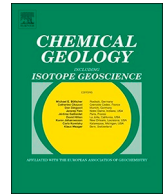




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journal homepage: www.elsevier.com/locate/chemgeoPaired analyses of oxygen isotope and elemental ratios within individual shells of benthic foraminifera genus *Uvigerina*Barbara Balestra^{a,b,c,*}, Ian J. Orland^{d,g}, Julianna Fessenden-Rahn^e, Galen Gorski^f, Rob Franks^c, Thom Rahn^d, Adina Paytan^c^a American University, Department of Environmental Science, Washington, DC 20016, USA^b National Museum of Natural History, (NMNH) Smithsonian, Paleobiology Department, Washington, DC 20560, USA^c University of California Santa Cruz, Institute of Marine Sciences Department, Santa Cruz, CA 95064, USA^d WiscSIMS, Department of Geoscience, University of Wisconsin-Madison, Madison, WI 53706, USA^e EES Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA^f University of California Santa Cruz, Earth and Planetary Sciences Department, Santa Cruz, CA 95064, USA^g Wisconsin Geological and Natural History Survey, University of Wisconsin-Madison, WI 53705, USA

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ABSTRACT

We compare different methodologies (in situ and bulk) for obtaining oxygen isotope ($\delta^{18}\text{O}$) and elemental ratios in the benthic foraminifera genus *Uvigerina* from ODP Site 1015, (California Margin), to assess what new information can be obtained with high-resolution in situ techniques. Specimens were prepared in epoxy mounts and exposed in cross-section such that multiple high-resolution analyses could be completed on the same shells using both Secondary Ionization Mass Spectrometry (SIMS) and Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS). We also measured elemental ratio data using LA-ICP-MS depth-profile measurements on whole, uncast foraminifera and elemental ratio and $\delta^{18}\text{O}$ with standard bulk techniques using the same species of benthic foraminifera from the same sediment sub-samples. Comparison of the data collected by the different methodologies indicates that there is a consistent offset of $\sim 0.9 \pm 0.1\%$ between SIMS and bulk analysis of $\delta^{18}\text{O}$ in these samples. The in situ laser data studied in epoxy mount is correlated with the foraminifera bulk measurements for both Mg and Sr, whereas the in situ depth-profile laser measurements of Mg and Sr from whole foraminifera are less correlated with the bulk measurements. We also observe that the intra-shell variability for each of the proxies is larger than the analytical error and does not follow chamber number. We propose that the $\delta^{18}\text{O}$, Mg, and Sr variability within and between single specimens at this site is linked to some combination of measurement bias, vital effects, and variable environmental conditions in the pore water where the tests were precipitated. This information can in turn be related to the regional setting of the site.

1. Introduction

The isotopic and elemental compositions of calcium carbonate tests (shells) of fossil foraminifera are widely used to infer past ocean chemistry and temperature (e.g., Nürnberg et al., 1996; Shackleton et al., 1984; Rosenthal et al., 1997; Lear et al., 2000; Wejnert et al., 2013; Mekik, 2018 and reference there-in). As recently as two decades ago, geochemical analysis of foraminiferal calcite was generally restricted to bulk sampling methods (i.e. data obtained on multiple tests combined into one sample). Since then, however, techniques for multi-element analysis of small sample volumes have been developed on sector field inductively coupled plasma mass spectrometry (ICP-MS) (Rosenthal et al., 1997; Marchitto, 2006) and quadrupole ICP-MS (Yu

et al., 2005; Harding et al., 2006). Over the last decade, high-resolution analytical methods for measuring both Mg/Ca and $\delta^{18}\text{O}$ have advanced such that micron-scale in situ analyses are now feasible by secondary ion mass spectrometry (SIMS) (Wycech et al., 2018a) and reference there-in) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (Fehrenbacher et al., 2015 and reference there-in). These technical advances allowed researchers to better understand empirical calibrations of element/Ca ratios used as proxies for paleo-environmental reconstruction (Nürnberg, 1995; Nürnberg et al., 1996; Eggins et al., 2003, 2004; Sadekov et al., 2005; Toyofuku and Kitazato, 2005; Pena et al., 2007; Groeneveld and Filipsson, 2013). They have also been used to assess post-depositional alteration (Kozdon et al., 2013; Wycech et al., 2018b), and to resolve short time scale (seasonal

* Corresponding author at: American University, Department of Environmental Science, Washington, DC 20016, USA.

E-mail address: balestra@american.edu (B. Balestra).<https://doi.org/10.1016/j.chemgeo.2019.119377>

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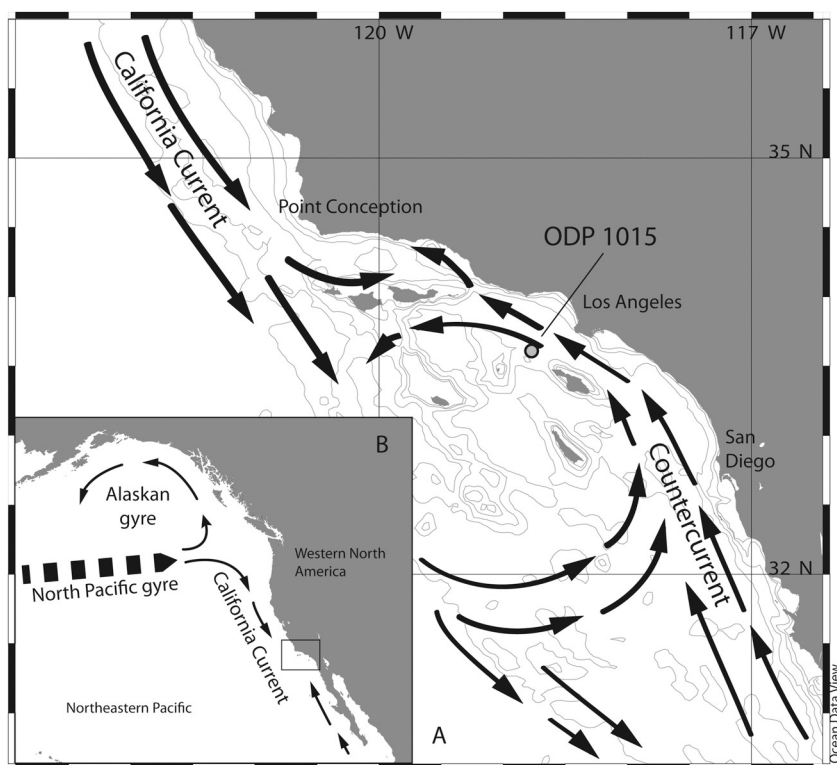


Fig. 1. A) Locations of ODP Site 1015 (blue circle) in Santa Monica Basin, California (901 m water depth); B) Generalized location and direction of the primary surface currents, the California Current and Countercurrent, are shown with arrows, as is the Northeast Pacific circulation in the northeast Pacific region. 1A and 1B are modified from White et al. (2013).

or decadal) environmental data for paleo-reconstructions (Ford et al., 2015), or for considering biomineralization processes (Branson et al., 2016).

