Highly resolved determination of Mg/Ca in single foraminifera shells using fs-LA-ICP-MS

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We have developed a high-resolution fs-LA-ICP-MS technique to determine Mg/Ca ratios in small and thin carbonate samples, such as foraminifers. A 200 nm fs laser was combined with a sector field ICP mass spectrometer. To facilitate fast peak switching (1 ms) by electrical scan, we determined the ion beams of the double charged $^{44}Ca^{++}$ and the single charged $^{25}Mg^{+}$, which are located at mass numbers 22 and 25, respectively. Our experiments show that the Ca^{++}/Ca^{+} ratio is 0.01, and nearly independent of experimental parameters and matrix. Correction was applied for the ^{22}Ne gas blank; however, the correction is low (< 5 % of the $^{44}Ca^{++}$ peak). Thus, several thousand measurements can be performed for one spot analysis using a spot size of 55 µm. To get low sample ablation and high depth resolution in the 5 – 10-nm range, we chose pulse repetition rates (PRR) of 1 and 5 Hz, respectively, at a fluence of about 0.5 J cm^{-2}. At a PRR of 1 Hz, the laser induced signal is shorter than the washout time of about 1 s. Therefore, the signal can be integrated, which significantly improves the reproducibility of the measurements (RSD of about 5 - 15 % for 0.3 ng ablation/pulse). Calibration was performed with the microanalytical carbonate reference material MACS-3.

The new technique has been applied for the analysis of multiple chambers of foraminifers. Mg/Ca ratios can be used as a paleo-seawater thermometer, because the incorporation of the trace element Mg depends on ambient water temperature. The analysis of the *Globorotalia inflata* from a sediment core of the Madeira Basin (KL88) yields a Mg/Ca ratio of about 0.9 mmol mol^{-1}, and significantly higher values of about 1.5 mmol mol^{-1} occur in the distal calcite layers of the shell.

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