

RESEARCH ARTICLE

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Key Points:

- Single-chamber Mg/Ca measurements of different foraminifera using femtosecond LA-ICP-MS
- Single-shot analysis to detect Mg/Ca variability of less than about 1 mmol/mol at a precision (RSD) of about 5%
- Femtosecond LA-ICP-MS depth profiles of foraminifer shells resemble information from 2-D NanoSIMS images

Supporting Information:

- Supporting Information S1

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High-Resolution Mg/Ca Measurements of Foraminifer Shells Using Femtosecond LA-ICP-MS for Paleoclimate Proxy Development

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Abstract Determination of Mg/Ca in foraminifer shells as a proxy of seawater temperature is of particular interest in paleoclimate reconstruction. Here we show that femtosecond–200 nm–laser ablation–inductively coupled plasma–mass spectrometry is a suitable technique to precisely and accurately determine Mg/Ca in the micrometer-sized calcareous chambers of foraminifera. At low fluence (0.3–0.6 J/cm²) the double-charged ⁴⁴Ca⁺⁺ and the single-charged ²⁵Mg⁺ ions are measured nearly simultaneously. Integrated single-shot measurements using a pulse repetition rate of 1 Hz enable precise analyses at a depth resolution of about 50–100 nm/pulse corresponding to an ablated material of 0.3–0.6 ng calcite/pulse for a spot size of 55 μm. High-resolution analyses can be performed until a depth of 10–20 μm and thus particularly suitable for thin-shelled foraminifera. Reproducibility (relative standard deviation) is about 5% as approved by homogeneous reference materials. Calibration is performed with the microanalytical synthetic reference material MACS-3. Magnesium and Ca data of different carbonate and silicate reference materials agree within uncertainties with reference values. The procedure has been successfully applied for detailed analyses of single chambers and shell-depth profiles of live individuals and empty planktic and benthic foraminifer tests from different ocean basins.

Plain Language Summary The ratio of magnesium and calcium (Mg/Ca) of the calcareous shells of single-celled marine microorganisms called foraminifera is used for temperature reconstruction of the past ocean and climate. We have been using very short laser pulses of 10^{−13} s to sample small amounts of calcite and Mg/Ca from very thin layers to analyze temperature at high accuracy and precision. Using low energy densities of 0.3–0.6 J/cm², Mg/Ca has been determined by mass spectrometry by applying a new single-shot analysis. Reproducibility of the analyses is about 5% as approved by homogeneous reference materials. The procedure has been successfully applied for detailed analyses of single chambers and shell-depth profiles of live individuals and empty planktic and benthic foraminifer shells from different ocean basins. The new method allows analyses of fossil shells to determine physiological processes and temperatures of ocean waters dating back several millions of years.

1. Introduction

In climate geochemistry, isotope ratios of oxygen ($\delta^{18}\text{O}$) and carbon ($\delta^{13}\text{C}$) as well as trace element data from paleoclimate archives are major proxies to reconstruct climates of the past at the seasonal scale and over millions of years (e.g., Fischer & Wefer, 1999; Haug et al., 2005; Lea, 2003). High-resolution measurements of calcareous skeletons, for example, foraminifera (with shell sizes of typically 20–500 μm and shell-wall thicknesses of about 5 to 50 μm), ostracods, ooliths, or corals, can only be investigated for major and trace elements by in situ nanoanalytical or microanalytical techniques, such as nanoscale secondary ion mass spectrometry (NanoSIMS; e.g., Spero et al., 2015; Fehrenbacher et al., 2017), electron microprobe (e.g., Kozdon et al., 2011; Sadekov et al., 2005; Toyofuku & Kitazato, 2005), and laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS; e.g., Reichart et al., 2003; Hathorne et al., 2009; Vetter et al., 2013; Steinhardt et al., 2015; Fehrenbacher et al., 2017).

Due to the high fossilization potential and ubiquitous abundance in calcareous sediments of most ocean basins over the past 100 Myr, foraminifera belong to the most investigated microorganisms utilized as archives in paleoceanography and climate reconstruction. Their calcareous shell is formed from the

seawater they thrive in, and the chemical composition depends on marine environmental parameters (e.g., temperature, salinity, and carbonate ion concentration; Shackleton & Opdyke, 1973; Lea, 1999; Rohling & Cooke, 1999; Spero et al., 1997; Katz et al., 2011). In particular, the Mg/Ca can be used as proxy for ambient seawater temperature at the time the shell was formed (Anand et al., 2003; Davis et al., 2017; Elderfield et al., 2002; Friedrich et al., 2012; Lea et al., 1999; Nürnberg, 1995; Nürnberg et al., 1996; Regenberg et al., 2009; Rosenthal et al., 2004). The chemical compositions of single foraminifer chambers provide proxies to reconstruct changes in the marine environment during the lifetime of the individuals such as water-depth related changes in ambient seawater temperature (for a review see Schiebel & Hemleben, 2017; Schiebel et al., 2018; Leduc et al., 2014; Jentzen et al., 2018). LA-ICP-MS profiles from single chambers provide data on the successive calcite layers of the foraminifer shell (high and low Mg/Ca bands) at high resolution (e.g., Eggins et al., 2004; Spero et al., 2015). LA-ICP-MS has become a commonly used microanalytical method for the investigation of solid geochemical and environmental samples (e.g., Davis et al., 2017; Reichart et al., 2003). However, there are some limitations to this technique, mainly with respect to analytical repeatability and measurement accuracy (Jochum et al., 2014). In particular, LA-ICP-MS has been applied for depth profile measurements of benthic and planktic foraminifers (e.g., Dueñas-Bohórquez et al., 2011; Eggins et al., 2003; Evans et al., 2015; Fehrenbacher et al., 2017; Hathorne et al., 2003; Leduc et al., 2014; Raitzsch et al., 2010; Sadekov et al., 2009; Spero et al., 2015; Wu & Hillaire-Marcel, 1995). Fehrenbacher et al. (2015) in detail present optimum procedures for this kind of analyses, emphasizing that high-resolution depth profiles require low fluence, low repetition rate, and a deep UV laser. In addition to these requirements, other properties have to be considered, such as matrix-matched calibration and high sensitivity of the mass spectrometer.

