

# MC-ICP-MS Isotope Measurements with Direct Injection Nebulisation (d-DIHEN): Optimisation and Application to Boron in Seawater and Carbonate Samples

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We report here an optimisation of the demountable direct injection high efficiency nebuliser (d-DIHEN) for isotopic measurements with a Neptune (ThermoFisher Scientific, Bremen, Germany) multi-collector inductively coupled plasma-mass spectrometer (MC-ICP-MS) and describe a method for boron isotopic ratio determination. With direct injection nebulisation 100% of the analyte was introduced into the ICP-MS plasma and wash times were drastically reduced for elements such as boron and thorium. Compared to the classical stable introduction system (SIS: double Scott/cyclonic spray chamber), sensitivity for boron was 2–5 times higher with d-DIHEN and wash times up to ten times shorter. Repeatability of  $^{11}\text{B}/^{10}\text{B}$  sample-calibrator bracketing measurements reached 0.25‰ (2s) for seawater and coral samples. Method accuracy and reproducibility were tested on mixed reference solutions having  $\delta^{11}\text{B}$  values in the ranges -90 to +40‰ and -2 to +2.5‰, demonstrating our ability to distinguish  $\delta^{11}\text{B}$  values with differences of only 0.25‰. The international seawater reference material NRCC NASS-5 (National Research Council, Ottawa, Canada), analysed in different sessions over a 10-month period, yielded an average  $\delta^{11}\text{B}$  value of  $+39.89 \pm 0.25\%$ , in the upper range of previously published seawater values. A comparison between  $\delta^{11}\text{B}$  determined by d-DIHEN MC-ICP-MS and positive-TIMS (P-TIMS) for four modern corals showed an excellent agreement (with bias of less than 0.4‰).

Keywords: direct injection, boron isotopes, MC-ICP-MS, seawater, carbonates.

*Nous présentons ici une optimisation du d-DIHEN (demountable direct injection high efficiency nebuliser) pour des mesures isotopiques avec le MC-ICP-MS Neptune (ThermoFisher Scientific, Bremen, Germany) et décrivons une méthode de détermination du rapport isotopique du bore. L'injection directe permet d'introduire 100% de l'échantillon dans un plasma d'ICP-MS et réduit de manière drastique le temps de lavage d'éléments comme B ou Th. En comparaison avec un système d'introduction classique (SIS, stable introduction system: chambre cyclonique doublée d'une chambre de Scott), la sensibilité du bore avec le d-DIHEN est 2 à 5 fois plus élevée et les temps de lavage jusqu'à 10 fois plus courts, la répétabilité des mesures de  $^{11}\text{B}/^{10}\text{B}$  par encadrement de standards (calibrator bracketing) est de 0.25‰ (2s) pour des échantillons d'eaux de mer et de coraux. La justesse et la reproductibilité de notre méthode ont été testées avec des solutions de référence mélangées tant sur la gamme de -90 à +40‰ (en  $\delta^{11}\text{B}$ ) qu'entre -2 et +2.5‰, nous permettant de discriminer des  $\delta^{11}\text{B}$  distants de seulement 0.25‰. La détermination du rapport  $^{11}\text{B}/^{10}\text{B}$  pour le matériel de référence international d'eau de mer NRCC NASS-5 répétée pendant 10 mois nous conduit à proposer une valeur moyenne de  $+39.89 \pm 0.25\%$ , dans la gamme supérieure des valeurs d'eaux de mer de précédentes publications. Les valeurs de  $\delta^{11}\text{B}$  déterminées par MC-ICP-MS et d-DIHEN pour quatre coraux modernes sont en très bon accord avec celles mesurées par P-TIMS (écarts de moins de 0.4‰).*

Multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has greatly improved sensitivity and sample analysis rate for isotopic composition measurements of many elements, and, despite its larger instrumental mass fractionation, has progressively become an attractive alternative to TIMS techniques. Because of their introduction as aqueous solutions, samples for ICP-MS do not have to be reduced to a few  $\mu\text{l}$  after chemical separation nor loaded onto a millimetric filament, saving considerable handling time. For similar individual measurement errors, one MC-ICP-MS measurement lasts for only a few minutes, against a few hours with TIMS.

The sample introduction system for MC-ICP-MS is critical, both in terms of ionisation efficiency and instrumental isotopic fractionation. The most common introduction system consists of a Meinhard nebuliser, creating a cloud of droplets injected into a spray chamber. The largest spray droplets aggregate onto the chamber walls and are removed, whereas the finest are introduced into the plasma torch. With such an introduction system, only about 5% of the sample actually reaches the plasma. Since the 1980s, most attempts focused on increasing the amount of sample introduced and ionised in the plasma. More recently, dry introduction through desolvation systems have been commonly used (such as APEX by ESI, Omaha, NE, USA; or Aridus by Cetac, Omaha, NE, USA) increasing the sensitivity by eliminating the solvent. Recent findings concerning wet introduction consist of, for example, a torch containing an in-built spray chamber (Todoli and Mermet 2002) or the use of commercial micro-concentric nebulisers directly mounted into the plasma torch (Westphal and Montaser 2006). Among the many existing introduction systems (spray chambers, desolvators, nebulisers), direct injection nebulisation (DIN) seems to be the most straightforward assemblage (e.g., review by Todoli and Mermet 2006). Key advantages of this method are that it has the lowest surface of contact between the inlet system and analytes, and the entire volume of solution entering the nebuliser is introduced into the plasma. However, because of the very high linear velocity of the spray, the sensitivity gain is much smaller than expected (e.g., Lawrence *et al.* 1984), despite a narrower droplet size distribution compared to a conventional nebuliser (e.g., Wiederin *et al.* 1991). The spray introduced into the plasma also contains large droplets up to 30  $\mu\text{m}$ , which are usually eliminated by spray chambers. Such droplets do not easily

evaporate nor ionise; thus, only 30% of the spray actually reaches the ion beam (Minnich *et al.* 2001). The spray quality is particularly critical with DIN techniques compared to any other introduction system as the spray is formed directly in the plasma. Large droplets are not discarded, unlike when using a spray chamber, and their injection into the plasma can lead to a sudden temperature increase and a potential torch melting. DIN has been used for ICP-MS and ICP-AES analysis (e.g., LaFreniere *et al.* 1985, 1987, Wiederin *et al.* 1991, Westphal *et al.* 2004). Improvements by McLean *et al.* (1998) led to the direct injection high efficiency nebuliser (DIHEN) and, latterly, its demountable version (d-DIHEN, Westphal *et al.* 2004).

DIN techniques are of great interest for elements such as boron with a high affinity for quartz surfaces. Because of this, DIN has already proved to be suitable for boron determination, for concentration measurements (Smith *et al.* 1991) as well as for MC-ICP-MS isotopic ratio measurements (Aggarwal *et al.* 2003, with a Cetac Microneb 2000). Other elements with a strong memory effect such as thorium (McLean *et al.* 2001), iodine and mercury (Wiederin *et al.* 1991), could benefit from this development, because DIN techniques could drastically shorten wash times.

