B}$ value
27 313 is calculated against the average of the two surrounding ratios. For each sample (whose
28 314 isotopic ratios are not shown), we calculate the average of the three $\delta^{11}\text{B}$ arising from the SSB
29 315 as explained in Fig. 1. We also show the repeatability of each sample (2SD of the 5 $\delta^{11}\text{B}$
30 316 values calculated by SSB). We notice that a remarkably good repeatability (black crosses)
31 317 was achieved for the seawater samples and that the carbonates and river water samples appear
32 318 less satisfying. Such a pattern is not systematic, as we experienced runs with not as low
33 319 repeatability for other seawater samples or, conversely, with much better repeatability for
34 320 carbonate and river water samples. One could expect worse repeatability for carbonate and
35 321 sediment samples as they undergo additional chemical treatment prior to B separation, but

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3 322 this was not unambiguously observed as shown by the comparison between carbonate and
4 323 river water samples (Fig. 4b and 4c, ESI data Tab. S1b).

5 324 We emphasize that the level of $\delta^{11}\text{B}$ precision required for geochemical studies of these
6 325 natural samples may vary. For river water and sediment studies, $\delta^{11}\text{B}$ values often span ranges
7 326 of tens of ‰ and a repeatability of 0.2 to 0.5‰ is generally sufficient. For carbonate and
8 327 seawater studies, better repeatability is usually necessary, as $\delta^{11}\text{B}$ variations are smaller, but
9 328 most likely not as low as 0.1‰.

10 329

11 330 **3.3 Blank levels and samples with low B content**

12 331 Blank levels of the chemical procedure were measured using ^{11}B intensity on the MC-ICP-
13 332 MS. These levels varied, according to the separation procedure (which depends on the sample
14 333 type) between 0.2 (for B chromatographic separation alone) and 8 ng of boron (for alkaline
15 334 fusion plus B separation). The $\delta^{11}\text{B}$ of these chemistry blanks typically varied between -10
16 335 and +10‰. Concerning the rock and soil samples mineralized by alkaline fusion, separation
17 336 blank correction was necessary when their B content was lower than 10 ppm. Altogether, B
18 337 chemical extraction blanks were low enough in concentration not to impair measurements
19 338 made on 200 ppb B solutions.

20 339 For samples with low B content (down to 10 ppb, *e.g.* rain waters or some carbonates) ,
21 340 internal standard error of the $^{11}\text{B}/^{10}\text{B}$ measured was generally below 0.0002 (0.04‰) and
22 341 repeatability of the $\delta^{11}\text{B}$ on three successive sample measurements below 0.15‰. However, at
23 342 such low concentrations, accurate B isotope determinations required an instrumental
24 343 background correction by on-peak zeroes. Influence of the instrumental blank over B isotope
25 344 measurements depends on two parameters: the difference between sample and blank $^{11}\text{B}/^{10}\text{B}$
26 345 ratios, and the signal to noise ratio between the sample and the blank. The closer the sample
27 346 and blank $\delta^{11}\text{B}$ are, the lesser the impact of blank on sample measurement is. Instrument
28 347 background $^{11}\text{B}/^{10}\text{B}$ was highly enriched in ^{10}B , with $\delta^{11}\text{B}$ values as low as -150‰.
29 348 Interference of Ar^{4+} on ^{10}B peak is not a possible explanation for low $\delta^{11}\text{B}_{\text{blk}}$ value, as those
30 349 peaks are well resolved (ESI, Fig. S2). Therefore, this background rather reflects instrument
31 350 memory, such as B potentially deposited onto the cones and undergoing thermo-ionization
32 351 with a strong isotope fractionation favouring light isotopes. In any case, for a small sample
33 352 with high $\delta^{11}\text{B}$, the variability induced by the blank correction could be significantly higher
34 353 than the repeatability of the measurement.

