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High precision MC-ICP-MS measurements of $\delta^{11}B$ from ng amounts in carbonate samples, using microsublimation and direct injection (µ-dDIHEN)

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The boron isotopic ratio ($\delta^{11}B$) of marine biogenic carbonates is a proxy for oceanic pH, provided that its measurement is precise enough (2SD ≤ 0.8 ‰ ≈ 0.1 pH-unit, magnitude observed for the ongoing ocean acidification). Indeed boron extraction and isotopic analysis present several difficulties: lightness, volatility in acidic environment, strong memory effect in ICP-MS (hence the risk of cross-contamination and high level blanks) and high energy of first ionisation. The $\delta^{11}B$ measurement of small samples with low [B] such as foraminifera (2-20 ppm and m_{sample} ≤ 5 mg), commonly used in palaeoceanography, is thus challenging. To overcome these difficulties, our new analytical protocol couples:

- an automated and miniaturised direct injection system, the µ-dDIHEN, allowing for the injection of small volumes (sample loop of 10-50 µL) at low flow rates (8-35 µL/min) to the MC-ICP-MS [1],
- boron extraction from the carbonate matrix through the fast-handling microsublimation method [2,3], that provides very low blanks (~10 pg),
- and the use of Jet sampler and X skimmer cones, boosting the sensitivity, together with two 10^{13} Ω amplifiers, improving the signal/noise ratio, for a precise measurement of small signals.

Only 240 µL of solution is required for a triplicate sample-standard bracketing measurement. Multiple $\delta^{11}B$ measurements of the carbonate MVS-1 reference material [4], with B amounts down to 1.2 ng, validated our protocol, reaching individual external precisions (2SD, n=5) of 0.1-0.3 ‰. We further measured modern biogenic carbonates, with various mineralogies and B contents, from which B was either extracted by microsublimation or by ionic chromatography. With B amounts down to 0.5-0.7 ng, we obtained 2SD between 0.1 and 0.5 ‰ and a good agreement between the two separation methods.

[1] Louvat *et al.,* 2019, *JAAS*, 34, 1553-1563
[2] Gaillardet *et al*., 2001, *GGR*, 25, 67-75
[3] Misra *et al.*, 2014, *GCA*, 140, 531-552
[4] Jurikova *et al.*, 2019, *GCA*, 248, 370-386