Boron isotopes have been applied to a number of questions in the geosciences. They provide a proxy for palaeo-pH variations in seawater (e.g., Vengosh *et al.* 1991, Hemming and Hanson 1992, Sanyal *et al.* 2000, Hönisch *et al.* 2004), despite certain problems (e.g., Pagani *et al.* 2005). Boron isotopes can also trace fluid circulation in accretionary prisms (You *et al.* 1995), as well as sources of anthropogenic pollution (Chetelat and Gaillardet 2005, Chetelat *et al.* 2005) or fluid-rock interactions (Lemarchand and Gaillardet 2006). They have also been applied in geothermal and environmental studies (Aggarwal *et al.* 2003, Peltola and Åström 2006, Pennisi *et al.* 2006, Millot and Négrel 2007). The low atomic mass of boron isotopes leads to a very high relative mass difference between  $^{11}\text{B}$  and  $^{10}\text{B}$  and thus to an important and variable mass bias in MC-ICP-MS as well as during separation chemistry. The instrumental mass bias is corrected through a sample-calibrator bracketing method (SSB) and the boron isotopic composition is commonly expressed relative to the average of the bracketing, as  $\delta^{11}\text{B}$  (in ‰):

$$\delta^{11}\text{B} = \left( \frac{\left( \frac{^{11}\text{B}}{^{10}\text{B}} \right)_{\text{sample}}}{\left( \frac{^{11}\text{B}}{^{10}\text{B}} \right)_{\text{cal1}} + \left( \frac{^{11}\text{B}}{^{10}\text{B}} \right)_{\text{cal2}}} \times 2 - 1 \right) \times 1000 \quad (1)$$

The reference boron solution used was the boric acid NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) SRM 951. Inter-comparison exercises between 2003 and 2009 (Gonfiantini *et al.* 2003, Aggarwal *et al.* 2004, 2009) demonstrated the analytical advances in boron isotope measurements by MC-ICP-MS, with similar or even better precisions and accuracy than with TIMS, and an increasing number of users. However, the latest inter-comparison tests by Aggarwal *et al.* (2009) proved the unfulfilled need for certified reference materials of natural composition to overcome the problem of bias in boron isotope measurements between different mass spectrometry laboratories.

Boron isotopes have long been measured using P-TIMS (Xiao *et al.* 1988, Nakamura *et al.* 1992, Gaillardet and Allègre 1995, Lemarchand *et al.* 2000) or N-TIMS (Spivack *et al.* 1987, Hemming and Hanson 1992, Pearson and Palmer 1999, Hönisch and Hemming 2004, Foster *et al.* 2006) techniques. The main advantage of P-TIMS is its good repeatability, whereas N-TIMS allows small samples (as low as a few ng) to be processed, without the need for preliminary chemical purification. For palaeo-pH reconstruction, precise analyses are needed, and most available coral or carbonate rock samples are large enough to yield several tens of ng of boron. Recently, boron isotopic ratios have also been measured by ICP-MS (e.g., Lécuyer *et al.* 2002) and MC-ICP-MS (e.g., Aggarwal *et al.* 2003, Foster 2008). Boron ionisation yields are higher in ICP-MS than in P-TIMS, decreasing the quantity of sample needed to obtain a given reproducibility (0.29‰, 1s,  $n = 9$ , Lécuyer *et al.* 2002; 0.19‰, 1s,  $n = 7$ , Aggarwal *et al.* 2003, 0.23‰, 2s,  $n = 7$ , Foster 2008). Moreover, MC-ICP-MS offers a more stable mass bias than TIMS, that allows for an easy correction of instrumental isotopic fractionation using a sample-calibrator bracketing method (Aggarwal *et al.* 2003). Nevertheless, boron isotopic determination by ICP-MS is hampered by the slow washout of the volatile  $\text{B}(\text{OH})_3$  species. Foster (2008, supplementary information) recently published one way to overcome this issue by adding a  $\text{NH}_3$  gas flux into a Teflon® (DuPont de Nemours, USA) spray chamber, thus reducing boron to the less volatile  $\text{B}(\text{OH})_4^-$  species. An alternative way to decrease such boron memory effects is to use inlet systems that offer less contact surface area with the introduced solution, such as DIN systems (Aggarwal *et al.* 2003).

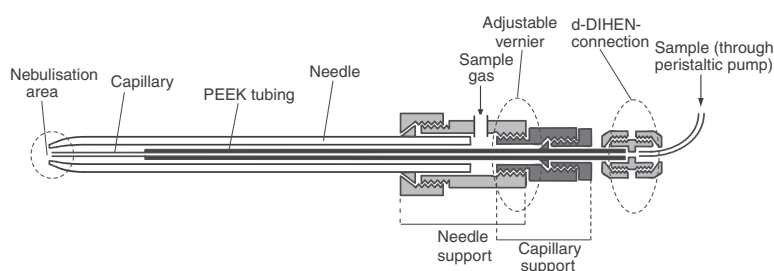
We report in this paper a feasibility study concerning the use of d-DIHEN (Analab, Strasbourg, France) for isotopic measurements with MC-ICP-MS Neptune (Thermo-Fisher Scientific, Bremen, Germany), and detail its performance for boron isotopes. With this technique, boron sensitivity was better than with the standard spray chamber introduction system. It was more accurate and more reproducible, and allowed a higher sample throughput. An intercomparison between N-TIMS and d-DIHEN MC-ICP-MS boron isotope analysis for four corals validated this d-DIHEN method. We also propose a boron separation protocol for carbonate samples, optimised for MC-ICP-MS measurements.

## d-DIHEN description and spray optimisation

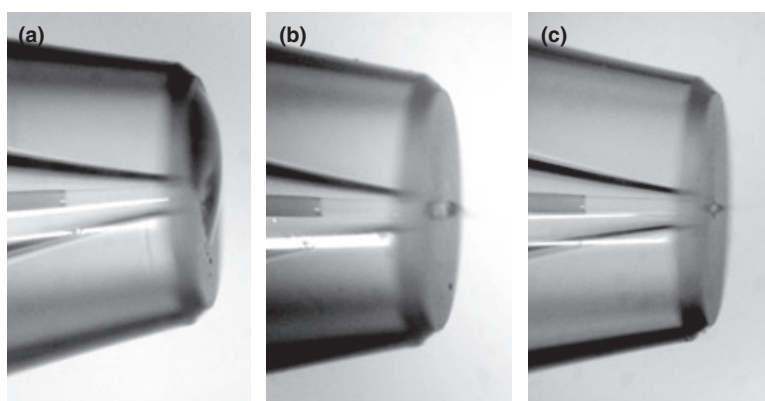
Direct injection nebulisation consists of injecting the analyte spray directly into the plasma, the nebuliser (a long Meinhard-like nebuliser) being introduced into the torch in place of the injector. One disadvantage of the DIHEN was its price and the risk of its melting, discouraging potential users. With the d-DIHEN, the spray is adjustable and both needle and capillary can be changed separately from the whole system, thus reducing the utilisation cost.