35 354 Figure 6 reports $\delta^{11}\text{B}$ measurements of boric acid SRM 951 solutions at B concentrations
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3 355 between 1 and 400 ppb, the bracketing solution being at 200 ppb (data and blank correction
4 356 equation in ESI, S2). Blank-corrected and uncorrected measurements are undistinguishable
5 357 for concentrations between 100 and 400 ppb. Blank corrections are needed for B
6 358 concentrations ≤ 50 ppb, which corresponds to a signal to noise ratio ≤ 170 . For solutions
7 359 with $[B] < 25$ ppb, the blank-corrected values seem to be over-corrected, with systematically
8 360 positive $\delta^{11}\text{B}$ values compared to the bracketing 200 ppb SRM 951 solution (by definition at
9 361 0‰). This shows that when samples with small B content are bracketed with solutions with
10 362 much larger $[B]$, the measured blank is too high compared to the actual blank as the
11 363 background after a 200 ppb B solution is higher than after solutions with $[B] < 25$ ppb. Based
12 364 on the results of Figure 6, we attempted to determine the blank $\delta^{11}\text{B}$ value of the instrument.
13 365 By calculating the $\delta^{11}\text{B}$ values resulting from a mixing equation (in ESI, S2) between the
14 366 blank and SRM 951 solutions at concentrations between 1 and 400 ppb, $[B]_{\text{blk}}$ and $\delta^{11}\text{B}_{\text{blk}}$ that
15 367 best fit the decreasing $\delta^{11}\text{B}$ curve on Figure 6 are between 0.1 and 0.3 ppb and between -250
16 368 and -100‰, respectively, in agreement with our previous estimation of $\delta^{11}\text{B}_{\text{blk}}$ at -150‰.

27 28 369 **3.4 Reproducibility of B chemical extraction**

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30 370 In order to assess the reproducibility of the B separation procedure for seawater samples, the
31 371 North Atlantic Surface Seawater NASS-5 was processed 12 times through ion
32 372 chromatography columns. For each of these 12 separations, $\delta^{11}\text{B}_{\text{NASS-5}}$ values were measured as
33 373 described previously. Two $\delta^{11}\text{B}$ values were more than 0.5‰ below the previously reported
34 374 value and were considered as outliers reflecting issues during B separation (ESI, Tab. S3).
35 375 The other 10 led to an average of $39.83 \pm 0.20\text{‰}$, in good agreement with our previous long-
36 376 term average $\delta^{11}\text{B}$ value of $39.85 \pm 0.25\text{‰}^{12}$. The 2SD uncertainty associated to the
37 377 reproducibility of chemical separation is twice as large as individual measurement
38 378 repeatability, and is comparable to the long-term reproducibility calculated for NASS-5
39 379 measurements (paragraph 3.2). This observation hints at a change of the stock solution
40 380 isotope composition during storage or repeating handling over time scales of several months,
41 381 and through possible contamination by atmospheric B.
42 382 For a river water sample processed 4 times through Amberlite resin 50 μL columns,
43 383 reproducibility was 0.3‰ (0.16‰ if one value was excluded, ESI, Tab. S3). For a coral
44 384 sample, four independent dissolutions and B separations led to a $\delta^{11}\text{B}$ value of $25.05 \pm 0.3 \text{‰}$
45 385 (2SD), comparable to previous determinations ($24.9 \pm 0.3\text{‰}^{19}$, $24.65 \pm 0.25\text{‰}^{12}$). Eight
46 386 independent preparations of the standard reference basalt JB2, by alkaline fusion, cationic

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3 387 exchange column and B separation led to an average $\delta^{11}\text{B}$ value of $7.25 \pm 0.47\%$ (2SD), in
4 388 good agreement with previously reported values ($6.83 \pm 0.52\%$ ²⁰, $7.23 \pm 0.47\%$ ²¹,
5 389 $7.0 \pm 0.5\%$ ²²). Measurement data for determining the reproducibility of B separations of the
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8 390 different natural samples considered here are reported in Table S3 (ESI).