For the first time, we describe a new cutting-edge LA-ICP-MS technique, which enables highly resolved, precise, and accurate signals of Mg/Ca in foraminifers using a femtosecond (fs)-LA system and applying a single-shot ablation technique. Recently, fs-laser ablation has only been applied for B/Ca by Howes et al. (2017). To demonstrate feasibility and applicability of this new technique, we discuss results of planktic and benthic foraminifers from different locations. Results are compared to Mg/Ca ratios measured on bulk planktic foraminifer samples using standard wet chemistry method for downcore paleoclimatic applications (e.g., Barker et al., 2003). NanoSIMS measurements on a selected specimen were performed to confirm the data and interpretations from fs-LA-ICP-MS.

2. Materials and Methods

2.1. Materials

The samples used for analysis comprise the planktic foraminifer species *Globorotalia menardii* from Arabian Sea (seafloor sediment) and *Orbulina universa* from Caribbean Sea (water column), as well as the benthic foraminifer species *Cibicides wuellerstorfi* from the North Atlantic Ocean (Table S1 in the supporting information; Lochte et al., 1996; Schönfeld et al., 2011; Repschläger et al., 2018). The shells of the three species *G. menardii*, *O. universa*, and *C. wuellerstorfi* are made of low-magnesium calcite (see Bentov & Erez, 2006, and references therein). The individuals of *O. universa* and *C. wuellerstorfi* were alive (cytoplasm bearing) during sampling. In addition to the foraminifer samples, international reference materials were analyzed for calibration and quality control purposes. These are as follows:

MACS-3: This reference material is a synthetic calcium carbonate powder produced by the United States Geological Survey and exists as a homogeneous pressed powder pellet for microanalytical purposes. It was used for calibration with the mass fractions of Mg = 1756 $\mu\text{g/g}$ and Ca = 37.69% m/m (Jochum et al., 2012).

JCT-1: JCT-1 is a giant clam (*Tridacna gigas*) powdered sample prepared from the Geological Survey of Japan. For this work pressed powder pellets were used. Concentration data of MgO (0.053% m/m), CaO (54.51% m/m), and other elements are listed in the GeoReM database (<http://georem.mpch-mainz.gwdg.de>; Jochum et al., 2005).

JCP-1: This is a recent *Porites* sp. coral powdered sample prepared from the Geological Survey of Japan. Analyses were performed with pressed powder pellets. Published data exist for MgO (0.16% m/m) and CaO (53.5% m/m; GeoReM).