Microanalytical methods such as SIMS and LA-ICP-MS are particularly useful when a limited number of specimens are available or when an assessment of chemical heterogeneity is required (Glock et al., 2012, and references therein). One clear advantage of micro-analytical in situ techniques over bulk analyses is that single foraminiferal tests can be re-analyzed multiple times by the same or different in situ techniques. As a result, it is technically feasible to integrate a diverse range of analytical approaches to better characterize the environmental signals recorded in single foraminiferal shells or to refine understanding of biomineralization or post deposition alteration processes. For example, laser ablation techniques on single foraminifera have been used to determine quantitative element/Ca ratios from depth-profiling analysis of single, whole specimens (Wu and Hillaire-Marcel, 1995; Hathorne et al., 2003; Reichart et al., 2003; Pena et al., 2005; Munsel et al., 2010; Fehrenbacher et al., 2017). SIMS and electron probe micro-analysis (EPMA) have been used to produce elemental maps, determine elemental ratios, and (for SIMS only) test novel isotopic proxies in foraminiferal calcite (Allison and Austin, 2003; Sano et al., 2005; Bice et al., 2005; Kunioka et al., 2006; Rollion-Bard and Erez, 2010; Glock et al., 2012; Vigier et al., 2015; Kozdon et al., 2009, 2013; Evans et al., 2015). More recently, SIMS methods have been further developed to permit analysis of planktonic foraminifera $\delta^{18}\text{O}$ (Kozdon et al., 2009, 2011, 2013; Vetter et al., 2013; Wycech et al., 2018a, b). Just one study, however, has analyzed intra-shell $\delta^{18}\text{O}$ variability in benthic foraminifera (Rollion-Bard et al., 2008). Rollion-Bard et al. (2008) analyzed $\delta^{18}\text{O}$ by SIMS in specimens of the benthic genus *Amphistegina*. They report that the thin layers of calcite that have elevated Mg/Ca and are associated with “primary calcite” precipitated within an organic matrix of a newly deposited chamber have markedly ($\sim 3\%$) lower $\delta^{18}\text{O}$ values than the “secondary” calcite that comprises 95% of the shell. They argue that the lower $\delta^{18}\text{O}$ of primary calcite is due to some “vital effect” that lowers the $\delta^{18}\text{O}$ of bulk analyses below the value predicted by inorganic experiments (e.g. Kim and O’Neil, 1997).

Given that the $\delta^{18}\text{O}$ of benthic foraminifera is a foundational global-scale paleoclimate proxy (Lisiecki and Raymo, 2005), further interrogation of benthic foraminifera is warranted. In this study, we leveraged updated SIMS methods developed over the last decade along with element/Ca analysis by LA-ICP-MS to evaluate two generalized hypotheses that emerge from the work of Rollion-Bard et al. (2008): 1) that at intra-shell resolution, Mg/Ca variability anticorrelates with $\delta^{18}\text{O}$, and 2) that at micron-scale, $\delta^{18}\text{O}$ anticorrelates with indicators of organic matrix. We investigated samples from ODP Site 1015 in the Santa Monica Basin representing two-time slices, the last 1000 years and the Younger Dryas (YD; 12.9–11.7 ky BP) (Rasmussen et al., 2006) focusing on the benthic genus *Uvigerina*, specifically *Uvigerina peregrina*, with ornamentation which is common to the California margin (Ohkushi et al., 2013; Davis et al., 2016; Balestra et al., 2018). The Santa Monica basin has been targeted as a region for paleoceanographic reconstructions because its location strategically links it to mechanisms of regional climate oscillations and ecosystem changes in the California Margin (Balestra et al., 2018). We measured both the Mg/Ca ratio (LA-ICP-MS) and $\delta^{18}\text{O}$ (SIMS) on single foraminifera tests that were embedded in an epoxy mount and exposed in cross-section. For comparison, we collected element/Ca ratio data with LA-ICP-MS measurements on whole uncast foraminifera, as well as element/Ca ratios and $\delta^{18}\text{O}$ values by standard bulk techniques for each time slice using the same foraminifera species (i.e. *Uvigerina*) from the same sediment samples. We ultimately aim to assess the utility of analyzing single-shells using paired, high spatial-resolution geochemical analyses in single *Uvigerina*, which is a benthic genus commonly used for paleoclimate studies.

2. Material and methods

2.1. ODP Site 1015 and *Uvigerina* spp.

ODP Site 1015, ($33^{\circ}42.925'N$, $118^{\circ}49.185'W$, water depth 901 m; Fig. 1) was drilled in the deepest part of Santa Monica Basin (Shipboard Scientific Party, 1997). Two holes were drilled at this site (A = 149.5 m and B = 98.7 m core lengths, Shipboard Scientific Party, 1997). In this

Table 1
Sample ID, sample core depths and estimated ages (from Balestra et al., 2018).

	Site	Core	Section	cm	Depth mbsf	Depth (mcd)	Age cal. y.b.p.
Late Holocene	1015A	1H	1W	4-6	0.04	0.04	197
	1015A	1H	1W	10-12	0.10	0.10	561
	1015A	1H	1W	100-102	1.00	1.00	1003
YD	1015A	3H	6W	30-32	23.25	24.24	12,115
	1015A	3H	6W	125-127	24.14	25.13	12,463
	1015A	3H	7W	137-139	25.76	26.75	12,976

study, sediment samples for analyses of the benthic foraminifera *Uvigerina* spp. were selected to avoid turbidite intervals (Romans et al., 2009). The age model for this core and thus the age of the samples utilized is based on Balestra et al. (2018) (Table 1). The average sedimentation rate for the late Holocene (0–11.7 ka) at this site is 2.0 mm/yr. For the Last Glacial Maximum (LGM) and deglacial period (22–11.7 ka) it is 3.6 mm/yr. Using this age model, two time-periods were chosen for this study, the last 1 ky of sediment accumulation and sediments deposited during the Younger Dryas (YD; 12.9–11.7 kyr B.P) (Rasmussen et al., 2006). The last 1 ky samples represent the “warm” interglacial period, while the YD is a period during the last deglaciation when Northern Hemisphere climate returned abruptly to near-glacial conditions (i.e. cold, dry and windy) for ~1.5 ky (Fairbanks, 1989; Bond et al., 1997).

The benthic foraminifera *Uvigerina* spp. selected for analysis is present in both time-slices and it is relatively insensitive to changes in carbonate ion concentrations ($\Delta[\text{CO}_3^{2-}]$) (Elderfield et al., 2010). This genus is commonly found in mesotrophic environments, often characterized by fine-grained sediments with elevated organic matter content (Van der Zwaan et al., 1986). *Uvigerina* spp. lives in shallow infaunal depth habitats (Van der Zwaan et al., 1986; Fontanier et al., 2002; Schweizer et al., 2005). The weaker sensitivity to carbonate ion changes of this genus when compared to epifaunal species (Elderfield et al., 2010, 2006), is probably because it calcifies from pore water at 1–2 cm depth within the sediment, where $\Delta[\text{CO}_3^{2-}]$ tends to be close to zero (Tachikawa and Elderfield, 2002; Martin and Saylaes, 1996; Elderfield et al., 2010). Therefore, there is limited influence of $\Delta[\text{CO}_3^{2-}]$ on shell Mg/Ca of this genus (Elderfield et al., 2010).