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10 391 Altogether, these results demonstrate that $\delta^{11}\text{B}$ determination in natural samples at sub 0.1‰
11 392 (2SD) level remains hampered by the B chemical separation procedures (and/or sample
12 393 heterogeneity for solid samples). The reproducibility of the separation procedures is now
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14 394 clearly the limiting step towards better B isotope measurements.
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18 19 396 **4. Conclusions**

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21 397 Automation of the solution delivery to the d-DIHEN by coupling a valve to the autosampler
22 398 (1) allows for the analysis of samples 24 hours per day, increasing sample throughput, and (2)
23 399 yields more stable conditions and thus allows us to reach an unprecedented sub-0.1‰
24 400 precision level (2SD, repeatability over five successive determinations), which is twice as
25 401 good as the best reproducibility reported to date (0.25% ^{11,12}). This level of precision has not
26 402 yet been achieved for long-term measurements nor for all natural samples. Particular care has
27 403 to be taken during extraction and purification of B from the sample prior to isotope
28 404 measurement. Blanks must be carefully checked, and even corrected for if small B quantities
29 405 are measured. Proper conservation of dilute B solutions might also be crucial at this level of
30 406 precision. Reproducibility of B isotope ratio measurements around 0.2 – 0.4‰ (2SD) is
31 407 sufficient for most geochemical applications, such as the study of water-rock interactions and
32 408 global B geochemical mass-budgets. However, tracing recent ocean acidification could
33 409 require a 0.1‰-precision level and novel scientific applications are likely to emerge if high-
34 410 precision analytical techniques make it possible. It is therefore critical not only to improve the
35 411 precision and accuracy, but also to develop new B extraction procedures for natural samples
36 412 that would reduce residual matrix effects and be more reproducible. The automated d-DIHEN
37 413 introduction technique might also be of great interest for elements other than boron, with
38 414 similar analytical limitations such as memory effects and/or loss within desolvation devices.
39 415 The higher sample throughput offered by automated d-DIHEN measurements, is likely to be
40 416 of great interest for environmental studies where monitoring and continuous screening are
41 417 more and more requested.
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431 **References**

- 432 1 N. Hemming and G. Hanson, *Geochim. Cosmochim. Acta* 1992, **56**, 537.
- 433 2 P.N. Pearson and M.R. Palmer, *Nature* 2000, **406**, 695..
- 434 3 B. Hönisch and N.G. Hemming, *Earth Planet. Sci. Lett.* 2005, **236**, 305
- 435 4 J.W.B. Rae, G.L. Foster, D.N. Schmidt and T. Elliott, *Earth Planet. Sci Lett.* 2011, **302**,
436 403.
- 437 5 N.R. Bates, M.H.P. Best, K. Neely, R. Garley, A.G. Dickson, and R.J. Johnson,
438 *Biogeosci.* 2012, **9**, 2509.
- 439 6 R. Gonfiantini and 30 others, *Geostand. Newslett.* 2003, **27**, 41.
- 440 7 J.K. Aggarwal, and 15 others, *J.Anal. At. Spectrom.* 2009, **24**, 825.
- 441 8 Y.K. Xiao, E.S. Bearly and J.D. Fassett, *Int. J. Mass Spectrom. Ion Proc.* 1988, **85**, 203.
- 442 9 W.P. Leeman, R.D. Vocke, E.S. Bearly and P.J.P. Paulsch, *Geochim. Cosmochim. Acta*
443 1991, **55**, 3901.
- 444 10 D. Lemarchand, J. Gaillardet, C. Göpel and G. Manhès, *Chem. Geol.* 2002, **190**, 123.
- 445 11 G.L. Foster, *Earth Planet. Sci. Lett.* 2008, **271**, 254.
- 446 12 P. Louvat, J. Bouchez and G. Paris, *Geostand. Geoanal. Res.* 2010, **35**, 75.
- 447 13 D.R. Wiederin, F.G. Smith, and R.S. Houk, *Anal. Chem.* 1991, **63**, 219.