Westphal *et al.* (2004) give a detailed description of the d-DIHEN. Briefly, a long borosilicate glass needle is mounted in a Teflon® (DuPont de Nemours, USA) tee support that also carries the nebuliser gas and a capillary in an adjustable vernier (Figure 1). The 100  $\mu\text{m}$  i.d. fused silica capillary in the middle of the nebuliser needle (polyimide coated except for the last 5 mm of the 'spray' extremity) is continuous from the Tygon® (SaintGobain Performance Plastics, USA) tube of the peristaltic pump to the nebuliser tip.

The d-DIHEN spray was first optimised outside of the torch. This optimisation was purely visual: a spray as 'light' as possible yet relatively dense is required (made of very small droplets) and without pulsation. Nebuliser gas flow rate was set to 0.2  $\text{l min}^{-1}$  and finely tuned afterwards to optimise signal intensity and stability. Sample uptake was achieved by a twelve-roller peristaltic pump with a 0.19 mm i.d. Tygon tube. After successive tests, we decided to work with a sample uptake rate of 15–60  $\mu\text{l min}^{-1}$ , with most of the tests presented in this paper at 50  $\mu\text{l min}^{-1}$  (a good compromise between increased sensitivity but longer wash time at lower uptake rate). The major parameter for the spray quality was the capillary-needle tip distance that controlled the droplet size, the spray strength and its regularity. It was adjusted under a four times magnification



**Figure 1.** The d-DIHEN device. This was introduced into the plasma torch, so as the needle tip was 4 mm behind the end of the auxiliary gas tube in the torch. Needle and capillary supports were fully demountable. The relative position of the capillary to the needle extremity was adjustable.



**Figure 2.** Optimisation of the d-DIHEN spray before its introduction into the plasma torch. Three positions of the capillary relative to the needle are described: (a) Nebuliser capillary behind the extremity of the needle: a water meniscus formed at the needle extremity surface, the spray was strong yet pulsated, wash time remained long. (b) Nebuliser capillary protruding from the needle tip: there was a water cone at the end of the capillary, a frail spray with very large droplets fell like a gentle rain. (c) Nebuliser capillary almost at the end of the needle (a few tenths of mm behind): we observed a small water cone without a meniscus at the needle extremity, the spray was very stable although not as heavy as in (a).

binocular microscope. In Figure 2, three capillary-needle tip positions are shown.

In Figure 2a the capillary was too far from the needle tip; the spray was powerful and consisted of relatively small droplets, but was unstable and pulsating; under the binocular microscope a large pulsating water meniscus was observed on the needle tip surface. Running ICP-MS measurements under such conditions led to unstable signal and longer wash times. Figure 2b shows a capillary protruding outside of the needle tip; large droplets (falling like gentle rain) were observed; under such conditions, the torch was likely to melt. Figure 2c shows the optimum capillary position. The capillary tip was almost at the needle tip, a few tens of  $\mu\text{m}$  behind; the spray was formed of fine droplets, less heavy than in the configuration of Figure 2a,

but very regular (no pulsation); under the binocular microscope the solution formed a small cone out of the capillary/needle, and there was no water meniscus on the needle tip surface.

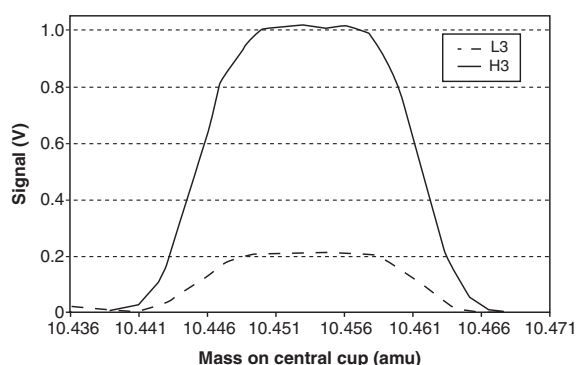
Another important parameter for d-DIHEN ICP-MS measurements is the distance between the end of torch intermediate gas tube and the d-DIHEN needle tip, which determines how close to the plasma the direct injection nebuliser is. With previous nebuliser gas flow and spray optimisation, we determined that a distance of 4 mm was optimal for both the sensitivity and stability of the signal, similar to the distance of 5 mm reported by Westphal *et al.* (2004). At 2 mm, plasma sputtering was dangerous for the torch, and for distances larger than 6 mm, a loss of sensitivity was clearly observed.

## MC-ICP-MS optimisation and measurements

### Optimisation and sensitivity

Once the d-DIHEN device was introduced into the plasma torch, the plasma ignited (with an operating power of 1200 W, cool and auxiliary gas flows of 15 and 1.5 l min<sup>-1</sup>) and the vacuum stabilised, the peristaltic pump was started and a boron solution was introduced into the plasma. Signal intensity and stability were optimised by adjusting the nebuliser and auxiliary gas flows (respectively around 0.2 and 1.5 l min<sup>-1</sup>), torch position, extraction and focussing lens voltages. For a 100 ng ml<sup>-1</sup> B solution, the sensitivity was about 1–1.5 V on <sup>11</sup>B (10<sup>11</sup> Ω Faraday cup amplifier resistance), which is similar to the sensitivity reported by Foster (2008) (10–15 V per μg ml<sup>-1</sup>). The <sup>11</sup>B peak was then centred, and its shape optimised using the quadrupole focus after the magnet. Peaks were slightly rounder than those obtained with a stable introduction system (SIS: double Scott/cyclonic spray chamber; Figure 3). This probably resulted from space charge effects and larger ion energy dispersion, as more water is introduced into the plasma when using DIN techniques.

In order to estimate d-DIHEN sensitivity gain, signal intensities of a multi-elemental solution (Li, B, Mg, Ca, Cu, Zn, Sr, Nd, Hf, Pb, Th, U) were measured and compared with those from SIS and APEX-HF (ESI, Ohama, NE, USA) (Figure 4). These elements are some of those commonly measured for isotope ratios in geochemistry. For most elements, a two- to threefold increase in sensitivity, compared with SIS, was observed (after signals had been scaled to

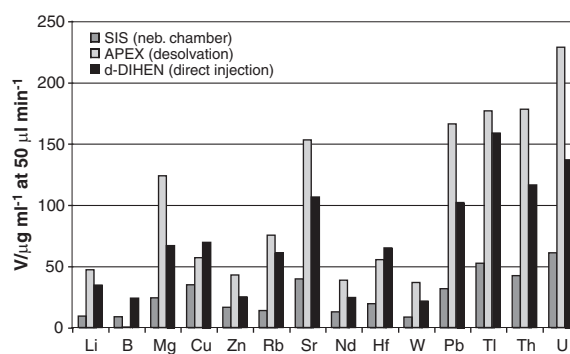


**Figure 3.** Peak shape of optimised <sup>11</sup>B (cup H3) and <sup>10</sup>B (cup L3) signal for MC-ICP-MS measurements. The peak shape was less well defined than with the SIS (stable introduction system: dual Scott/cyclonic spray chamber).

the same uptake rate and solution concentrations). However, d-DIHEN sensitivities were comparable to APEX-HF or even lower. It is surprising that, despite almost complete transfer of the aspirated sample to the plasma by direct injection, the sensitivities only increased by a factor of 2–3 compared with SIS. The higher velocity and larger size of the spray droplets in the case of d-DIHEN induces lower ionisation efficiency within the plasma (e.g., Lawrence *et al.* 1984). We tested d-DIHEN at a higher torch power (up to 1600 W) and observed that sensitivity was enhanced for most elements, but the plasma was not sufficiently stable for precise isotopic measurements.