2.2. SIMS measurements of $\delta^{18}\text{O}$ and OH/O

For SIMS analysis, six sediment samples representing the selected time intervals were soaked overnight in deionized water (pH = ~8.0, buffered), washed over 63 μm and 250 μm sieves, and oven dried at 45 °C (as by Kozdon et al., 2013). The > 250 μm fraction was then examined for benthic foraminifera (i.e., *Uvigerina* spp.). Sample cleaning consisted of multiple ultrasonication steps in MilliQ water and methanol, with additional rinses in MilliQ water between and after sonication. The cleaned tests were embedded along with two grains of UWC-3 calcite standard ($\delta^{18}\text{O} = 12.49\text{‰}$ Vienna Standard Mean Ocean Water, VSMOW; Kozdon et al., 2009) in a single 25-mm diameter, round epoxy mount. This mount was made with Buehler EpoxyCure® 2 hardener and resin (before the product formulation changed in 2016). After embedding, the epoxy mount was ground to the level of best sample exposure (Kozdon et al., 2011, 2013) and polished to a topographic relief of < 1 μm (Kita et al., 2009). The sample mounts were gold-coated for scanning electron microscope (SEM) imaging and SIMS analyses. Since the genus *Uvigerina* adds a new layer of calcite to all existing chambers every time that a new chamber is formed (Grunlund and Hansen, 1976) we acquired high-resolution SEM images of all samples before SIMS analysis to facilitate targeting of the appropriate calcite layers. SEM images were taken after the in situ measurements to record the relative spot positions (Figs. 2 and 3, right panels).

In situ $\delta^{18}\text{O}$ data were acquired from the *Uvigerina* spp. test walls at the WiscSIMS Laboratory (University of Wisconsin-Madison) with a

CAMECA IMS 1280 large-radius multi-collector SIMS (Kita et al., 2009; Valley and Kita, 2009). Analytical conditions on the SIMS are like those reported for the 10- μm spot analyses by Kozdon et al. (2013). A $^{133}\text{Cs}^+$ primary ion beam with an intensity of ~1.3 nA was focused to a beam-diameter of ~10 μm . The typical secondary $^{16}\text{O}^{--}$ intensity was 2.5×10^9 counts per second (cps), and $^{18}\text{O}^{--}$, $^{16}\text{O}^1\text{H}^{--}$, and $^{16}\text{O}^{--}$ ions were simultaneously recorded by three Faraday cup detectors. Charging of the sample surface was compensated by gold coating and by an electron flood gun focused on the analysis site. Four to six consecutive measurements of UWC-3 calcite standard were performed before and after every set of 5–16 sample analyses. The precision (spot-to-spot reproducibility) for each sample analysis is calculated as the 2 s.d. of the bracketing UWC-3 analyses. Across the entire session, the average spot-to-spot reproducibility (1 s.d.) of $\delta^{18}\text{O}$ analyses in the UWC-3 standard was $\pm 0.15\text{‰}$.

Between three and seven 10- μm spots were analyzed for $\delta^{18}\text{O}$ on each of 38 tests (16 tests from < 1 ky and 22 tests from the YD, for a total of 144 10- μm spots). The ratio $^{16}\text{OH}^{--}/^{16}\text{O}^{--}$ (OH/O, hereafter) was measured simultaneously during all $\delta^{18}\text{O}$ analyses. The average OH/O of bracketing UWC-3 (an anhydrous marble) measurements was used to measure “background” $^{16}\text{OH}^{--}$, which was subtracted from each sample analysis in the intervening block to calculate “background-corrected” OH/O (Wycech et al., 2018a, b). Following SIMS analysis, data were screened for outliers in secondary ion yield and background-corrected OH/O, and pit morphologies were examined by SEM for irregularities. Following these quality control measures, out of a total of 144 SIMS spots measured in the calcite tests just 1 was removed from interpretation. An additional 39 SIMS spots were removed from our paired-analysis interpretation because they did not have a matching LA-ICP-MS analysis of Mg/Ca for comparison (see below in Section 2.4). A data table including all raw and corrected sample and standard measurements is included as Appendix A.

2.3. Oxygen isotope analysis by isotope ratio mass spectrometry

To compare the high-resolution SIMS data with typical whole-test analysis, we analyzed $\delta^{18}\text{O}$ in *Uvigerina* spp. from the same core sections by conventional means (Kiel-device with Isotope Ratio Mass Spectrometer IR-MS). The foraminifera were analyzed at the University of California Santa Cruz, Stable Isotope Laboratory using a Finnigan Isotope Ratio Mass Spectrometer (IR-MS, MAT-256) with a Kiel auto-carbonate device (using an in-house crystalline Carrera Marble standard, CM12, calibrated against international standards and NBS-19 crystalline carbonate standards). The tests used for conventional analysis were picked from the same vial/split as the tests used for SIMS analysis but are not the identical individuals. Between 12 and 15 specimens were picked from each sample, cleaned and gently crushed. Individuals between 355 and 250 μm size fraction were used to eliminate variability based on size. All the data are expressed using standard delta (δ) notation in per mil (‰) relative to Vienna Pee Dee Belemnite standard and the reproducibility (1σ) of the NBS-19 standard was $\pm 0.05\text{‰}$ for $\delta^{18}\text{O}$ during these analyses (Appendix B).