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3 448 14 C.S. Westphal, K. Kahen, W.F. Rutkowski, B.W. Acon and A. Montaser, *Spectrochim.*
4 449 *Acta (B)* 2004, **59**, 353.
5
6
7 450 15 E.J. Catanzaro, C.E. Champion, E.L. Garner, G. Malinenko, K.M. Sappenfeld and W.R.
8 451 Shields, *US Nat. Bur. Stand. Spec. Pub.* 1970, **260**, 17.
9
10 452 16 A. Galy, N. Belshaw, L. Halicz, and R. O’Nions, *Int. J. Mass Spectrom.* 2001, **208**, 89.
11
12 453 17 G. Paris, A. Bartolini, Y. Donnadiou, V. Beaumont and J. Gaillardet, *Chem. Geol.* 2010,
13 454 **275**, 117.
14
15
16 455 18 J. Vogl and M. Rosner, *Geostand. Geoanal. Res.* 2011, **36**, 161.
17
18 456 19 J. Gaillardet and C.J. Allègre, *Earth Planet. Sci. Lett.* 1995, **136**, 665.
19
20 457 20 D. Lemarchand, D. Cividini, M.-P. Turpault and F. Chabaux, *Geochim. Cosmochim.*
21 458 *Acta* 2012, **98**, 78.
22
23 459 21 S. Tonarini, M. Pennisi and W.P. Leeman, *Chem. Geol.* 1997, **142**, 129.
24
25 460 22 C. Boschi, A. Dini, G.L. Fruh-Green and D. S. Kelley, *Geochim. Cosmochim Acta*
26 461 2008, **72**, 1801.
27
28 462 23 B. Chetelat and J. Gaillardet, *Envir. Sci. Technol.* 2005, **39**, 2486.
29
30 463 24 P. Louvat, J Gaillardet, G. Paris and C. Dessert, *Appl. Geochem.* 2011, **26**, 576.
31
32 464 25 D. Cividini, D. Lemarchand, F. Chabaux, R. Boutin and M.-C. Pierret, *Geochim.*
33 465 *Cosmochim. Acta* 2010, **74**, 3143.
34
35 466 26 D. Lemarchand, J. Gaillardet, C., E. Lewin and C.J. Allègre, *Nature* 2000, **408**, 951.
36
37 467 27 G. Paris, J. Gaillardet and P. Louvat, *Geology* 2010, **38**, 1035.
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5 469 **Tables and Figures captions**

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10 471 **Table 1:** Operating parameters for boron isotope ratios measurement by MC-ICP-MS,
11 472 using direct injection nebulizer d-DIHEN as an introduction system.

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14 473 **Table 2:** Automation program of the FAST valve. This program is designed to avoid
15 474 introduction of air bubbles into the d-DIHEN nebulizer.

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18 475 **Table 3:** $\delta^{11}\text{B}$ measurements of boric acid reference materials AE120, AE121, and
19 476 AE122¹⁸ measured 4 times over 5 months. Individual data and 2SD are calculated from the 5
20 477 $\delta^{11}\text{B}$ values determined from three successive measurements of each solution.

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24 478 **Figure 1:** Sample-Standard Bracketing sequence (SSB) for the measurement of a sample
25 479 thrice successively, allowing for a statistical determination of average $\delta^{11}\text{B}$ and repeatability
26 480 (2SD) over five values. The same symbols are used in Figure 4.

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30 481 **Figure 2:** d-DIHEN nebulizer / FAST valve / autosampler assembly, for the LOAD (a)
31 482 and INJECT (b) positions of the valve. During autosampler operation (sample change and
32 483 wash), the valve is in LOAD and a carrier solution feeds the direct injector, preventing air to
33 484 be injected to the plasma.