In addition to enhanced sensitivity, sample uptake rates as low as 15 μl min<sup>-1</sup> can be attractive for some elements where the available quantity of sample is critical (e.g., cosmochemistry samples, mineral separates in geochemistry, or foraminifera). Moreover, sensitivity does not decrease linearly with uptake rate, and is comparatively better with d-DIHEN at lower uptake rates. A twofold decrease in uptake rate gave approximately three-quarters of the previous signal.

Oxide production was controlled by measuring the NdO<sup>+</sup>/Nd<sup>+</sup> ratio. Ratios up to 30% (6–30%, mostly depending upon the distance between the torch and the sampler cone) were measured, much higher than those obtained by SIS or APEX (typically 9% and 3% respectively), and those reported by Westphal *et al.* (2004) on Ce for quadrupole ICP-MS with direct injection (4% at 85 μl min<sup>-1</sup> sample uptake rate). Doubly charged ion



**Figure 4.** Comparison of sensitivities for many elements between <sup>7</sup>Li and <sup>238</sup>U for three introduction systems: SIS (stable introduction system = dual Scott/cyclonic spray Chamber), APEX desolvation system and direct injection nebulisation d-DIHEN. Sensitivities are in V/μg ml<sup>-1</sup> of the element (10<sup>11</sup> Ω amplifiers) for a constant uptake rate of 50 μl min<sup>-1</sup>.

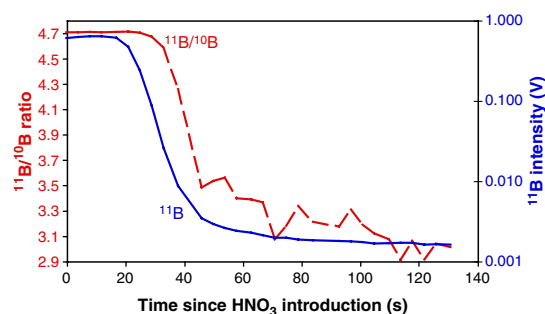
production, estimated using the  $U^{2+}/U^+$  ratio, was 0.5–1%, slightly lower than values from SIS and APEX (1.5% and 3%, respectively), and comparable with Westphal *et al.* (2004) for  $Ba^{2+}/Ba^+$ .

### Performance for neodymium isotope measurement

As neodymium isotope ratios were measured very precisely on a Neptune MC-ICP-MS (2s reproducibility of 10–20 ppm for  $^{143}Nd/^{144}Nd$  over 3 years), Nd was used as the reference element for testing the quality of isotope measurements with d-DIHEN. A 200 ng ml<sup>-1</sup> standard solution yielded a 12 V signal on  $^{142}Nd$ . The same solution of the JMC (Johnson Matthey Chemicals, London, UK) reference sample was measured using d-DIHEN on Neptune and TIMS Triton instruments, and gave  $^{143}Nd/^{144}Nd$  ratios of 0.511457 (Triton instrument) and 0.511454 (Neptune instrument), with a 2s internal reproducibility (standard error) of 5 ppm (10 min measurement, using  $^{146}Nd/^{144}Nd$  as the normalisation ratio and an exponential mass fractionation law). Other Nd isotopic ratios were also comparable between TIMS and MC-ICP-MS, except for  $^{150}Nd/^{144}Nd$ , which was also observed with SIS or APEX (due to the limits of mass bias correction with the exponential mass fractionation law in MC-ICP-MS compared with TIMS, e.g., Wombacher and Rehkämper 2003). Neodymium isotope ratios were accurately measured using d-DIHEN, and internal standard errors were identical to those obtained with SIS or APEX introduction systems. The general optical transmission and signal collection performances of the Neptune MC-ICP-MS were thus not affected by direct injection of the spray into the plasma. Only the isotope peak shape showed a difference, being slightly rounder with d-DIHEN than with the classical SIS inlet system.

### Wash time and bracketing procedure

A critical point concerning boron measurement in ICP inlet systems is the memory effect. With SIS, 15–20 min long washes with 0.5 mol l<sup>-1</sup> HNO<sub>3</sub> were needed to reach a blank signal below 1% of the  $^{11}B$  signal previously measured. With d-DIHEN, 100 s washout times (with 0.5 mol l<sup>-1</sup> HNO<sub>3</sub>) were sufficient to reach a blank  $^{11}B$  signal as low as 1‰ of the previous signal (Figure 5). The much lower contact surface area between the sample and the inlet system has a large impact upon the wash time necessary between samples. Foster (2008) ruled out the boron wash problem by blowing NH<sub>3</sub> into the spray chamber to decrease the volatility of boron in the inlet system. The use of gaseous NH<sub>3</sub>, however, requires some



**Figure 5. d-DIHEN wash in 2% v/v HNO<sub>3</sub> after NIST SRM 951 reference solution at 200 ng ml<sup>-1</sup> was measured for 10 min (black line for  $^{11}B$  intensity and grey line for  $^{11}B/^{10}B$  isotopic ratio).**

precautions because of its toxicity for users and reactivity towards metals and alloys present in the spectrometer. Moreover, this technique is not necessarily suitable for other elements with long washout times (e.g., Hg). d-DIHEN, however, by design, may decrease the wash time of any element, and is potentially useful for those with high memory effects, such as Th (McLean *et al.* 2001) or Hg (Powell *et al.* 1992).

To account for mass discrimination and its variation through time, boron isotopes were measured by sample-calibrator bracketing, using NIST SRM 951 (0‰ by definition), at either 100 or 200 ng ml<sup>-1</sup>. The samples and calibrator solutions were measured using the same method. The baseline was measured by defocussing the signal for 10 s, and then  $^{11}B$  and  $^{10}B$  were simultaneously collected over 2 min. A peak centring was performed every hour. No on peak zero was subtracted. Between two consecutive analytes, when the introduction capillary was moved from one vial to another, the peristaltic pump was switched off, to avoid any aspiration of air bubbles into the direct injection device that would lead to systematic plasma extinction.

Combined with the necessary wash and uptake times, a calibrator-sample sequence lasted for 10–12 min, an elapse time for which the variation of instrumental mass fractionation was small (0.1‰ on average) and could be considered as linear. Our technique enabled five to six sample  $\delta^{11}B$  measurements per hour, more than twice as many samples as could be measured using the method of Foster (2008). The accuracy of  $\delta^{11}B$  measurements was verified by measuring an enriched reference sample at -43.1‰ and seawater NASS-5, processed through the chemistry, every ten samples.