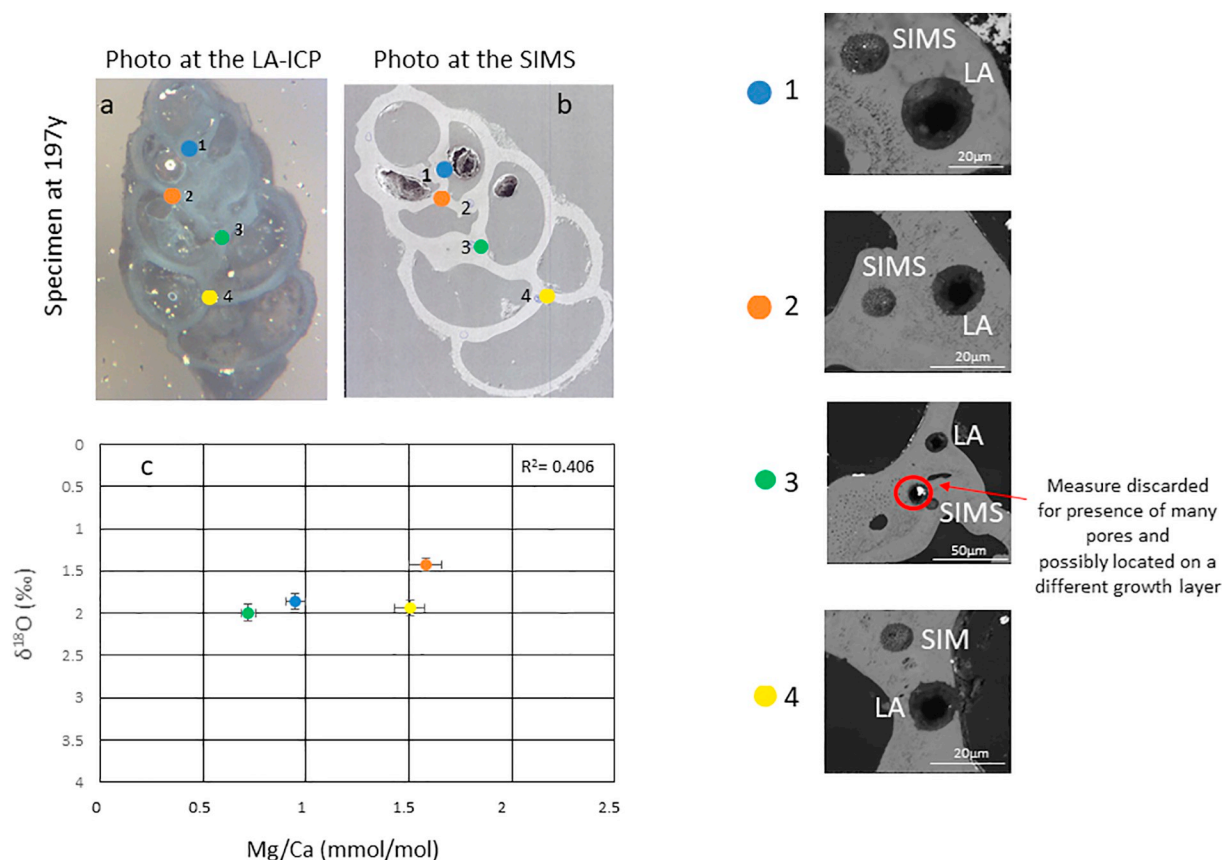


Fig. 2. Example of analyzed foraminifera from the last 1000 years; a) photo taken with the LA-ICP-MS camera showing the four spots analyzed on a test embedded in epoxy; b) SEM image of the same individual showing spots after SIMS analysis; c) linear correlation graph between $\delta^{18}\text{O}$ and Mg/Ca, error bars represent 1sd based on analytical errors of the standard. The SEM photos on the right part of the figure, show more clearly the locations of measurements. Note that different colors correspond to different spot analyses. The colors and the numbers are consistent between the plot and all the photos. (For the interpretation of the references to color in the figure legend, the reader is referred to the web version of this article).

2.4. Analysis by LA-ICP-MS (12 μm spots and 50 μm spots)

We performed LA-ICP-MS analysis on *Uvigerina* spp. specimens with a Teledyne Photon Machines Analyte Excite laser (193 nm) and Thermo X Series II ICP-MS. Laser analysis spots were targeted to be adjacent to the SIMS analysis using the same epoxy mounts (i.e. same tests). Between SIMS and LA-ICP-MS analysis, the mounts were gently polished to remove the gold coating required for SIMS analysis. The advantage of measuring the samples by both techniques is that it allows for a more direct comparison between analytical methods and the various geochemical tracers obtained using these methods. One disadvantage of using epoxy mounts for LA-ICP-MS analysis is that the spot size, and thus analytical sensitivity, is spatially limited by the exposed cross-section of the test wall. Thus, we use a 12 μm spot size, which is smaller than the typical 50- μm spot used for non-epoxy mounted LA-ICP-MS analyses. The 12 μm spots were carefully targeted to be in test areas with no pores, and well inside the edge of the test walls to avoid contamination bias in the measurements. To the best of our ability, laser spots were placed as close as possible to the SIMS analyses pits, however, this was not possible for some tests since the sample exposures were slightly altered during polishing between the two procedures (see Figs. 2 and 3). Pre-ablation of the spots (5 Hz, 5 shots, 0.4 J/cm²) was performed to clean the surface area. Approximately two to six laser spots (10 Hz, 200 shots, 1.83 J/cm²), 12 μm in diameter, were ablated on each of the tests. These data are presented in the supplemental material as Appendix C, and were acquired for masses 24-Mg, 44-Ca, and 88-Sr. NIST 610 was analyzed with the same parameters and used for elemental calibration. Long-term reproducibility of the Mg/Ca ratio in NIST 610 (nominal values of 432 ppm, GeoRem, 6/2011), was

$8.66 \pm 0.14 \text{ mmol mol}^{-1}$ (1σ , $n = 150$ over 5 analytical days). We assume that the analytical reproducibility using the standards is equivalent to that of the foraminifera, which we cannot assess directly since each measurement of the foraminifera destroys that portion of the sample, and repeated measurements are not possible. Repeated measurements on different locations in the same foraminifera are subject to larger variability inherent to the organism (representing short term environmental changes over the life span of each individual and vital effects).

We then obtained 50- μm spot analyses by the more traditional depth-profiling LA-ICP-MS procedure on uncast, whole foraminifera taken from the same sediment samples. Specimens were picked from the same six sediment splits from which tests were picked to make the epoxy mount used for LA-ICP-MS and SIMS analysis (but different individuals). Individuals of similar size were analyzed to ensure the least variability based on size (250–355 μm). Because of low sample availability, it was not possible to depth-profile the same number of tests for each time slice (in total 29 tests were used versus the 38 that were measured in the epoxy mounts). For consistency and to allow direct comparison with the procedure used for the foraminifera mounted in epoxy, the sample cleaning consisted of multiple ultrasonication steps in MilliQ water and methanol and additional rinses with MilliQ water. The tests were adhered to a glass slide using carbon tape (rather than embedded and polished in the epoxy). The sampling spots were pre-ablated (5 Hz, 5 shots, 0.4 J/cm²) before data acquisition to clean the surface area. Approximately two to six laser spots (10 Hz, 200 shots, 1.83 J/cm²), 50 μm in diameter, were ablated on each of the tests. All the data are presented in supplemental material as Appendix D, and were acquired for masses 24-Mg, 44-Ca, 55-Mn, and 88-Sr. NIST 610