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38 485 **Figure 3:** Long-term $\delta^{11}\text{B}$ measurement of solutions SE43 (in-house pure $\text{B}(\text{OH})_3$ mixed
39 486 solution) and NASS-5 (international seawater reference material), before and after
40 487 automation. 2 standard deviations (error bars) are reported only for automated measurements,
41 488 as previously only one measurement was done for each solution (internal errors for these
42 489 measurements were smaller than data points, and long-term reproducibility is considered the
43 490 same for all data before automation, *i.e.* 0.25‰).

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49 491 **Figure 4:** Typical evolution of the instrumental fractionation observed during an
50 492 overnight measurement session. Samples were measured by standard-sample bracketing 3
51 493 times in a row (Fig 1). All solutions had 200 ppb B concentration. Three runs with different
52 494 types of natural samples are shown (data are reported in Table S1 of ESI): a/ seawater
53 495 samples; b/ carbonate samples, and c/ river water samples. Blue squares represent measured
54 496 $^{11}\text{B}/^{10}\text{B}$ ratios of the bracketing standard solution (left Y-axis); sample ratios are not shown.

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3 497 Small red dots show $\delta^{11}\text{B}$ values (right Y-axis) of the bracketing standard solution (calculated
4 498 with $^{11}\text{B}/^{10}\text{B}$ of previous and next standards). Large black circles (and associated 2SD error
5 499 bars, right Y-axis) are averages of three standard solution $\delta^{11}\text{B}$ values for the stability of 3
6 500 successive measurements of one sample (Fig 1 and paragraph 3.2). Black crosses present the
7 501 repeatability on $\delta^{11}\text{B}$ (2SD, n=5, see Fig 1, right Y-axis) measured for each sample, in ‰ on
8 502 the right Y-axis scale. The dotted lines indicate the $\pm 0.1\%$ repeatability achieved on pure
9 503 boric acid solutions. For all data represented, outlier values were not rejected.

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16 504 **Figure 5:** Matrix effects on SRM 951 solutions at a concentration of 200 ppb doped with
17 505 Na, Ca, Fe, SiO_2 and mannitol at concentration between 10 and 1000 ppb. Na, Fe and SiO_2 -
18 506 doped solutions at 100 and 1000 ppb were measured twice two days apart (red dots for the
19 507 second measurements).

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23 508 **Figure 6:** SRM 951 solutions measured at concentrations between 1 and 400 ppb against
24 509 a bracketing SRM 951 solution at a concentration of 200 ppb. Black dots represent
25 510 uncorrected values. White dots are for blank-subtracted $^{11}\text{B}/^{10}\text{B}$ ratios (for each solution,
26 511 correction is done with the average of the preceding and following blanks, see ESI section 2).
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Instrument	Operating parameters
MC-ICP-MS	Neptune, ThermoScientific
Cones	Ni: standard sampler and X-skimmer
Introduction system	direct injection nebulizer (d-DIHEN)
Uptake rate	50 $\mu\text{L}\cdot\text{min}^{-1}$
Autosampler	SC (ESI)
Automation valve	6-port valve FAST (ESI)
RF Power	1200 W
Ar Cool Gas	15 $\text{L}\cdot\text{min}^{-1}$
Ar Auxiliary Gas	1.2 to 1.6 $\text{L}\cdot\text{min}^{-1}$
Ar Sample Gas	0.2 $\text{L}\cdot\text{min}^{-1}$
Cup Configuration	^{10}B in L3, ^{11}B in H3
Amplifier resistors	$10^{11} \Omega$
Resolution	low (400)
Integration time	8 s
Block/Cycles	1B/15C
Uptake Time	1 min
Wash Time	3 min
Oxides	$\text{NdO}^+/\text{Nd}^+ \leq 30\%$ — $\text{BO}^+/\text{B}^+ \leq 2\%$
Sensitivity	20 to 50 V/ppm of B, on mass ^{11}B