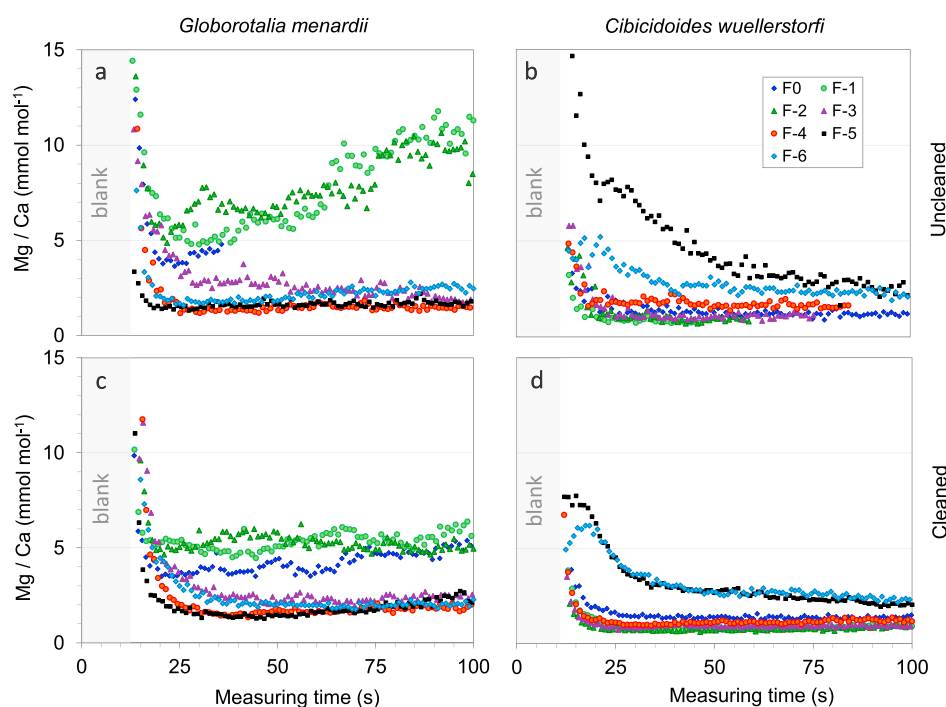


Figure 1. Mg/Ca fs-LA-ICP-MS profiles of *G. menardii* (men-20) and *C. wuellerstorfi* (wuell-2) collected from core top sediments (Table S1 in the supporting information). (a and b) Mg/Ca profiles of uncleaned foraminifera. (c and d) Mg/Ca profiles of oxidative cleaned foraminifera. Single chambers (F0 final chamber to F-6) were ablated from the outside of the shells toward the inside (left to right). See supporting information for further fs-LA-ICP-MS profiles (Figures S3 and S4).

The preparation of the pressed powder pellets of JCT-1 and JCP-1 (13 mm in diameter and 2 mm in thickness) was conducted at the University of Mainz using a vacuum hydraulic press (PerkinElmer). The setup was evacuated for 5 min. After evacuation a pressure of 5 t is applied and hold for 15 min.

SRM 610: This reference sample is a silicate glass produced by the National Institute of Standards and Technology (NIST). It is commonly used for microanalytical purposes. Certified and quasi-certified concentration values of Mg (432 $\mu\text{g/g}$) and CaO (11.4% m/m) and other elements are published by Jochum et al. (2011).

2.2. Preparation of Foraminifera

For geochemical analyses, the foraminifer tests were prepared in different ways.

1. For LA-ICP-MS analyses, single unbroken tests of *G. menardii*, *O. universa*, and *C. wuellerstorfi* were picked and placed on a carbon adhesive tape or in a sandbox (pure 200–500- μm -sized quartz grains) in order to avoid contamination from the tape. After the first runs, some specimens were cleaned with buffered hydrogen peroxide solution (100 μL 30% H_2O_2 and 10 mL NaOH) according to Barker et al. (2003) to determine the influence of the oxidative cleaning step (Figures 1 and 2 and Figure S1 in the supporting information).
2. Four bulk samples (10 individuals/sample) of *G. menardii* were cleaned for Mg/Ca analyses following the protocol of Barker et al. (2003), whereas two samples were further treated with an additional reductive cleaning step. Mg/Ca analysis of the bulk samples was performed on an axial-viewing ICP-OES (VARIAN 720-ES) at GEOMAR, Kiel (Table S2 in the supporting information).
3. One uncleaned *O. universa* (uni14) was additionally analyzed with NanoSIMS to confirm the LA-ICP-MS data (Figure 3). This *O. universa* was embedded in resin (Epoxy Cure™ 2) and ground until a flat and even cross section.

We performed secondary ion images of $^{26}\text{Mg}^+$ and $^{40}\text{Ca}^+$ from selected sample areas in multicollection mode with the NanoSIMS 50 ion probe (Hoppe et al., 2013) at the Max Planck Institute for Chemistry. With a recently installed Hyperion RF plasma oxygen primary ion source, a primary O^- beam ($d \sim 250$ nm,

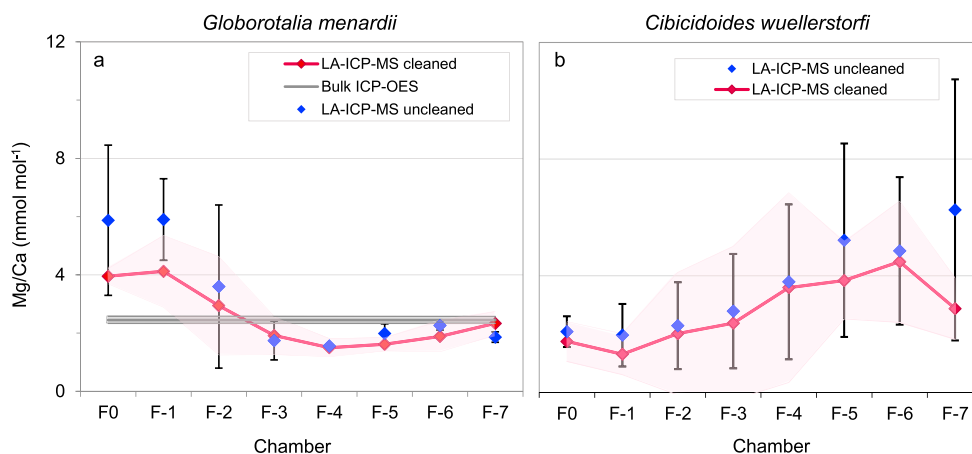


Figure 2. (a) Average Mg/Ca values (1SD) determined by spot analyses of the eight final chambers of four *G. menardii* specimens (cleaned and uncleaned). F0 is the final chamber, and F-1 to F-7 are penultimate to seventh from last chambers, respectively. Grey shaded bar: average Mg/Ca of four bulk samples. (b) Average Mg/Ca (1 SD) determined by spot analyses of the eight final chambers of five *C. wuellerstorfi* specimens (cleaned and uncleaned). The cleaned foraminifera show on average lower Mg/Ca for both *G. menardii* and *C. wuellerstorfi*, respectively. See supporting information for data.