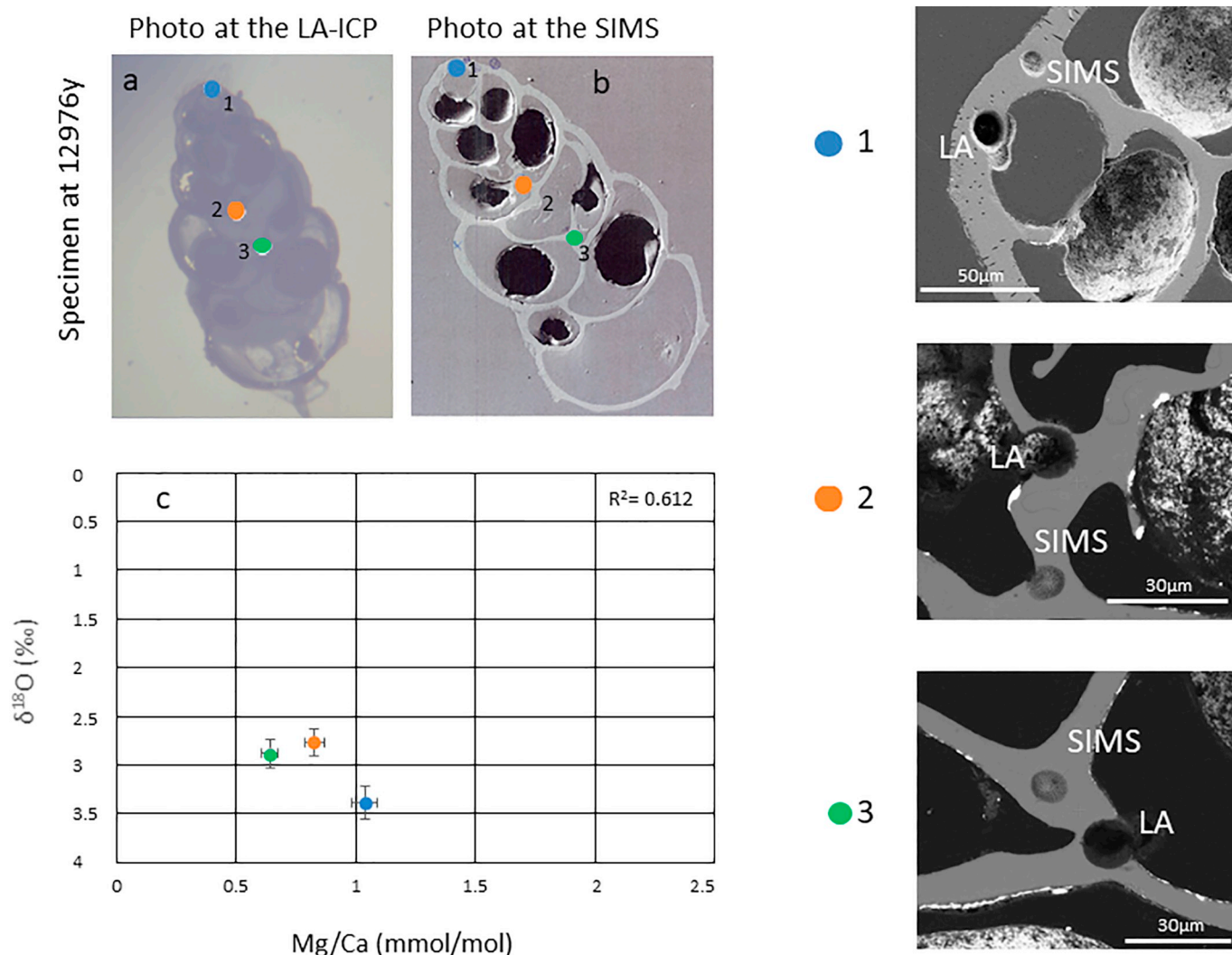


Fig. 3. Example of analyzed foraminifera from the YD. a) photo taken with the LA-ICP-MS camera showing the three spots analyzed on a test embedded in epoxy; b) SEM image of the same individual showing SIMS spots; c) linear correlation graph between $\delta^{18}\text{O}$ and Mg/Ca error bars represent 1sd based on analytical errors of the standard. The SEM photos in the right part of the figure, show in more detail the location of the measurements. Note that different colors correspond to different spot analysis. The colors and the numbers are consistent between the plot and all the photos. (For the interpretation of the references to color in the figure legend, the reader is referred to the web version of this article).

was analyzed with the same parameters used for the epoxy mount and used for elemental calibration (reproducibility of the Mg/Ca ratio in NIST 610 analyzed with these samples was $8.74 \pm 0.14 \text{ mmol mol}^{-1}$ (1σ , $n = 150$ over 5 analytical days)). As noted above the reproducibility of different spots obtained on each test is much lower than that of the standard as it incorporates real natural variability and unknown vital effects.

2.5. Bulk ICP-MS element ratio measurements

Bulk Mg/Ca and Sr/Ca ratios were measured by ICP-MS (Finnigan Elemental XR) at UCSC using the procedure described in Quintana Krupinski et al. (2017). Between 9 and 12 specimens were picked from each of the six time-intervals, from the same samples used for LA-ICP-MS and SIMS analysis. Individuals of similar size were analyzed to ensure the least variability based on size (250–355 μm). The specimens were crushed, and sample cleaning consisted of multiple ultrasonication steps in MilliQ water and methanol, a reductive and oxidative step and additional rinses with MilliQ water following the protocol by Quintana Krupinski et al. (2017). The reductive step was included in the cleaning procedures to remove Mg associated with remnant organic

matter and adsorbed phases (Boyle and Keigwin, 1985; Bian and Martin, 2010; Quintana Krupinski et al., 2017). The cleaned tests were transferred to acid-cleaned Eppendorf vials on the day of analysis and dissolved in 400 μL of 0.075 HNO_3 (Optima grade) prior to analysis. The between-run reproducibility (based on measurement of the liquid consistency standard and blank after every 3 samples) was $\pm 0.3\%$ (1σ) for both Mg/Ca and Sr/Ca, and the in-run reproducibility was $\pm 0.4\%$ (1σ). These data are presented in the supplemental material Appendix B.

2.6. Data treatment

Images of each specimen analyzed by SIMS and LA-ICP-MS were taken using a Scanning Electron Microscope (SEM). These high-resolution images helped ensure that the measurements were taken on the same layer of growth of the shell and to avoid contamination due to the presence of pores and/or channel on the shell analyzed (see examples in Figs. 2 and 3). Moreover, all the elemental ratio measurements (12- and 50- μm spots) are time-resolved. Thus, every measurement has been manually examined making sure to identify contaminant phases or anomalous spikes. Most of the time-resolved trace element profiles

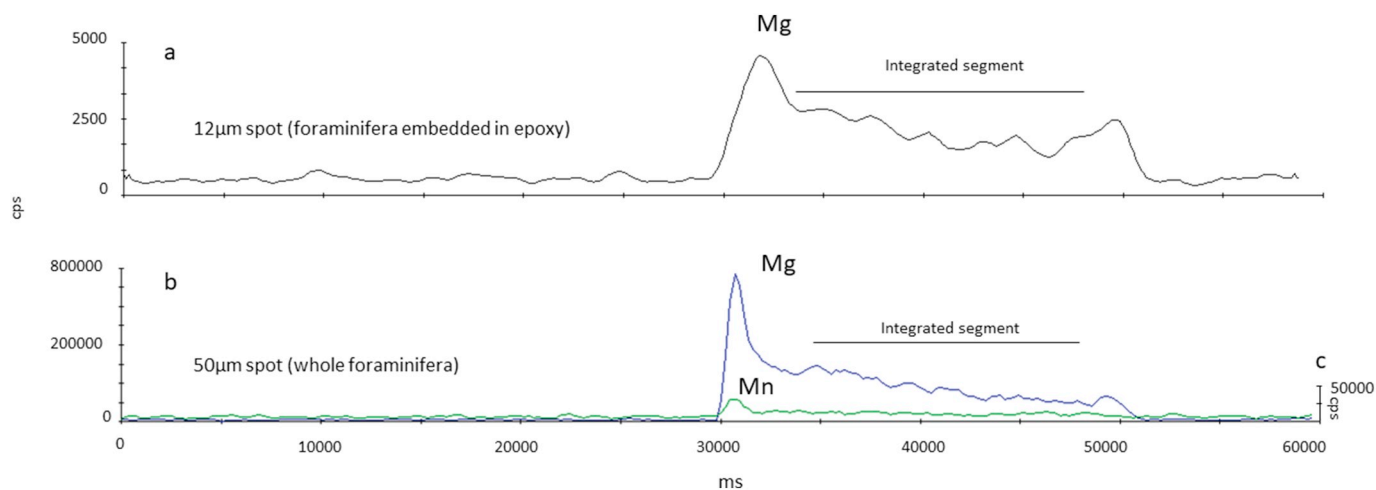


Fig. 4. a) example of Mg depth profile through foraminifera embedded in epoxy.; b, c) example of Mg and Mn depth profile through whole foraminifera. In both figures a surface veneer that is rich in Mg in a) and rich in Mg in b) and Mn in c) is clear and it has not been considered. Note the different intensity scale on a), b) and c).