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514 Table 1

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Event	Action	Param	Comment
On Probe Down	Load 1		when autosampler goes to the next sample, FAST valve switches to LOAD position
Probe in Sample	Time A	18s	from this moment, wait 18 seconds until the next instruction
Timer A Expires	Inject 1		after these 18 s, the FAST valve switches to INJECT position
On Rinse Type 2	Move Rinse		when the sample measurement is finished, the autosampler goes to rinse
On Rinse Type 2	Load 1		when the autosampler goes to the rinse position, the FAST valve switches to LOAD position
On Rinse Type 2	Timer B	18s	from this moment, wait 18 seconds until the next instruction
Timer B Expires	Inject 1		after these 18 s, the FAST valve switches to INJECT position

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519 Table 2

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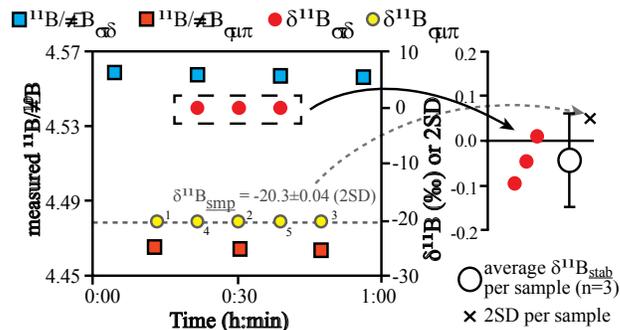
	$\delta^{11}\text{B}$ (‰)	2SD
	-20.43	0.08
AE120	-20.36	0.08
	-20.34	0.09
	-20.30	0.06
average	-20.36	0.11
certified	-20.2	0.6
	19.50	0.04
AE121	19.72	0.11
	19.72	0.12
	19.51	0.11
average	19.61	0.25
certified	19.9	0.6
	39.37	0.05
AE122	39.37	0.09
	39.44	0.16
	39.46	0.06
average	39.41	0.09
certified	39.7	0.6

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522 Table 3

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Standard-Sample Bracketing sequence:
(the same sample is measured three times)



Average $\delta^{11}\text{B}_{\text{qut}}$ is calculated from 5 values:

$$\begin{aligned} \text{standard 1} & \rightarrow \delta^{11}\text{B}_{\text{qut}'} = \{2R_{\text{qut}'} / (R_{\text{std}'} + R_{\text{qut}'}) - 1\} \times 1000 \\ \text{sample 1} & \rightarrow \delta^{11}\text{B}_{\text{qut}'} = \{2R_{\text{qut}'} / (R_{\text{std}'} + R_{\text{qut}'}) - 1\} \times 1000 \\ \text{standard 2} & \rightarrow \delta^{11}\text{B}_{\text{qut}''} = \{2R_{\text{qut}''} / (R_{\text{std}''} + R_{\text{qut}''}) - 1\} \times 1000 \\ \text{sample 2} & \rightarrow \delta^{11}\text{B}_{\text{qut}''} = \{2R_{\text{qut}''} / (R_{\text{std}''} + R_{\text{qut}''}) - 1\} \times 1000 \\ \text{standard 3} & \rightarrow \delta^{11}\text{B}_{\text{qut}'''} = \{2R_{\text{qut}'''} / (R_{\text{std}'''} + R_{\text{qut}'''}) - 1\} \times 1000 \\ \text{sample 3} & \rightarrow \delta^{11}\text{B}_{\text{qut}'''} = \{2R_{\text{qut}'''} / (R_{\text{std}'''} + R_{\text{qut}'''}) - 1\} \times 1000 \\ \text{standard 4} & \rightarrow \delta^{11}\text{B}_{\text{qut}''''} = \{2R_{\text{qut}''''} / (R_{\text{std}''''} + R_{\text{qut}''''}) - 1\} \times 1000 \end{aligned}$$

with $R = ({}^{11}\text{B}/{}^9\text{B})_{\text{measured}}$

$$\delta^{11}\text{B}_{\text{smp}} = \text{average} (\delta^{11}\text{B}_{\text{qut}'}, \delta^{11}\text{B}_{\text{qut}''}, \delta^{11}\text{B}_{\text{qut}'''}, \delta^{11}\text{B}_{\text{qut}''''}, \delta^{11}\text{B}_{\text{qut}'})$$