## Boron chemical separation

Before isotope measurements were made, boron was extracted from seawater and carbonate samples by ion exchange chromatography following a method adapted from Gaillardet and Allègre (1995) and Lemarchand *et al.* (2002). Two modifications from the previous methods were carried out: (a) replacement of HCl and NaCl respectively by HNO<sub>3</sub> and NaNO<sub>3</sub> during the whole process, and (b) removal of the final 'micro-sublimation' to discard organic matter (Gaillardet *et al.* 2001), which was strictly necessary for TIMS measurements. Elimination of HCl avoided a possibly critical evaporation step at the end of the separation, performed to modify the media from HCl to HNO<sub>3</sub> (which is the introduction medium in ICP-MS). The influence of any organic matter that might be present in the samples on the measurement of boron isotope ratios has, however, been tested and is apparently not critical. Skipping this micro-sublimation step also reduced the risk of losing boron and made the whole process faster and easier.

In seawater, the boron concentration is sufficiently high that only very small test portions are required. Between 50 and 100 µl of sample (200–500 ng B) were loaded directly onto a 10 µl Amberlite® IRA-743 (Rohm and Haas, Philadelphia, PA, USA) column at pH 7–9 (adjusted with distilled ammonia). After H<sub>2</sub>O and 0.6 mol l<sup>-1</sup> NaNO<sub>3</sub> washing steps, boron was eluted with 50 µl of 0.5 mol l<sup>-1</sup> and 100 µl of 0.1 mol l<sup>-1</sup> HNO<sub>3</sub>. The final 150 µl were diluted to 100–200 ng ml<sup>-1</sup> B solutions (in 0.05 mol l<sup>-1</sup> HNO<sub>3</sub>), ready for measurement by MC-ICP-MS.

For carbonate samples, the dominant Ca-matrix was first removed on a AGW-50X8 (BioRad Laboratories Inc., Hercules, CA, USA) resin (which does not retain boron) and the fraction containing boron was then passed through a 50 µl Amberlite IRA-743 column, with the same wash and elution reagents as for 10 µl columns (using only larger volumes).

The validity of the extraction procedure was tested for each new column by purification and measurement of δ<sup>11</sup>B for both NIST SRM 951 boric acid and NASS-5 seawater (Table 1). Procedural replicates of the NASS-5 yielded δ<sup>11</sup>B = 39.88 ± 0.27‰ (2s, n = 10). The reproducibility was very similar to that of Foster (2008) (2s = 0.25‰, n = 7). For NBS SRM 951 boron standard solution, the replicates yielded δ<sup>11</sup>B = -0.02 ± 0.28‰ (2s, n = 16). This repeatability was only slightly higher than that external reproducibility without chemical separation.

**Table 1.**

**Measured values of δ<sup>11</sup>B for different chemical extractions of boron from seawater NASS-5 and NIST SRM 951 through 10 µl Amberlite IRA-743 columns**

| RM No. | δ <sup>11</sup> B (‰) | NASS-5 No. | δ <sup>11</sup> B (‰) |
|--------|-----------------------|------------|-----------------------|
| 1      | 0.13                  | 1*         | 39.85                 |
| 2      | -0.09                 | 2*         | 39.72                 |
| 3      | 0.14                  | 3*         | 39.87                 |
| 4      | 0                     | 4*         | 39.83                 |
| 5      | -0.08                 | 5*         | 39.85                 |
| 6      | 0.07                  | 6          | 39.69                 |
| 7      | 0.19                  | 7          | 39.89                 |
| 8      | -0.03                 | 8          | 39.97                 |
| 9      | -0.23                 | 9          | 40.02                 |
| 10     | -0.09                 | 10         | 40.15                 |
| 11     | 0.22                  | Av. NASS-5 | 39.88 ± 0.27          |
| 12     | 0.01                  |            |                       |
| 13     | -0.2                  |            |                       |
| 14     | -0.03                 |            |                       |
| 15     | -0.12                 |            |                       |
| 16     | -0.18                 |            |                       |
| Av. RM | -0.02 ± 0.28          |            |                       |

\* sample volume: 200µl of NASS-5 instead of 50µl for the other extractions.

Extraction blanks for the 10 µl column purification step were 0.25 ± 0.05 ng of boron (2s, n = 4). As we generally extracted at least 100 ng of boron from our samples, this blank represented less than 0.3% of the sample. We measured an average δ<sup>11</sup>B of ~-2‰ for these extraction blanks. By mass balance, such a blank could lower the δ<sup>11</sup>B of 200 ng boron seawater samples by -0.06‰ (taking into account both purification and instrumental blanks).

## Performance of MC-ICP-MS boron measurement with d-DIHEN

### Stability of the <sup>11</sup>B/<sup>10</sup>B ratio

Generally, a loss of 30% of the signal was observed during the first hour after plasma ignition and first signal optimisation, with a drift of around -2‰ in the <sup>11</sup>B/<sup>10</sup>B ratio of a boron standard solution. After a stabilisation time (~2 hr after plasma ignition), during which the signal was regularly re-optimised when <sup>11</sup>B intensity dropped, the instrument was ready for sample boron isotope measurement, as <sup>11</sup>B/<sup>10</sup>B only varied by 0.1–0.3‰ per hour. The ion beam might have to be refocused after 2–3 hr (by tuning only torch position, not gas flows or optical lenses). The within-run standard error of one measurement varied between 0.00007 and 0.00025 on the <sup>11</sup>B/<sup>10</sup>B ratio (between 0.015‰ and 0.05‰) for 200 ng ml<sup>-1</sup> sample and standard solutions (2 min measurement time). For 50 ng ml<sup>-1</sup> sample solutions, the measurement standard

error was larger (0.00020–0.00050 or between 0.04‰ and 0.1‰). This internal standard error was close to that given by Foster (2008) on a similar instrument, and yielded an estimate for the short-term stability of the  $^{11}\text{B}/^{10}\text{B}$  ratio. The bracketing of calibrators relative to their two neighbouring calibrators gave a mean value of  $0.0 \pm 0.25\%$  (2s, averaged over 10 hr of sample-calibrator bracketing measurements). This provided an estimate of the long-term stability of the  $^{11}\text{B}/^{10}\text{B}$  ratio of 0.25‰, identical to the reproducibility of NASS-5 and NIST SRM 951 solutions.