15 pA) was rastered over 10×10 - to 20×20 - μm^2 -sized sample areas. During these measurements, six image planes (256×256 pixels) were acquired, with integration times of 10 ms/pixel each. Prior to analysis, fields of 14×14 to 22×22 μm^2 (always larger than the fields of the respective subsequent measurements) were sputtered with a high current primary beam (~ 40 pA) to remove the gold coating on selected sample areas. From the ion images, $^{26}\text{Mg}^+ / ^{40}\text{Ca}^+$ images were generated, using in-house software developed at the Max Planck Institute for Chemistry.

2.3. Analytical Techniques

2.3.1. Laser Ablation

We used the 200-nm wavelength–NWR femtosecond fs-laser ablation system NWRfemto from ESI combined with the SF Thermo Element2 ICP mass spectrometer (Jochum et al., 2014). Important operating

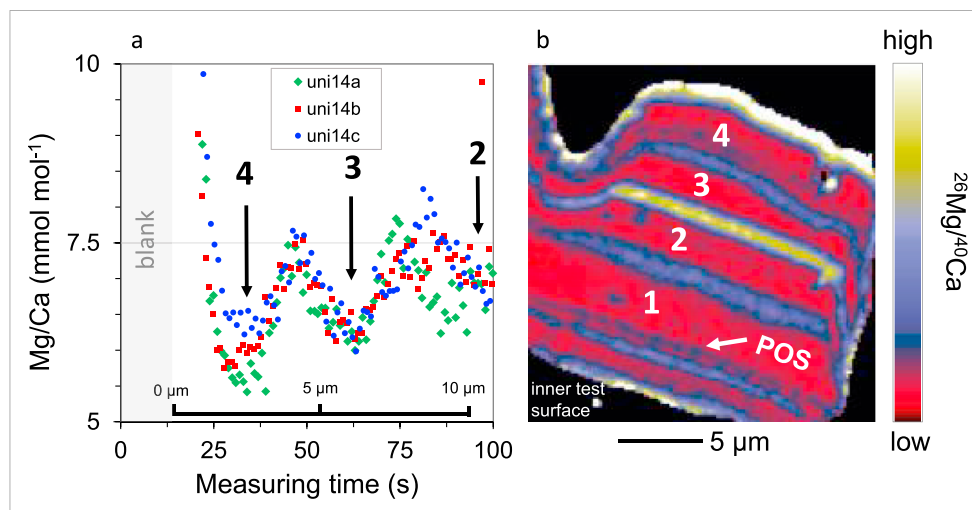


Figure 3. *Oboluna universa*. (a) Varying Mg/Ca values with ablation time as a measure of test depth (scale bar 10 μm) from the (left) outer test surface (15 s) to the (right) inner test surface (100 s). The same test was ablated 3 times (uni14-a, -b, -c). (b) Mg/Ca data from 20 to 100 s of ablation time correspond to Mg/Ca data from NanoSIMS, with low (red color) and high-Mg/Ca layers (yellow and blue colors). The first layer is not well resolved in the fs-LA-ICP-MS data because of the count rates from ablation holes deeper than about 10 μm are too low (at the applied setup, at 1 Hz, fluence of 0.6 J/cm^2 , and hole diameters of 55 μm). POS: primary organic sheet.

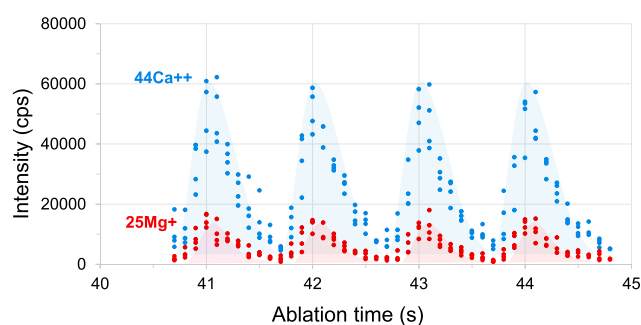


Figure 4. Time-resolved $^{25}\text{Mg}^+$ and $^{44}\text{Ca}^{++}$ signals of single laser shots of the reference material MACS-3 ($\text{Mg} = 1756 \mu\text{g/g}$, $\text{Ca} = 37.69\% \text{ m/m}$). Maximum peak signal intensities of $^{25}\text{Mg}^+$ and $^{44}\text{Ca}^{++}$ at a PRR of 1 Hz evenly range at about 15 and 60 kcps, respectively.

