Application note | 001006

Mass spectrometry

Boron isotope ratio measurements in carbonates via LA-ICP-MS

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Introduction

Boron isotopes are an important proxy used in paleo-climate research, often used to understand ocean acidification in the past, in particular during times of high atmospheric CO_2 (e.g. Paleocene-Eocene Thermal Maximum, PETM[1, 2], or during the warming after the last deglaciation[3-5]). The fractionation of boron isotopes (^{10}B and ^{11}B) between borate and boric acid in seawater is pH dependent. Biogenic carbonate (e.g. foraminifera or corals), which are understood to incorporate borate into their skeletons[6,7], are therefore a good archive of past ocean pH[8].

In this field of research, where sample material is unique and limited, laser ablation techniques have become a novel way to map variations in boron isotopic composition across biogenic carbonates[9-12]. However, the precision and accuracy to which boron isotope ratios could be accurately mapped in carbonate materials has previously been affected by the scattering of Ca ions[10].

Here, we show the advantage of using the Thermo Scientific™ Neoma™ MC-ICP-MS and the Thermo Scientific™ Neoma MS/MS™ MC-ICP-MS for boron LA-ICP-MS analysis of carbonate samples.

Methods

Instrumentation

An ESL™ NWR™ 193 UC laser ablation system equipped with a TwoVol 2 ablation cell was connected to the Neoma and Neoma MS/MS MC-ICP-MS (Figure 1). Both MC-ICP-MS systems were equipped with the Jet Interface using the high sensitivity X-skimmer and Jet-sampler cones.

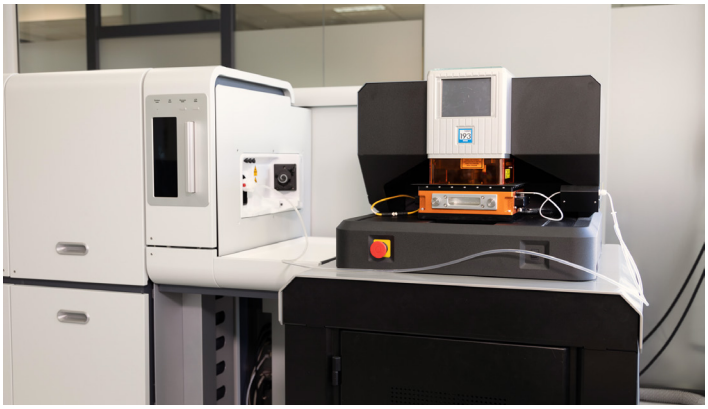

Figure 1. Neoma MC-ICP-MS connected to ESL NWR 193 LA

A raster ablation of the reference material NIST® SRM® 610 was used to tune the LA-MC-ICP-MS. The B cup configuration (Table 1) was used and laser conditions (Table 2). The Neoma tune parameters were tuned to achieve high sensitivity.

Table 1. B isotope cup configuration

C. Cup	L5	L4	L3	L2	L1	C	H1	H2	H3	H4	H5
^{10}B	^{9}Be					^{10}B					^{11}B
^{11}B	^{10}B					^{11}B					^{12}C
10.5			^{10}B						^{11}B		

Table 2. Laser set-up conditions

Fluence (J/cm^2)	6
Repetition Rate (Hz)	13
Circle spot size (µm)	100
Gas flows: He (L/min) N_2 (ml/min)	 0.75 4

Many laser parameters were controlled via the NWR Laser plugin supplied within the Thermo Scientific™ Qtegra ISDS™ Software in Neoma MC-ICP-MS. This allows bi-directional communication between the two platforms, useful for sharing sample lists, triggering and data processing. Similar plugins for Qtegra are available for other laser ablation systems.

The reference material NIST SRM 610 was used to tune and test the overall performance of the LA-MC-ICP-MS. and served as the normalizing standard using published δ^{11}B values[10]. Boron isotope analysis was then carried out on a pressed carbonate pellet of JCp-1[2].

Results

Laser sensitivity

Sensitivity of the Neoma and Neoma MS/MS MC-ICP-MS was determined by measuring 60 repeats of 2 second integration time of a 50 ppm pressed carbonate pellet a total of 5 times. A sensitivity of 0.008 V/ppm (total B) was achieved with the chosen laser settings (See table 3). This is a factor 2 better than previous generations of MC-ICP-MS, where a maximum of 0.004 V/ppm was previously achievable (for the same laser and gas settings).