## Repeatability

In order to evaluate the best repeatability of the sample-calibrator bracketing technique with d-DIHEN, we bracketed the standard solution against itself for one night, without any peristaltic pump shutdown or retuning of the instrument. During this 12 hr experiment, the  $^{11}\text{B}$  intensity and  $^{11}\text{B}/^{10}\text{B}$  ratio drifted by 7% and 0.5‰ respectively. The measurements were grouped by blocks of thirty cycles of 2 s in order to simulate our classical sample-calibrator measurement and we calculated bracketed  $\delta^{11}\text{B}$  values of the calibrator for intervals of 6, 12, 18, 24 and 30 min (e.g., for the 6 min interval, one block was bracketed by the two blocks measured 6 min before and 6 min after). The results of this statistical grouping are given in Table 2. We observed that the  $^{11}\text{B}/^{10}\text{B}$  ratio was relatively independent of the time interval between bracketing calibrators. It is worth noticing that gathering the measurement cycles by blocks of 60 or even 120 s led to a slightly better repeatability (i.e., 0.2‰ instead of 0.25‰ for a 12-min interval between two calibrators). During boron isotope measurement of the samples, we integrated thirty cycles of 2 s and the interval time between sample and calibrator was 5–6 min (wash plus uptake times).

## Mixed reference solutions to verify accuracy

We tested the accuracy of boron isotopic measurements with d-DIHEN by analysing a set of mixed reference solutions. A solution of NIST SRM 951 ( $^{11}\text{B}/^{10}\text{B} =$

$4.04362 \pm 0.00137$ , Catanzaro *et al.* 1970) was mixed in various proportions with NIST SRM 952 ( $^{11}\text{B}/^{10}\text{B} = 0.05348$ , Nakamura *et al.* 1992) on the one hand, and with purified NASS-5 seawater on the other. This resulted in solutions of calculated  $\delta^{11}\text{B}$  between -90‰ and 40‰ ( $\pm 1.4$ – $1.6\%$ ). Measured and calculated  $\delta^{11}\text{B}$  agreed, within analytical and weighing uncertainties, as shown in Figure 6a. Another set of mixed reference solutions with  $\delta^{11}\text{B}$  isotopic ratios ranging from -2.0 to +2.5‰ was prepared in order to confirm our capacity to discriminate between isotopic differences as small as 0.25‰ (at the limit of the estimated repeatability). Results (average of three measurements) are presented in Figure 6b. We observed an excellent correlation between measured and calculated  $\delta^{11}\text{B}$  for this second series of enriched reference solutions, with a linear correlation coefficient  $R^2$  greater than 0.99; all data points fell on the 1:1 slope.

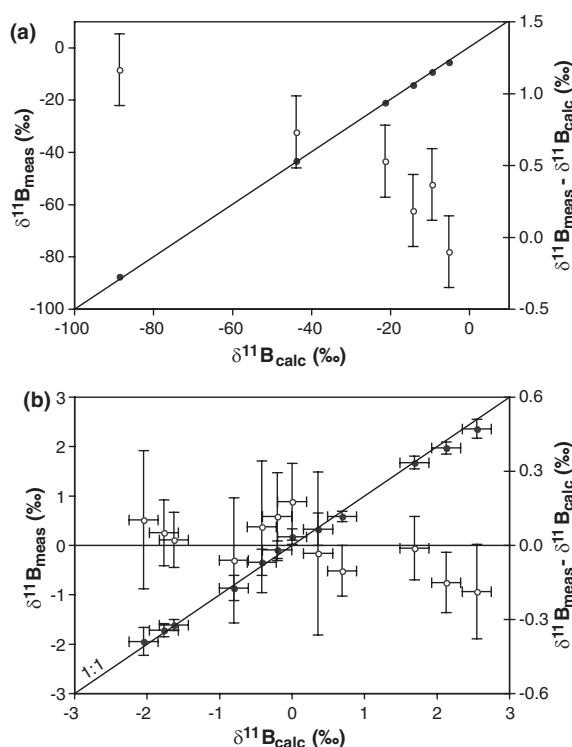
## Long-term repeatability

The accuracy of our method was verified on a daily basis by bracketing a synthetic calibrator with  $\delta^{11}\text{B}$  of -43.1‰ (SE43) and a NASS-5 seawater sample (processed through separation chemistry) every ten samples. Measurements of the SE43 standard solution over a 10 month period gave an average  $\delta^{11}\text{B}$  of  $-43.15 \pm 0.25\%$  (2s,  $n = 74$ ) (Figure 7a). The same repeatability (0.25‰, 2s,  $n = 61$ ) was obtained for NASS-5 seawater solution over 9 months (Figure 7b). This is also the repeatability we determined for the standard solution alone (Table 2, for 12 min between two standard solutions). Boron extracted from NASS-5 seawater did not give less repeatable results than a synthetic standard solution, not processed through purification chemistry. There was, therefore, no apparent matrix effect due to chemical extraction, and the separation was sufficient to remove matrix ions that could perturb the measurement. We propose a NASS-5  $\delta^{11}\text{B}$  value of  $39.89 \pm 0.25\%$ . Previously published seawater  $\delta^{11}\text{B}$  ranges from 39.40 to 40.26‰, with an average of 39.70‰ (Vengosh *et al.* 1991, Hemming and Hanson 1992, Gaillardet and Allègre 1995, Spivack and You

**Table 2.**  
Bracketing of the NIST SRM 951 boron reference material against itself for one night

| Bracketing interval               | 6 min | 12 min | 18 min | 24 min | 30 min |
|-----------------------------------|-------|--------|--------|--------|--------|
| Mean $\delta^{11}\text{B}$ (‰)    | 0     | 0      | 0      | 0      | 0      |
| 2s (‰)                            | 0.23  | 0.25   | 0.27   | 0.29   | 0.25   |
| Highest $\delta^{11}\text{B}$ (‰) | 0.31  | 0.29   | 0.32   | 0.27   | 0.35   |
| Lowest $\delta^{11}\text{B}$ (‰)  | -0.3  | -0.33  | -0.33  | -0.4   | -0.23  |

The mean bracketed  $\delta^{11}\text{B}$  was calculated for 30 cycles measured every 6, 12, 18, 24 and 30 min. The best repeatability that could be expected for B measurement with our d-DIHEN set-up was 0.23‰. During this 12 hr experiment, the  $^{11}\text{B}$  intensity and  $^{11}\text{B}/^{10}\text{B}$  ratio drifted by 7% and 0.5‰, respectively.