parameters for both instruments are listed in Table S3 in the supporting information. The typical laser systems currently used for the analysis of foraminifers are 193-nm ArF excimer (e.g., Eggins et al., 2003, 2004; Evans et al., 2015; Fehrenbacher et al., 2015; Jentzen et al., 2018) and 213-nm Nd:YAG lasers (e.g., Hathorne et al., 2003). Both laser types have pulse lengths of several nanoseconds, which can cause matrix-related problems, especially for volatile elements (Jochum et al., 2014). Several publications (e.g., Fernández et al., 2007; Poitrasson et al., 2003; Shaheen et al., 2012) have shown that fs-laser ablation avoids sample heating and enabled ablation in a “controlled way” (Koch & Günther, 2007; Vanhaecke et al., 2010). Predominantly, nonthermal ablation processes allow stoichiometric aerosol generation (Hergenhörder et al., 2006). The formation of fine particles leads to enhanced signal intensity and stability in the ICP-MS (Shaheen et al., 2012). Especially for fs lasers with short wavelengths of 200 nm, elemental and isotopic fractionation effects are

minimized or nearly absent for carbonates, silicates, and phosphates (Jochum et al., 2014). Therefore, matrix-matching calibration is less important in fs laser ablation than in nanosecond laser ablation. This means that, for example, homogeneous silicate reference glasses can be used reliably for calibration of calcium carbonate samples. To get highly resolved depth profiles of the shell, low fluence of about $0.3\text{--}0.6 \text{ J/cm}^2$ has been chosen for all measurements. As already mentioned, Fehrenbacher et al. (2015) investigated in detail optimum procedures for depth profiling of foraminifers using an excimer LA system and a quadrupole mass spectrometer. In their study, the authors emphasize that high-resolution depth profiles require low fluence, low repetition rate, and a deep UV laser. In the present study, using a fs-LA system, all these requirements are fulfilled to an even higher degree than in the study of Fehrenbacher et al. (2015). The laser system has a short wavelength of 200 nm, and the laser pulse is much shorter ($<130 \text{ fs}$) than that of an Nd:YAG, or an excimer laser (several nanoseconds). The pulse repetition rate (PRR) of 1 Hz is as low as possible. The fluence ($0.3\text{--}0.6 \text{ J/cm}^2$) is lower than that used in other LA-ICP-MS investigations of foraminifers (e.g., $1\text{--}4.5 \text{ J/cm}^2$; Steinhardt et al., 2014; Fehrenbacher et al., 2015; Evans et al., 2015). This has the great advantage of an extremely gentle ablation of the shell; that is, shooting off of parts of the shell (“beating”; Müller et al., 2009) is avoided. The small volume of the ablated matter leads to a fast washout time, and single-shot measurements can be conducted with a pulse repetition rate (PRR) of 1 Hz.

One of the most important changes made to improve precision of isotope ratios using LA-ICP-MS is the application of single-shot analysis. Cottle et al. (2009) used this method for in situ Pb/U geochronology to simultaneously measure ^{206}Pb , ^{207}Pb , and ^{238}U peaks. We apply this method in a similar way for the determination of Mg/Ca in calcareous materials. Ion beam measurements of $^{25}\text{Mg}^+$ and $^{44}\text{Ca}^{++}$ are performed with a pulse repetition rate (PRR) of only 1 Hz to separate one laser pulse from another (Figure 4). Most other LA-ICP-MS applications use higher PRR, for example, 2–7 Hz (e.g., Dueñas-Bohórquez et al., 2011; Evans et al., 2015; Fehrenbacher et al., 2015; Hathorne et al., 2009; Steinhardt et al., 2014). In such cases, signal-smoothing devices or mathematical smoothing procedures can be applied.

We used an automated Excel application to start the evaluation of the data at a minimum of $^{44}\text{Ca}^{++}$ and $^{25}\text{Mg}^+$ count rates, respectively. Automated evaluation is done for each second. Because the peaks have a length of about 0.9 s, which is less than the washout time of 1 s of the ESI Large Format Cell used here, the individual peaks are separated. The short washout time has been substantially achieved using a localized ablation concept, where ablation occurs in a cylinder. Calibration is performed with the microanalytical calcium carbonate reference material MACS-3, which was analyzed continuously during a session. Rare but obvious, short (0.01 s) signal spikes are mainly electronically induced and automatically eliminated by an outlier routine, if Mg/Ca deviates from the median of the 30–40 values within one single shot by a given factor (e.g., 5). The single-shot analysis using low fluences of $0.3\text{--}0.6 \text{ J/cm}^2$ and a laser spot size of $55 \mu\text{m}$ enables a depth resolution of about 50–100 nm/pulse (corresponding to an ablated material of $0.3\text{--}0.6 \text{ ng}$ calcite/pulse) at reasonable spatial resolution of $55 \mu\text{m}$ up to a depth of about 10–20 μm of the ablation crater. Measurements would also be possible with smaller spot sizes of 10–20 μm , providing higher spatial resolution, but lower depths, and reduced reproducibility would provide less representative results of the entire shell or chambers.