show an enriched zone of high Mg/Ca at the start of each analysis, followed by an interval of relatively constant and lower Mg/Ca, consistent with observations reported in previous *in situ* laser ablation studies of foraminifera (Creech et al., 2010 and references there-in). The software that was utilized, Thermo PlasmaLab, permits screening the raw data and thus filtering each laser profile to remove suspect contaminate interferences, usually represented by sudden peaks of Mg or Mn (example in Fig. 4; Mn was monitored only for the 50 μm spots due to a weak signal from the 12 μm spots). We then compared the screened measurements from the different spot sizes (12- μm in epoxy versus 50- μm in uncast whole foraminifera) and for the bulk analysis. To compare the different spot sizes obtained with the LA-ICP-MS methodologies (12- μm spot in epoxies ($N = 38$ tests in total) versus 50- μm spot on whole foraminifera ($N = 29$ tests in total) and bulk analyses ($N =$ between 9 and 12 tests for each sample)) we calculated element/Ca means and standard deviations using the R software package. To compare $\delta^{18}\text{O}$ and trace element results, we generated regressions utilizing the average composition of each foraminifer and for each time slice while also indicating the different chambers in which the measurements were taken, (two examples in Figs. 2 and 3). The bivariate least-square regressions were generated using PAST software (Hammer et al., 2001).

3. Results

3.1. *In situ* $\delta^{18}\text{O}$ measurements

In situ SIMS $\delta^{18}\text{O}$ measurements (reported on the VPDB scale) vary between 0.7 and 2.6‰ in the Holocene and between 1.4‰ and 3.0‰ during the YD (Appendix A). The background-corrected OH/O ratios varied between 0.005 and 0.01 within the *Uvigerina* tests measured in this study (Appendix A). Simultaneous measurement of OH/O routinely accompanies carbonate $\delta^{18}\text{O}$ analyses at WiscSIMS. Its measurement was originally intended for use during data screening to monitor the relative amount of H-bearing species (i.e., not calcite) included within a sputtered spot. Over time, OH/O observations in many carbonate types (biologically mediated and abiotic) have revealed some intriguing patterns, including intra- and inter-sample anticorrelations between $\delta^{18}\text{O}$ and OH/O (Orland et al., 2015; Wycech et al., 2018a, b; Helsler et al., 2018). In carbonate samples, OH/O likely indicates the amount of water and/or organic material included in each SIMS spot, but it is unknown if there is causality between elevated OH/O and lower $\delta^{18}\text{O}$ values. As such, quantitative interpretation of the OH/O metric remains unclear and is beyond the scope of this study.

3.2. Traditional $\delta^{18}\text{O}$ measurements

$\delta^{18}\text{O}$ data measured with the bulk technique are systematically higher than those measured by SIMS, ranging from 2.8–2.9‰ in the Holocene, and from 3.1–3.4‰ in the YD (Appendix B). The relative difference between average $\delta^{18}\text{O}$ measurements from the Early Holocene and YD is $\sim 1.0\%$ for both techniques (Appendix B).

3.3. *In situ* elemental ratios

Values for Mg/Ca of individual specimens for the 12- μm spot analyses ranged from 0.6 to 1.3 mmol mol^{-1} in the Holocene, and between 0.5 and 1.7 mmol mol^{-1} in the YD (Fig. 5, Appendix C). For 50 μm spot analyses, Mg/Ca values are between 0.6 and 2 mmol mol^{-1} in the Holocene and between 0.8 and 1.7 mmol mol^{-1} in the YD (Appendix D). The Sr/Ca measurements ranged from 1 to 1.4 mmol mol^{-1} for the analyses on the epoxy mounts (12 μm spots) as well as from the depth-profiled foraminifera with 50 μm spots (Appendix C and Appendix D). To test for diagenetic overprinting, we monitored Mn/Ca during depth-profile analyses on the whole foraminifera (50 μm spot) after the pre-ablation (Appendix D). Mn/Ca values were relatively low (average 0.01 and 0.14 mmol mol^{-1}) and within the generally used level of Mn/Ca confirming the absence of diagenetic coatings (between 0.05 mmol mol^{-1} and $\sim 0.15 \text{mmol mol}^{-1}$ (Boyle, 1983; Boyle and Keigwin, 1985; Delaney, 1990; Ohkouchi et al., 1994; Glock et al., 2012)).

3.4. Traditional elemental ratio

The foraminifera bulk measurements are similar and correlated to the *in situ* laser data (12 μm spot) studied in epoxies for both Mg and Sr ($r^2 = 0.8$ and 0.9 respectively). However, the *in situ* depth-profile laser measurements of Mg and Sr from whole foraminifera (50 μm spot) show less correlation with the bulk measurements ($r^2 = 0.2$ and 0.02 respectively) (Fig. 6, Appendix C).

4. Discussion

4.1. Geochemical variability within and between *Uvigerina* tests

For both time intervals (i.e. last 1000 years and YD), the SIMS $\delta^{18}\text{O}$ values span a range of 1.9‰, which is remarkably high if we consider that the species is benthic and hence seasonal environmental changes