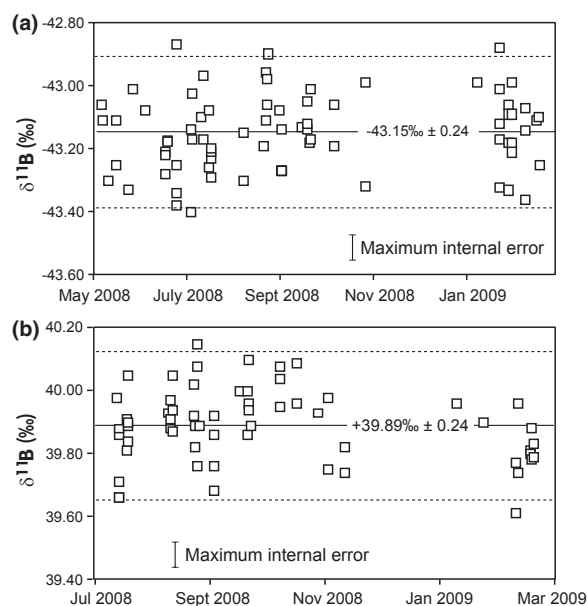


**Figure 6. Accuracy of MC-ICP-MS boron isotopic measurements with the d-DIHEN tested by mixed reference solutions: calculated and measured  $\delta^{11}\text{B}$  of calibrator-spike weighed mixtures were compared for two  $\delta^{11}\text{B}$  ranges: (a) from -90 to 0‰ and (b) from -2 to 2.5‰. Closed symbols are for measured  $\delta^{11}\text{B}$  and open ones for the difference between measured and calculated  $\delta^{11}\text{B}$ . For both series the agreement was very good (even excellent for the second one), suggesting the ability to distinguish  $\delta^{11}\text{B}$  to as little as 0.25‰.**

1997, Barth 1997, Aggarwal *et al.* 2003, Lécuyer *et al.* 2002, Hönisch *et al.* 2004, Foster 2008). Our data are, therefore, consistent with the literature, but in the upper part of the range. NASS-5 could be used as reference sample in future seawater boron studies, and inter-compared to other precise  $\delta^{11}\text{B}$  determinations by other laboratories.

### Boron concentration, acidity and matrix effects

A set of standard solutions with B concentrations ranging from 50 to 300 ng ml<sup>-1</sup> were bracketed by the 'reference' standard solution at 200 ng ml<sup>-1</sup> (Figure 8a). Deviation of the  $\delta^{11}\text{B}$  from the internal variability of the instrument was more than 0.25‰ when the concentrations differed by more than 10–20% from the bracketing calibrator. It even reached 10‰ at 10 ng ml<sup>-1</sup>. However,

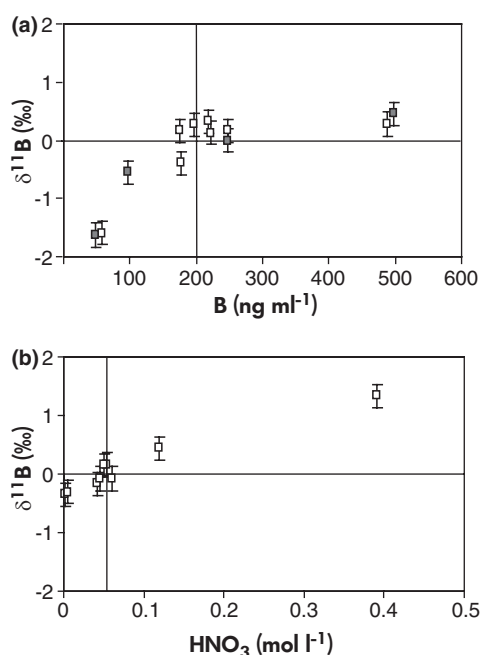


**Figure 7.  $\delta^{11}\text{B}$  evolution of SE43 synthetic standard solution (a) and NASS-5 seawater (b) (processed through purification chemistry). These two solutions were measured at the beginning of each measurement session and then every ten samples. Solid lines represent the average ratios and dotted lines the 2s intervals.**

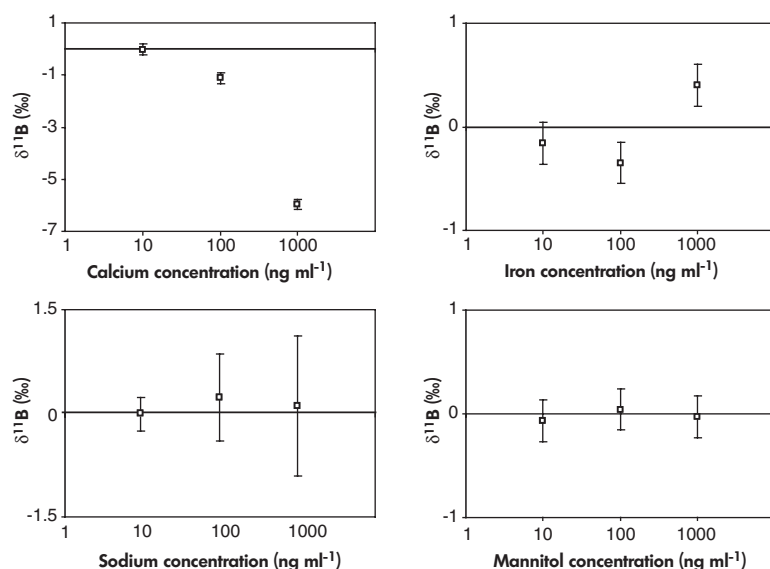
bracketing of the previous SE43 solution at 200, 100, 50 and 25 ng ml<sup>-1</sup> by standard solutions at the same concentrations gave fairly reproducible  $\delta^{11}\text{B}$  measurements (respectively -43.1‰, -43.3‰, -42.9‰ and -42.7‰). It was, therefore, of primary importance to use the same concentration for standard solutions and sample solutions. Measurements were still accurate (but less precise) even at low concentration. The effect of the instrumental blank was identical for both sample and calibrator, and was therefore corrected for by the bracketing protocol.

Standard solutions with HNO<sub>3</sub> concentrations from 0.01 to 0.09 mol l<sup>-1</sup> were also bracketed with the 'reference' standard solution at 0.05 mol l<sup>-1</sup> HNO<sub>3</sub> (Figure 8b). Measured  $\delta^{11}\text{B}$  were linearly correlated to the HNO<sub>3</sub> concentration. A variation in HNO<sub>3</sub> concentration of  $\pm 20\%$  was tolerated, as its effect was within the repeatability of the measurement method.

Finally, we assessed matrix effects by measuring the NIST SRM 951 boron reference solution at 200 ng ml<sup>-1</sup> mixed with various quantities of Fe, Ca, Na and mannitol. Although never detected in our samples, Fe and Ca could potentially be present after the chemical separation of B from carbonate samples, as well as Na from the NaNO<sub>3</sub>



**Figure 8.** NIST SRM 951 reference material  $\delta^{11}\text{B}$  variations with boron (a) and  $\text{HNO}_3$  (b) concentrations. Open squares are bracketed relative to a  $200 \text{ ng ml}^{-1}$  solution and closed squares relative to a  $250 \text{ ng ml}^{-1}$  solution. Best bracketing measurements were achieved when sample and standard solutions had similar boron concentration and acidity (within 20%). Repeatability errors calculated by error propagation were lower than  $0.06\text{‰}$ .



