High-resolution Mg/Ca measurements of foraminifers using microanalytical techniques

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The Mg/Ca ratio in foraminifer shells is a proxy of seawater temperature. Microanalytical techniques, such as LA-ICP-MS, NanoSIMS, 2D, and 3D scanning are suitable to perform such investigations.

A recently developed single-shot technique using fs - 200 nm – LA-ICP-MS with low fluence (< 0.6 J cm^{-2}) enables a depth resolution of about 50 – 100 nm/pulse with a precision (1 RSD) of about 5 %. Calcium carbonate nano-pellets with grain sizes reaching the range of nanoparticles (such as the microanalytical reference material MACS-3 np with a precision of <1 % RSD) help to improve the accuracy of the Mg/Ca data by using them as calibration material. NanoSIMS ion probe measurements are useful to perform images of $^{25}Mg^{+}$ and $^{40}Ca^{+}$ in selected areas (e.g., 20 x 20 μm^2) with a resolution of 0.2 µm. 2D and 3D scanning techniques using LA-ICP-MS help to identify the variability of Mg, Ca and other elements of the entire species and to test homogeneity of microanalytical reference materials.

Femtosecond-LA-ICP-MS has been applied for high-resolution analyses of single chambers and depth profiles of individual planktic and benthic foraminifer tests. Mg/Ca variabilities of less than about 1 mmol mol^{-1} can be detected for ablation hole-depths up to 20 µm. The limit of detection (LOD) of Mg/Ca is 0.05 mmol mol^{-1}. NanoSIMS measurements on selected specimen were performed to confirm the data and interpretation. Depth profiles of shells of *O. universa* display layers of high and low Mg/Ca bands (Spero et al., 2015) indicating night and day calcification cycles, respectively.