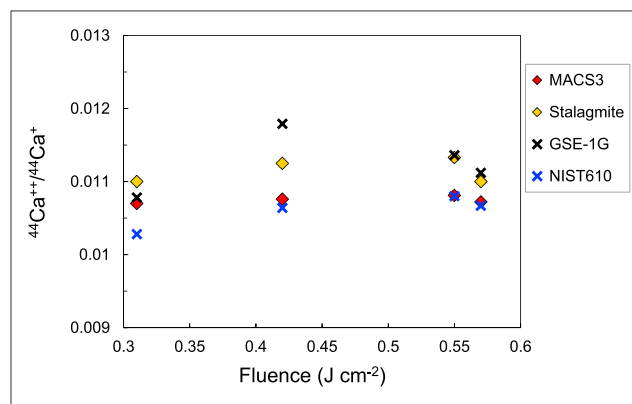


Figure 5. $\text{Ca}^{++}/\text{Ca}^{+}$ values uniformly range around 1.1% independent of the fluence and material analyzed, but slightly affected by slight differences of the day-to-day performance (e.g., tuning, strength of the vacuum).

Depth profile resolution depends on the shape of the ablation crater (Figure S2 in the supporting information). The fs-laser beam has a Gaussian energy profile, where crater profiles are not identical to the spatial resolution of laser intensity. Proper alignment of optics and the use of high-quality objective lenses help to improve the beam profile and crater quality, which may be less predictable compared to ArF excimer lasers. To test the use of fs-LA for depth profile measurements, we performed experiments on the reproducibility of our analyses using foraminifer shells with inherent Mg variability during ablation. Because multiple analyses cannot be conducted on the same location, but at distances of about 100 μm , possible variations in thickness of the single calcite layers, laser entrance angles, and nonparallel Mg-enriched layers can cause differences in the depth profiles. Figure 3 shows as an example three measurements of *O. universa* (spherical chamber). The maximum peaks of the three measurements are within 4 s of the ablation pulses corresponding to a resolution of better than about 200 nm.

2.3.2. ICP Mass Spectrometry

The Element2 ICP mass spectrometer is a double-focusing SF instrument with electric and magnetic fields. In low mass resolution mode ($M/\Delta M = 300$), the SF mass spectrometer delivers flat top peaks in contrast to quadrupole instruments. The SF mass spectrometer has the advantage of higher sensitivity (a factor of about 8; Jochum et al., 2014) compared to a quadrupole instrument used in most applications (e.g., Dueñas-Bohórquez et al., 2011; Fehrenbacher et al., 2015, 2017; Hathorne et al., 2009; Reichart et al., 2003; Spero et al., 2015). In addition, flat top peaks in low mass resolution improve precision of the measurements compared to quadrupole mass spectrometer (Jochum et al., 2014). A disadvantage of the double-focusing SF mass spectrometers is the lower scan speed in comparison to a quadrupole instrument. To improve precision of the Mg/Ca measurements, the time-consuming 0.031-s magnetic jump between the masses of $^{25}\text{Mg}^{+}$ and $^{44}\text{Ca}^{+}$ needs to be avoided. We chose the fast <0.001-s electric jump and measured the double-charged $^{44}\text{Ca}^{++}$, which is in the same mass range ($m/2e = 22$) as $^{25}\text{Mg}^{+}$ ($m/e = 25$). Fast electrical scan measurements (<1 ms) can only be performed when the mass range of the masses of interest is within about 30%. In practice, this means that the ^{44}Ca and ^{25}Mg measurements need to be carried out on the less abundant double-charged ^{44}Ca ions than single-charged Ca ions. Because one isotope is measured within 0.0125 s (using five repeated measurements each), approximately 40 Mg and 40 Ca measurements can be performed nearly simultaneously over a scan time of 1 s. Even with single-shot measurements also $^{23}\text{Na}^{+}$ and $^{27}\text{Al}^{+}$ can be measured quasi simultaneously together with $^{44}\text{Ca}^{++}$. The $^{25}\text{Mg}^{+}$ and $^{44}\text{Ca}^{++}$ blanks are determined for 10 s at the beginning of each measurement before ablation. For evaluation, the count rates of both isotopes have to be blank-corrected. The blank measurements of $^{44}\text{Ca}^{++}$ comprise a $^{22}\text{Ne}^{+}$ peak because of the presence of Ne in the Ar and He sample gases. However, this amount is small with $^{22}\text{Ne}^{+}/^{44}\text{Ca}^{++} < 0.01$. Detailed investigations using samples of different matrices and operating parameters show that $\text{Ca}^{++}/\text{Ca}^{+}$ is uniformly present at an average of about 1.1% (Figure 5) and does not change during a measurement series.

2.4. Measurement Precision

The measurement precision (1 relative standard deviation in percent (1 RSD)) of the Mg/Ca data is determined using repeated measurements of homogeneous calcium carbonate reference materials. Six independent analyses of the pressed powder pellets of MACS-3, Jct-1, and Jcp-1 samples yield uncertainties (1 RSD) in Mg/Ca between 2% and 7%. Similar results are obtained from different foraminifer specimens and different species analyzing homogeneous parts of the shells. Because of the more controlled ablation on glassy reference materials, such as NIST SRM 610, precision is significantly better (0.4%) than in pressed powdered materials of carbonates.