**Figure 9.** NIST SRM 951 reference material  $\delta^{11}\text{B}$  variations with addition of different compounds (Fe, Ca, Na and mannitol as an organic matter analogue). These ions could potentially pollute the boron fraction after its chemical separation. For sodium, samples were measured twice and error bars represent the repeatability. For the other added elements, error bars on  $\delta^{11}\text{B}$  are  $2\times$  standard error of one measurement.

added during the separation. Mannitol was used as an analogue for organic matter. Sodium-enriched measurements were triplicated. The results of these experiments are presented in Figure 9. The reported error bars are 'external'  $2s$  for the Na-spiked solutions and 'internal'  $2s$  for the other experiments (Fe, Ca and mannitol). Iron-, Na- and mannitol-enriched standard solutions did not systematically deviate from the  $\delta^{11}\text{B}$  of the 'reference' standard solution with increasing concentration, but tended to give less repeatable measurements. This was particularly obvious for Na, for which triplicate measurements showed a decrease in precision with increasing concentration. The  $\delta^{11}\text{B}$  value of the standard solution was shifted towards increasingly negative values with increasing Ca concentration in the standard solution. Wash times after mannitol-enriched solutions were longer than usual, but the absence of a  $\delta^{11}\text{B}$  shift compared with the reference standard solution confirmed that the final micro-sublimation step of the purification protocol of Gaillardet *et al.* (2001) (dedicated to the removal of potentially present organic matter) was not required for B isotope measurements by MC-ICP-MS. We also tested acetic acid as an organic matter analogue (and used for carbonate dissolution) and no shift of  $\delta^{11}\text{B}$  with increasing concentrations of acetic acid added ( $0.002\text{--}0.01 \text{ mol l}^{-1}$ ) was observed.

## Application to modern corals

Four modern corals, previously analysed by Gaillardet and Allègre (1995), were chosen for a comparison

between P-TIMS and d-DIHEN MC-ICP-MS boron isotope measurements. A detailed description of corals COM1, COM4, COM5 and COM6, all with different origins, can be found in Gaillardet and Allègre (1995). Finely crushed samples (10–20 mg) were washed in distilled H<sub>2</sub>O and dissolved in 0.1 ml of 4 mol l<sup>-1</sup> HNO<sub>3</sub> in a closed beaker plunged for 30 min in an ultrasonic tank. The resulting solution was diluted with 0.4 ml of H<sub>2</sub>O, centrifuged and boron was extracted according to the procedure described above. To test the repeatability of this B separation on carbonate samples, we carried out three different chemical separations for sample COM6. Boron isotopic compositions were measured at least three times for each sample. Results are given in Table 3 and represented in Figure 10.

MC-ICP-MS and P-TIMS data were in good agreement; differences were lower than 0.4‰ between our determinations and the P-TIMS values of Gaillardet and Allègre (1995), thus validating our MC-ICP-MS measurement using d-DIHEN.

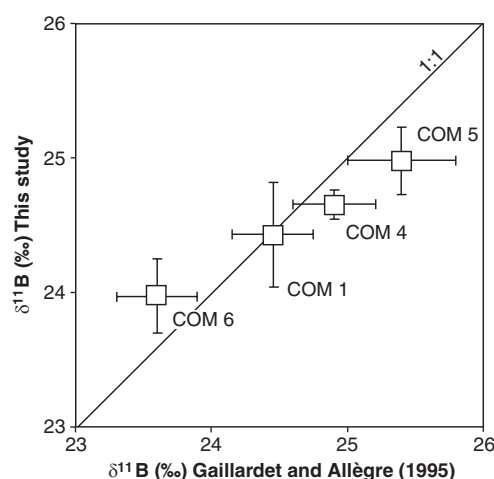
This is the first time that MC-ICP-MS and TIMS data for δ<sup>11</sup>B measured in bulk carbonate samples have agreed so well (differences between MC-ICP-MS and P-TIMS data were respectively 0.04‰, 0.25‰, 0.39‰ and 0.37‰ for COM1, COM4, COM5, COM6). The most recent comparison of boron isotope ratio measurement by MC-ICP-MS and TIMS is that of Kasemann *et al.* (2009) with differences between the two methods between 0.4‰ and 1.1‰.

Boron isotopic measurements carried out on carbonates were not limited by sample size. We did not try to measure the smallest possible quantity of boron. For a duplicated analysis, a solution of 400 μl at a minimum concentration of 50 ng ml<sup>-1</sup> was needed, equivalent to 20 ng of boron. The optimum test portion size of boron to

**Table 3.**  
Comparison of values for δ<sup>11</sup>B from four modern corals from this study and a previous one for the same corals by Gaillardet and Allègre (1995)

| δ <sup>11</sup> B | This study   | n  | Gaillardet and Allègre (1995) |
|-------------------|--------------|----|-------------------------------|
| COM1              | 24.41 ± 0.35 | 4  | 24.45 ± 0.3                   |
| COM4              | 24.65 ± 0.11 | 3  | 24.9 ± 0.3                    |
| COM5              | 25.01 ± 0.20 | 7  | 25.4 ± 0.3                    |
| COM6              | 23.97 ± 0.28 | 11 | 23.6 ± 0.3                    |

Three different chemical separations were processed for COM6. n is the number of measurements. Uncertainties are 2s.



**Figure 10.** δ<sup>11</sup>B of four different corals measured by MC-ICP-MS with d-DIHEN (this study) and by P-TIMS (Gaillardet and Allègre 1995). Vertical error bars represent instrumental repeatability for COM1, COM4 and COM5 and method repeatability (three different separation chemistries) for COM6.

perform high quality boron isotope determination by MC-ICP-MS with direct injection was found to be 50–100 ng. This was slightly larger than that in Foster (2008), who performed boron determinations on 1–3 mg of foraminiferal carbonate, yielding 30–50 ng of boron.

## Conclusions

The boron measurement protocol using d-DIHEN direct injection nebulisation detailed in this paper was accurate and precise. The major advantage of d-DIHEN for boron determination was the shorter wash time, reducing the interval between sample and calibrator in the bracketing procedure to 5 min. For most elements between the masses of Li and U, a three- to fourfold sensitivity gain with d-DIHEN relative to classical spray chamber was observed, similar or slightly smaller than that with the APEX desolvation system.

Accuracy was tested by measuring boron in two series of mixed reference solutions of known isotopic compositions between -90‰ and 40‰ and between -2‰ and 2.5‰. We demonstrate that we could distinguish δ<sup>11</sup>B values at the level of 0.25‰. Intermediate precision of one enriched reference sample SE43 and of NASS-5 measured every ten samples during many months gave a 2s standard deviation 0.25‰, which is also the repeatability of a standard solution bracketed against itself for 12 hr. We propose a δ<sup>11</sup>B mean value for NRCC NASS-5 seawater

of  $39.89 \pm 0.25\%$ . Replicate chemical separations of standard solutions and seawater solutions gave  $\delta^{11}\text{B}$  repeatability of  $0.28\%$  and  $0.27\%$ , respectively. This indicates that, with the increasing precision of MC-ICP-MS boron isotope measurements, boron chemical separation becomes the critical point in the precision tests. The P-TIMS previously published data on four modern corals and our d-DIHEN MC-ICP-MS were in good agreement, and our protocol led to a total repeatability for these corals (chemistry plus analysis) of between  $0.1\%$  and  $0.5\%$  (2s). Finally, preliminary sensitivity tests on other elements than boron and the accuracy of Nd isotopes measurements demonstrate the potential for using d-DIHEN for a large range of applications on MC-ICP-MS.

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