Boron isotopes by femtosecond LA-ICP-MS with application to pH reconstruction in biogenic carbonates

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In this study, we explore the capability of our customized UV femtosecond laser ablation system coupled to a Nu Plasma II MC-ICP-MS to determine B isotope composition by investigating standard materials of various matrices and foraminifera and coral samples. Boron isotope ratios were determined on ion counters using NIST SRM 610 as reference material. Multiple analysis of silicate and carbonate standard materials including NIST SRM 612, the MPI-DING series (komatiite to rhyolite glasses), IAEA-B-8 (clay) and JCp-1 (coral) reveal average $\delta^{11}B$ values, which agree well with published data. The reproducibility is better than 0.8‰ (2 SD). Investigations of the benthic foraminifera species (*C. wuellerstorfi*) from the ODP core 1092 show little inter- and intra-shell variability in $\delta^{11}B$. However, average $\delta^{11}B$ values reveal variation between 13.5 and 14.7‰ at the time of cooling of Antarctica ~14 Myr ago, which indicate a change in deep water pH of 0.2 pH units. Furthermore, we studied recent cold-water corals (*D. dianthus*) from the Comau Fjord (Chile), a field site showing spatial and seasonal variation in seawater pH (7.63 to 7.85). $\delta^{11}B$ values ranges between 23.5 and 27.0‰ corresponding to an internal pH up-regulation for calcification of 0.78 to 1.14 pH units, which is likely controlled by ambient seawater pH and nutrient availability. Our results demonstrate that fs-LA-ICP-MS provides a unique technique to determine B isotope ratios at high spatial resolution for pH reconstruction.