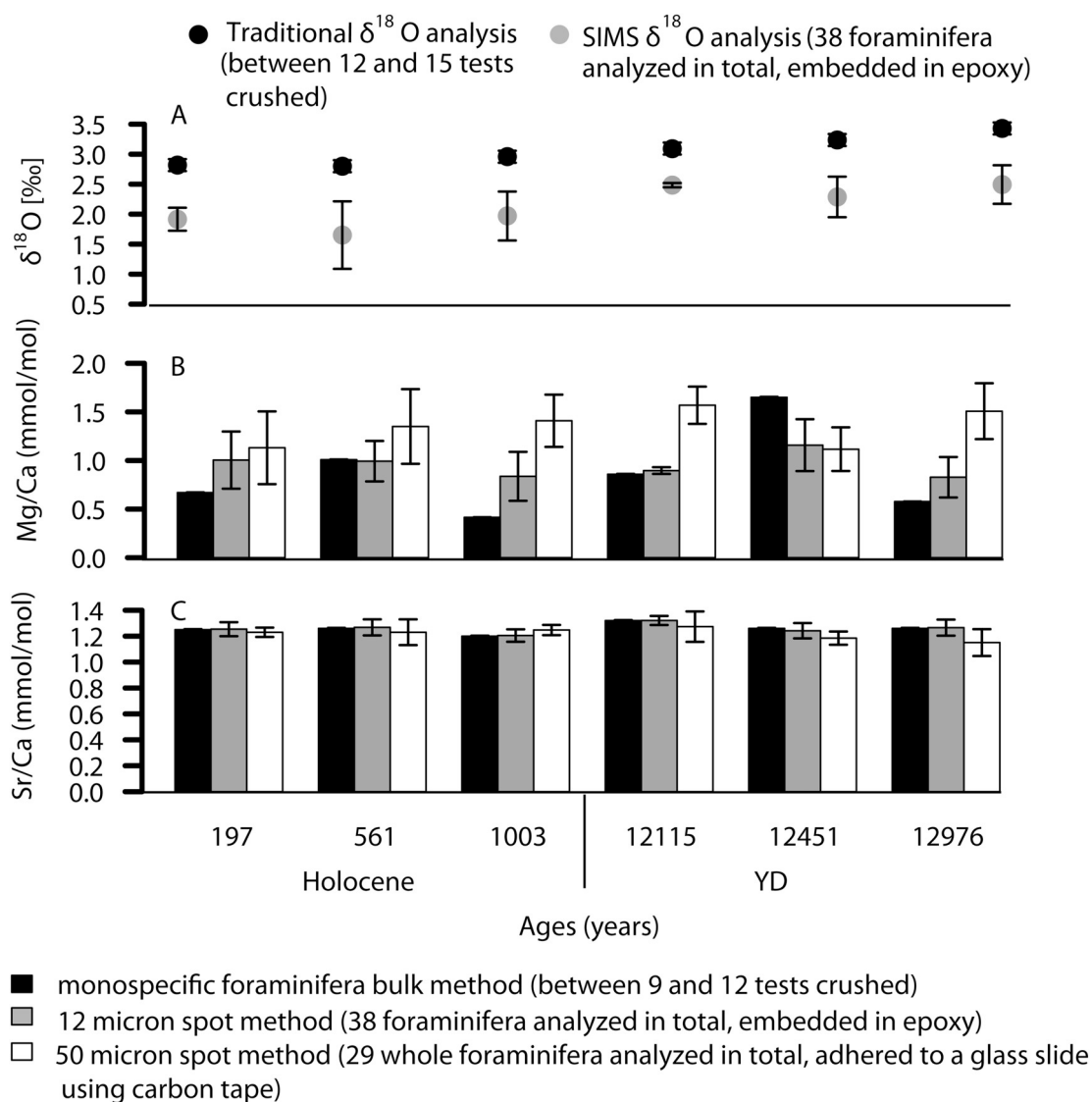


Fig. 5. Average $\delta^{18}\text{O}$ (A), Mg/Ca (B) and Sr/Ca (C) values for each time slice using different measurement methods. In panel A, circles show $\delta^{18}\text{O}$ data collected by traditional whole-shell analysis on aliquots of 12–15 shells from each depth interval (black circles) and the average of multiple (i.e. all the available tests for each sample) SIMS $\delta^{18}\text{O}$ analyses (gray circles) on shells from the same depth interval. Error bars are 1sd analytical error for the whole shell analyses and 1sd of the range of data obtained for the population of the SIMS analyses averaged at each time interval. Black bars represent bulk analysis of multiple shells, gray bars represent 12 μm spots and white represents 50 μm spots obtained using LA-ICP-MS. Note that the analytical error on the single foraminifer analyses (based on repeat analyses of the standard) is much smaller than the range of values depicted in the figure.

and habitat depth are not expected to vary much. Specifically, *Uvigerina* generally prefers a shallow infaunal habitat (Corliss and Emerson, 1990; Ernst and van der Zwaan, 2004; Davis et al., 2016) and samples were obtained from sediments at a depth of 901 m of seawater. However, the difference in the average values between the two time-intervals is consistent with lower temperatures or higher salinity (higher $\delta^{18}\text{O}$) in the YD bottom waters (Rickaby and Elderfield, 2005). The Mg/Ca data, in contrast, do not show a significant difference in the values or the range between the two time-intervals. Assuming Mg/Ca data represent bottom water temperatures, the $\delta^{18}\text{O}$ difference between the two time-periods suggests that the $\delta^{18}\text{O}$ of bottom water and/or porewater decreased between the YD and Late Holocene.

The in situ analyses allow us to calculate a correlation coefficient between Mg/Ca and $\delta^{18}\text{O}$ within single foraminifera (see Figs. 2 and 3 as two examples). In contrast to the finding of Rollion-Bard et al. (2008) for the benthic foraminifera *Amphistegina*, no correlation is observed in any *Uvigerina* test between the in situ Mg/Ca and $\delta^{18}\text{O}$ measurements (Fig. 7). Furthermore, considering the growth mechanism of the genus

Uvigerina (Grunlund and Hansen, 1976), and that the paired analysis are within the same growth layer, we do not see any apparent correlation between either geochemical proxy and chamber number, implying that there is no consistent age- or size-related impact on Mg/Ca and $\delta^{18}\text{O}$ (Figs. 2 and 3). Our results suggest species-specific responses, which warrant further research comparing different benthic foraminifera genus.

Our analyses of *Uvigerina* individuals demonstrate considerable within-genus variability. Other than bias due to the utilized methodologies, there are several effects that could contribute to the observed variability, including biological or “vital” effects and changes over time in the porewater chemistry. We have not used the data to derive temperatures because we expect that the bottom water temperatures varied little within each time slice and thus is not relevant for the aims of this research (e.g., to compare among analytical techniques and between time slices). Theoretically, if both proxies record the temperature of the pore water, we would expect a strong correlation since bottom water $\delta^{18}\text{O}$ is assumed to change little in the open ocean within the time scale