$$2\text{SD} = 2 \times \text{standard deviation} (\delta^{11}\text{B}_{\text{qut}'}, \delta^{11}\text{B}_{\text{qut}''}, \delta^{11}\text{B}_{\text{qut}'''}, \delta^{11}\text{B}_{\text{qut}''''}, \delta^{11}\text{B}_{\text{qut}'})$$

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525 Figure 1

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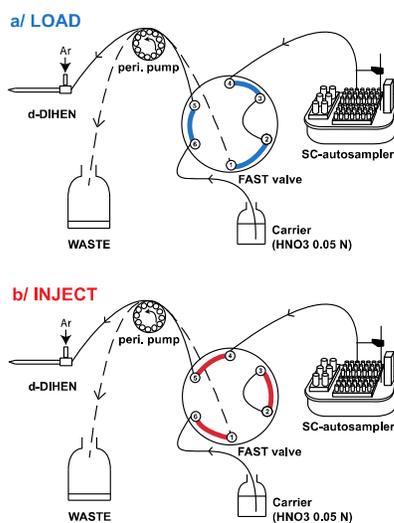


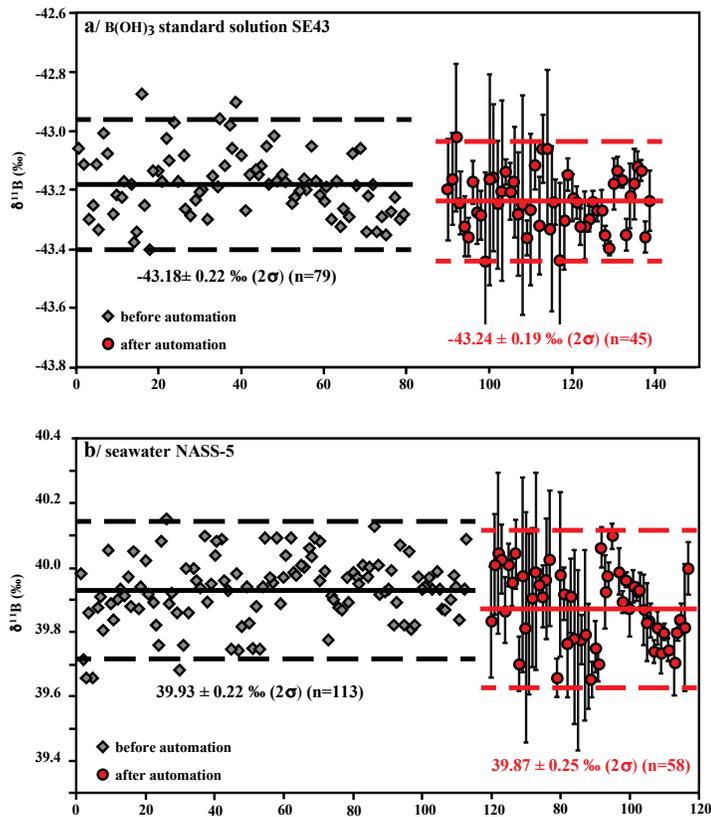
Figure 2

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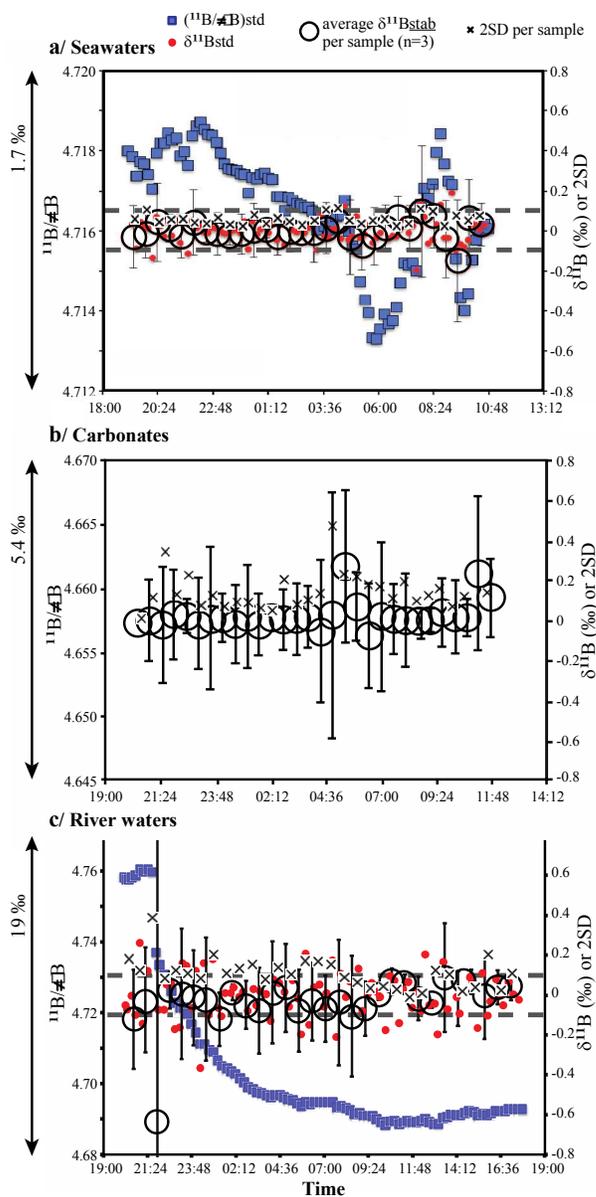