Boron baseline

On previous generations of MC-ICP-MS, an elevated baseline around ^{10}B has been observed that extended up to mass 11 (Figure 2 purple line)[10]. This elevated baseline was thought to be due to scattering of Ca^{4+} ions when ablating carbonate samples [10]. This results in an offset of the δ^{11}B value from the accepted value by > 4‰ (Figure 3).

Table 3. Laser sensitivity of Neoma MC-ICP-MS for 50 ppm pressed carbonate pellet

Label	Type	^{10}B (cps)	SE	^{11}B (cps)	SE	^{11}B/^{10}B	SE
Pellet_01	SMP	4.61E+06	5.37E+04	2.14E+07	2.52E+05	4.6490	0.0009
Pellet_02	SMP	4.83E+06	5.53E+04	2.24E+07	2.54E+05	4.6387	0.0011
Pellet_03	SMP	3.84E+06	4.01E+04	1.78E+07	1.72E+05	4.6408	0.0008
Pellet_04	SMP	4.65E+06	6.83E+04	2.15E+07	3.11E+05	4.6339	0.0015
Pellet_05	SMP	4.29E+06	4.45E+04	1.99E+07	2.03E+05	4.6380	0.0013
	Average (cps)	**4.44E+06**	**5.24E+04**	**2.06E+07**	**2.38E+05**		
	Average (V)	**0.07**	**0.0008**	**0.33**	**0.0038**		
	Total B (V)	**0.40**					
	Sensitivity (V/ppm)	**0.008**					

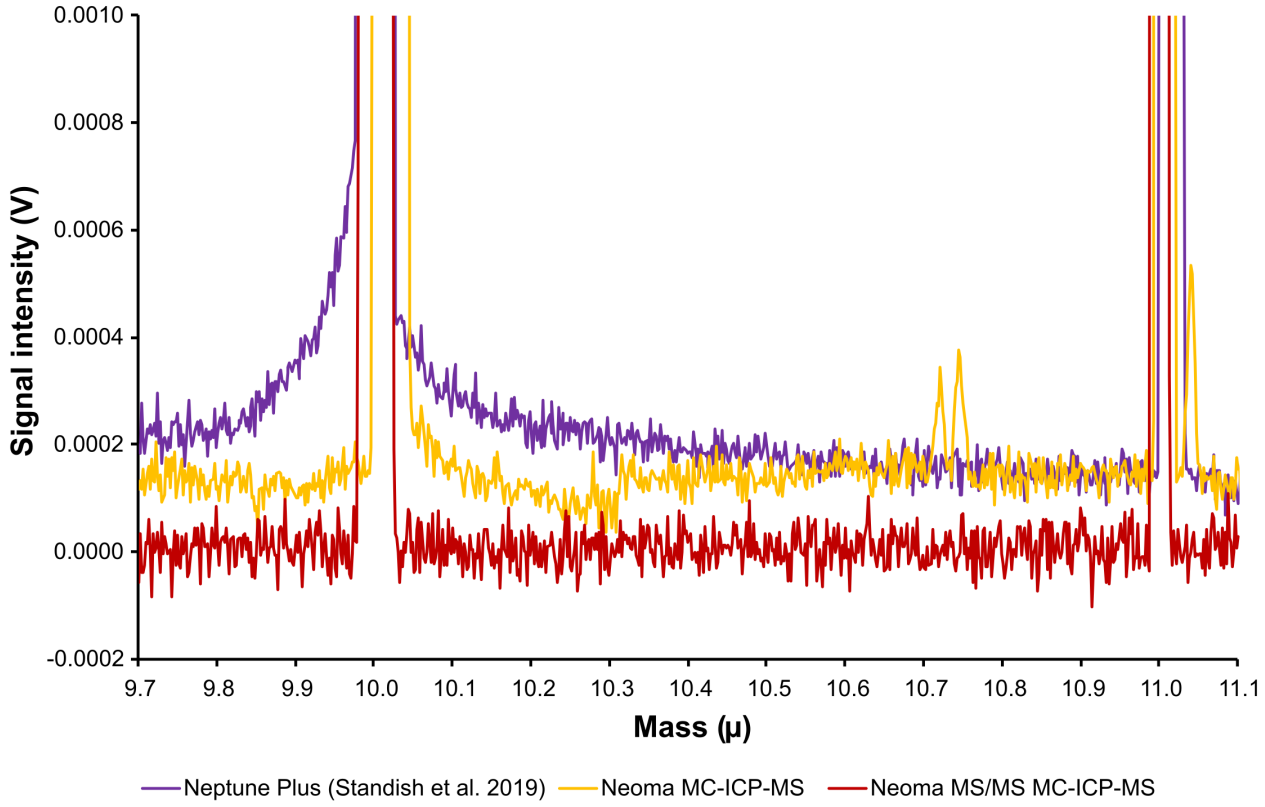

Figure 2. Mass scan across ^{10}B and ^{11}B when ablating the carbonate pellet JCp-1