2.5. Measurement Accuracy

To evaluate the measurement accuracy of the single-shot fs-LA-ICP-MS analysis, we analyzed the international reference materials Jct-1, Jcp-1, NIST SRM 610, and MACS-3 having different Mg/Ca. MACS-3

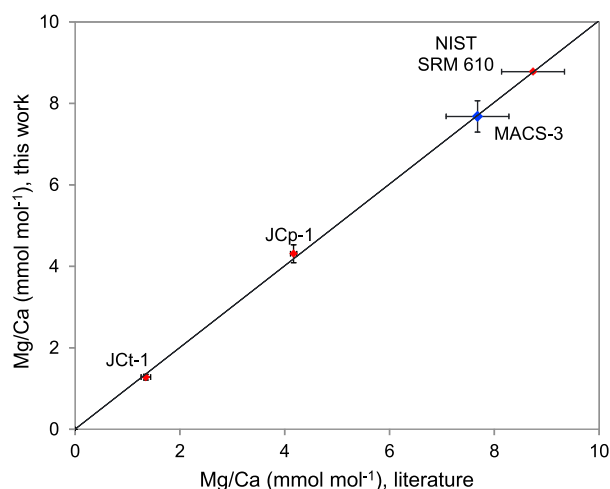


Figure 6. Comparison of fs-LA-ICP-MS data shows a good agreement of fs-LA-ICP-MS Mg/Ca data (mmol/mol) of reference materials with the respective reference values (GeoReM database).

was used for calibration. Figure 6 shows the results together with the overall analytical uncertainty, comprising the analytical uncertainties of sample and MACS-3 measurements as well as the uncertainty of the published Mg/Ca reference value of MACS-3 ($\text{Mg/Ca} = 7.68 \pm 0.60$ mmol/mol; United States Geological Survey reference values published in Jochum et al. (2012)). We obtained the following Mg/Ca data (mmol/mol) for the three samples JCT-1 with 1.35 ± 0.16 , JCp-1 with 4.17 ± 0.48 , and NIST SRM610 with 8.78 ± 0.71 . Within overall analytical uncertainty of fs-LA-ICP-MS analyses and reference values between 7% and 12%, the measured and the published data sets (e.g., Hathorne et al., 2013) agree well, indicating good accuracy of the single-shot method (Figure 6).

2.6. Limit of Detection

The limit of detection (LOD) is estimated by the mean of the blank and the 3σ standard deviation of the blank. For an element ratio, it is difficult to establish, because the LODs of two elements have to be evaluated. However, for calcareous samples, such as foraminifers, corals, and ostracods, the Ca content is high and uniform at about 40% m/m. Therefore, the LOD of Mg/Ca mainly depends on the LOD of Mg. Our experiments demonstrate that the LOD of Ca by using the doubly charged $^{44}\text{Ca}^{++}$ sig-

nal for detection is about 1,000 $\mu\text{g/g}$, which is 400 times lower than the Ca mass fraction in calcium carbonates. The LOD of Mg using the single-charged $^{25}\text{Mg}^{+}$ for analysis is much lower at about 10 $\mu\text{g/g}$. Consequently, the LOD of Mg/Ca is $10 \mu\text{g/g} / 400,000 \mu\text{g/g} \times (\text{ratio of rel. atomic mass Ca and Mg})$, which is about 0.05 mmol/mol.

3. Applications

Planktic foraminifers are floating in surface waters of the oceans, whereas benthic foraminifers live at the ocean floor (e.g., Murray, 2006; Schiebel & Hemleben, 2017). Single-shot fs-LA-ICP-MS analyses of Mg/Ca of the individual chambers of two different planktic foraminifer species and one benthic foraminifer species are discussed for variations in ambient seawater temperature and ecological effects. Mg/Ca values of cleaned tests only are considered only for the discussion below. Uncleaned foraminifers have elevated Mg/Ca values (Figures 1 and 2), which is most likely caused by contamination of the foraminiferal shells (e.g., organic tissue).

3.1. Chamber-to-Chamber Mg/Ca Variability in the Planktic Foraminifer *G. menardii*

Mg/Ca values of four individuals of the species *G. menardii* with similar ontogenetic ages, from core top sediment in the Arabian Sea, show significant Mg/Ca differences among the final eight chambers (Figures 1a, 1c, and 2a). Calculated ambient seawater temperatures from Mg/Ca, applying the calibration $\text{Mg/Ca} = 0.38 \exp(0.090 T)$ of Anand et al. (2003), reveal variability in calcification temperatures within and between tests and chambers, as well as systematic similarities. The chambers from F0 to F-7 yield an average Mg/Ca value of 2.5 mmol/mol, consistent with Mg/Ca temperatures around 21 °C, which is similar to Mg/Ca values from the bulk samples (~ 2.4 mmol/mol; Figure 2a). The Mg/Ca of the final two chambers F0 and F-1 are much higher (~ 4 mmol/mol) compared to the preceding chambers F-2 to F-7 (average ~ 2 mmol/mol), yielding Mg/Ca temperatures of 26 °C and 18.5 °C, respectively. These results indicate either environmental (e.g., temperature, preservation/dissolution) effects or biological processes during calcification (e.g., ontogenetic effects in the planktic foraminifers such as *Globigerinoides sacculifer*; see Dueñas-Bohórquez et al., 2011; Jentzen et al., 2018) or a combination of both. If the differences of Mg/Ca between the chambers were temperature related our data would indicate that *G. menardii* individuals (1) had built their shells when ascending from the colder waters at subthermocline depth of ~ 150 m to the warmer surface mixed layer (under stratified conditions), or (2) experienced a temporal (e.g., seasonal) change in seawater temperature caused by upwelling (cold) versus stratified (warm) conditions, or (3) both (Schiebel et al., 2004). Leduc et al. (2014) observed a similar behavior, namely, different Mg/Ca values of chambers of the planktic species *Globigerina bulloides*, which indicate either surface or subsurface temperatures and vertical migration through the water column.