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533 Figure 3

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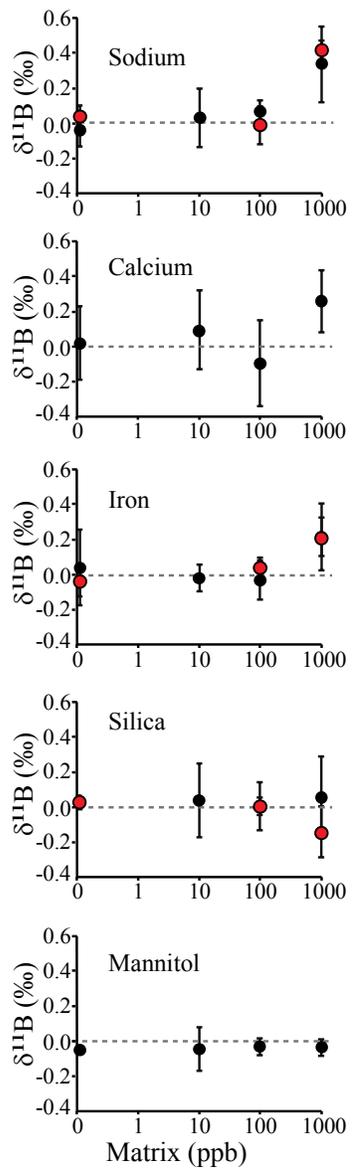


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537 Figure 4

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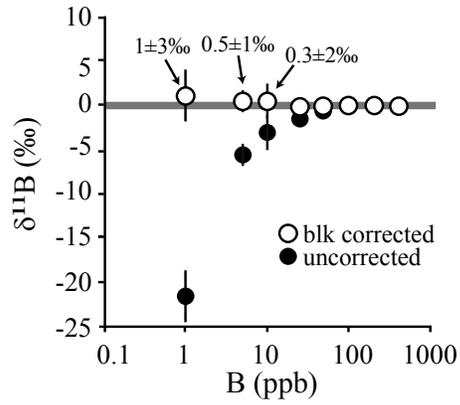
541 Figure 5

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547 Figure 6

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