The new geometry and design of the Neoma MC-ICP-MS eliminates the majority of scattered Ca ions interfering with the ^{10}B peak (Figure 2 yellow line). This is further improved with the pre-cell mass filter of Neoma MS/MS MC-ICP-MS, which filters out the Ca signal before isotopic separation. Through this technology, the elevated ^{10}B baseline is completed eradicated (Figure 2 red line). This means that the $\delta^{11}B$ value acquired using NIST610 for mass bias correction matches the accepted value of JCp-1 without need for any secondary isotopic correction (Figure 3).

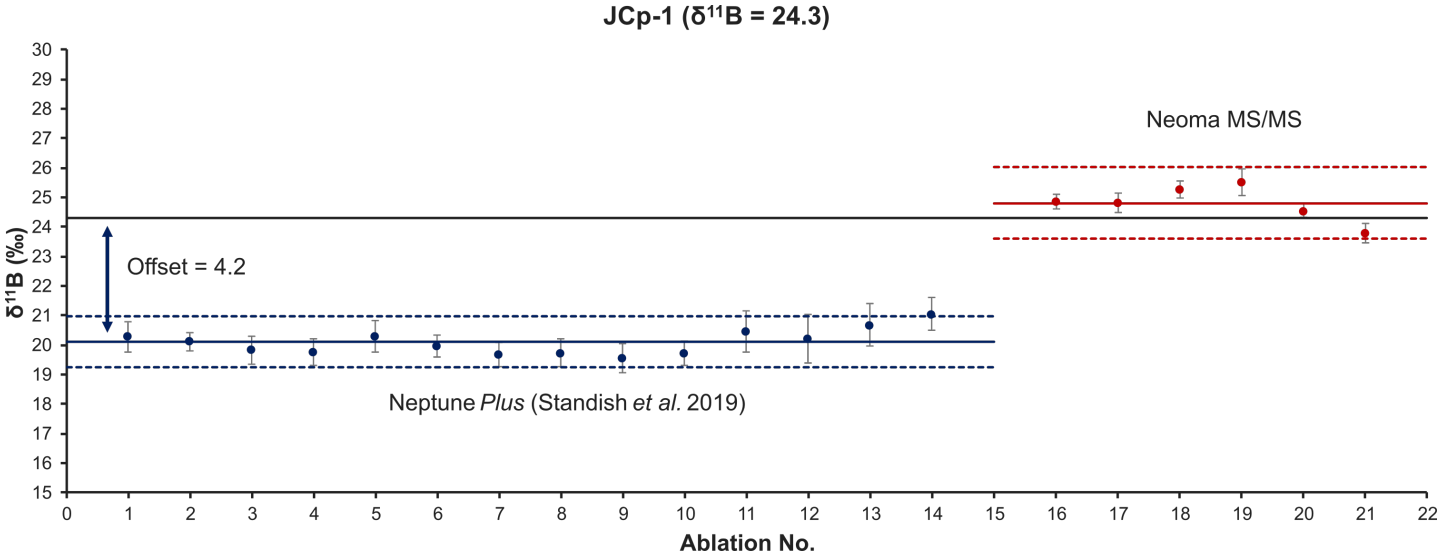

Figure 3. Comparison of boron isotopic composition of carbonate standard JCp-1 measured with the previous generation of MC-ICP-MS and with Neoma MS/MS MC-ICP-MS. All error bars are 2SE. External reproducibility (dash lines) are 2SD.

Conclusion

Boron isotope analysis of carbonate samples via LA-ICP-MS has previously been challenged by elevated ^{10}B baselines due to the interferences from scattered Ca^{4+} ions. The pre-cell mass filter of Neoma MS/MS MC-ICP-MS eliminates this problem by filtering out Ca ions before isotopic separation. This means that measured boron isotope ratios of carbonate samples are accurate and do not require a secondary matrix correction.

By eliminating the interference from scattered Ca ions, the Neoma MS/MS MC-ICP-MS allows for accurate boron isotope analysis of carbonate samples, precluding the requirement for well matched standards. This should allow researchers to investigate a wider range of samples and provide confidence in the accuracy of the boron isotope ratio.

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