Furthermore, Mg/Ca dissolution affects the foraminifer tests and a decreasing calcite-saturation state below $\Delta[\text{CO}_3^{2-}] = 21.3 \mu\text{mol/kg}$ causes decreasing Mg/Ca in the tests (Regenberg et al., 2014). The deep basins ($>1,000\text{-m}$ water depth) in the Arabian Sea have a low calcite saturation state ($\Delta[\text{CO}_3^{2-}] < 20 \mu\text{mol/kg}$; Schiebel et al., 2007), which most likely effects the outer and inner shell walls and pores of specimens from this site resulting in lower Mg/Ca (Ivanova et al., 2003; Schiebel, 2002; Schiebel et al., 2007).

3.2. Intrashell Mg/Ca Heterogeneity in Planktic Foraminifer *O. universa*

Intrashell heterogeneity of the chemical composition in single chambers of foraminifer shells can be determined, for example, from the fs-laser ablation depth profiles and NanoSIMS images. Mg/Ca variability in single chambers most likely indicate physiological variations in the calcification processes, such as diurnal changes in the incorporation of Mg^{2+} (e.g., Fehrenbacher et al., 2017; Spero et al., 2015). Depth profiles of shells of *O. universa* (Figure 3 and Table S1 and Figure S1 in the supporting information) display layers of high and low Mg/Ca bands (Eggins et al., 2004; Spero et al., 2015) indicating day (low-Mg bands) and night (high-Mg bands) cycles. Three different measurements performed on different locations of the same spherical test of *O. universa* show similar patterns with small differences of less than 4-s ablation time, corresponding to less than $0.2 \mu\text{m}$ in shell depth difference. These small differences are presumably caused by the different laser entrance angles and have only little relationship to crater shape. Figure 3 shows that the single-shot fs-LA-ICP-MS technique is capable to resolve layers with less than about 1-mmol/mol difference in Mg/Ca.

3.3. Mg/Ca Heterogeneity in the Benthic Foraminifer *C. wuellerstorfi*

Mg/Ca variations in shell depths and between chambers of the benthic foraminifer *C. wuellerstorfi* from the North Atlantic (Figures 1b, 1d, and 2b) show increasing Mg/Ca values from the final chamber F0 (1.7 mmol/mol Mg/Ca) to F-6 (4.5 mmol/mol), and lower Mg/Ca values again in chamber F-7 (Figure 2b). The chambers F0 to F-7 yield an average Mg/Ca temperature of 5.2°C (Mg/Ca value of 2.78 mmol/mol) applying the species-specific Mg/Ca calibration of Healey et al. (2008) ($\text{Mg/Ca} = 0.781 \exp(0.230 T)$ for *C. wuellerstorfi*). This average Mg/Ca temperature is 1.2°C higher than the deep ocean bottom temperatures around 4°C (e.g., Repschläger et al., 2015). However, the first three chambers (F0 to F-2) yield Mg/Ca values between 1.3 and 2.0 mmol/mol, which are comparable to Mg/Ca bulk samples of Repschläger et al. (2015) (1.7 mmol/mol). Increasing Mg/Ca from the youngest to older chambers in *C. wuellerstorfi* was also shown in the study of Raitzsch et al. (2011). Such heterogeneity in benthic foraminiferal tests is most likely related to biological processes during ontogeny, because bottom water environments are stable compared with the surface ocean, and large variation of temperature and/or CO_2 is unlikely. In addition, Raitzsch et al. (2011) showed that B/Ca in single chambers behave opposite to Mg/Ca, which is related to pH of the calcifying fluid.

4. Conclusions

LA-ICP-MS using a 200-nm femtosecond laser combined with a SF ICP mass spectrometer is a suitable technique for highly resolved measurements of Mg/Ca in calcareous microorganisms, such as foraminifers, which can be used as a proxy for ambient seawater temperature during shell formation. Advantages of this technique are the nearly nonmatrix matched calibration for carbonates, silicates, and phosphates; high precision and accuracy using a single-shot analysis and measuring flat top peaks; high sensitivity of the mass spectrometer; and the high depth resolution of about 50–100 nm/pulse using low fluences. The high depth resolution of fs-LA-ICP-MS enables detection of Mg/Ca variabilities of less than about 1 mmol/mol at a precision (RSD) of about 5%, but only for ablation hole depths up to 10–20 μm for single-shot analysis. Therefore, this technique is especially useful for thin-shelled specimens. A major disadvantage of fs-LA-ICP-MS to get high-precision data of heterogeneous samples is the long measuring time of the magnetic jump using single-charged Mg and Ca ions. However, this problem can be evaded by using double-charged Ca ions for analysis. Besides the Gaussian profile of the fs-laser spot, a reproducibility of depths measurements of about 50–100 nm depending on the fluence can be achieved.

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