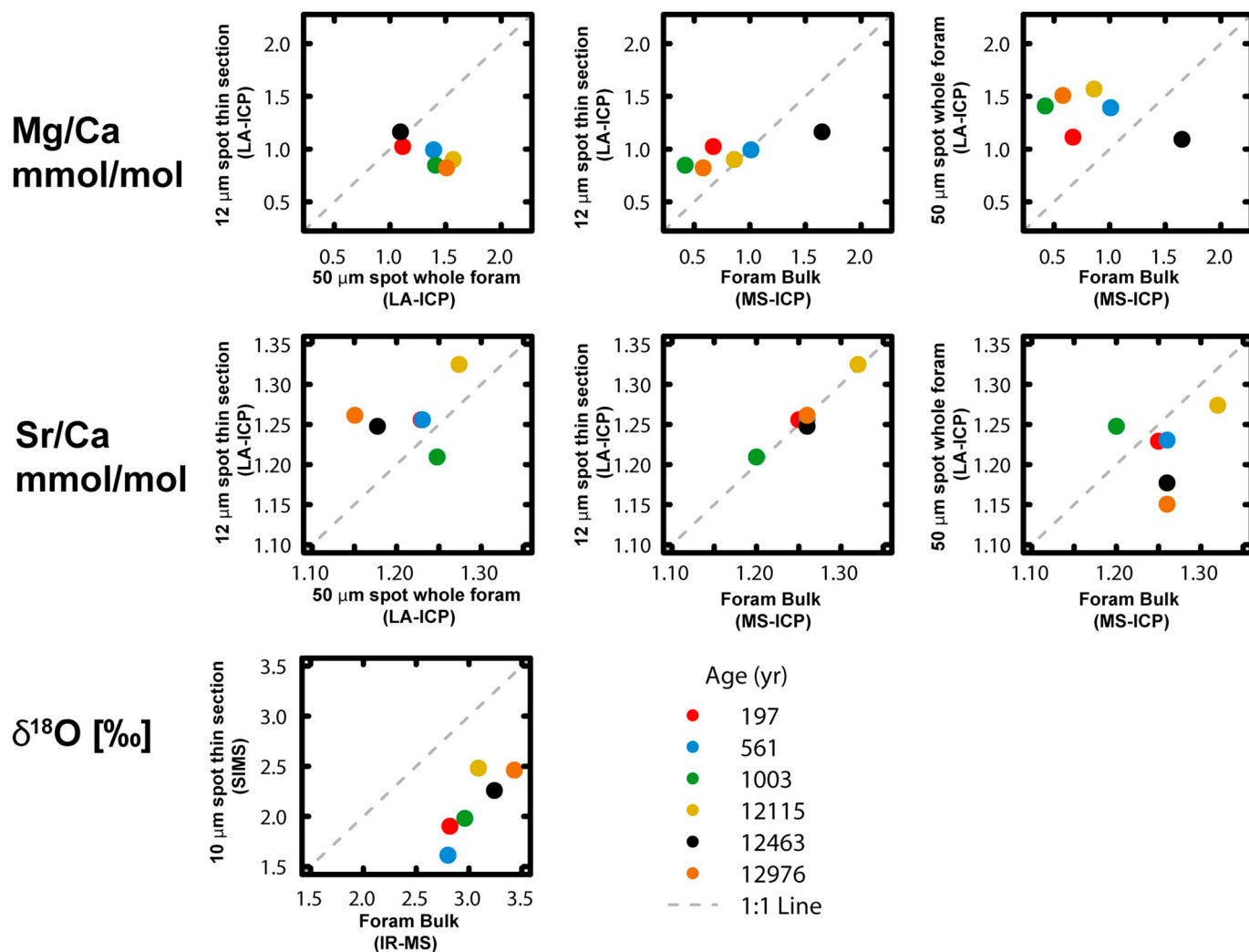


Fig. 6. Comparison plots of in situ and bulk methods for Mg/Ca, Sr/Ca, and $\delta^{18}\text{O}$. Each colored spot represents data averaged over multiple measurements on multiple specimens and grouped by age. (For the interpretation of the references to color in the figure legend, the reader is referred to the web version of this article).

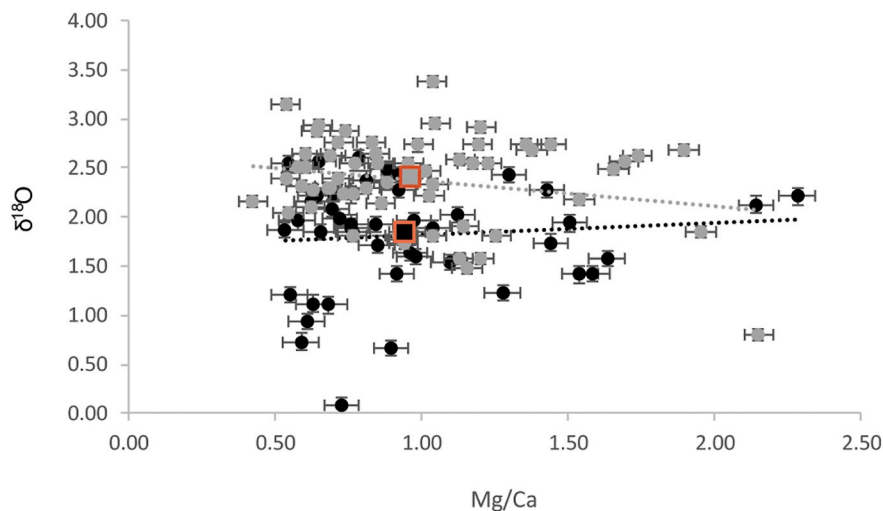


Fig. 7. Bivariate least square regression of the in situ paired analyses of $\delta^{18}\text{O}$ (SIMS on 10 μm spot) and Mg/Ca (LA-ICPMS on 12 μm spot). The different color represents the two-time periods (Holocene/black versus YD/gray). The two squares represent the average value for each time periods with the same legend color (Holocene/black versus YD/gray).

Grey = YD $R^2 = 0.053$

Black = Holocene $R^2 = 0.0076$

represented by each time interval used. One of the causes for the lack of correlation could be the specific location of Site 1015 (i.e. Santa Monica Basin) and the sensitivity of this location to environmental changes that are then recorded in the genus utilized for this study. Specifically, the basin is relatively deep and different water masses with distinct characteristics of temperature, salinity and origin may have filled the basin during the different time slices analyzed here and contributed to the lack of correlation between Mg/Ca and $\delta^{18}\text{O}$ when comparing data from the last 1000 years to that of the YD (Fig. 7). It has been shown that the benthic foraminifera investigated in this study can calcify in low bottom water oxygenation levels (Moffitt et al., 2014, 2015; Ohkushi et al., 2013). Thus, it is also possible that Mg/Ca ratios in *Uvigerina* particularly at this location, are sensitive to different growth and calcification conditions, such as food availability or carbonate chemistry (Wit et al., 2010), which could contribute to the lack of correlation seen in the data.

4.2. Comparison of bulk and in situ analytical techniques

4.2.1. $\delta^{18}\text{O}$

An offset of $\sim 1\%$ is observed between the $\delta^{18}\text{O}$ values of *Uvigerina* measured by SIMS and those measured by traditional bulk gas isotope ratio mass spectrometry (IRMS) (Fig. 5). This offset, (SIMS $\delta^{18}\text{O}$ values $\sim 1\%$ lower than measured by IRMS) and the average background-corrected OH/O ratio of 0.008 (Appendix A) are consistent with IRMS-SIMS comparison studies reported in other low-temperature carbonates, including foraminifera (Orland et al., 2015; Wycech et al., 2018a). Here, the existence of a 1% offset is notable because it matches the offset observed by Rollion-Bard et al. (2008) between the secondary calcite in their cultured benthic foraminifera and the expected $\delta^{18}\text{O}$ value. The IRMS-SIMS $\delta^{18}\text{O}$ offset is likely the result of matrix effects on the SIMS data (i.e., the inclusion of water and/or organic materials within the sputtered sample volume (Orland et al., 2015; Wycech et al., 2018b), and possibly the related effect of trace element content on the SIMS measurements (Sliwinski et al., 2017). While experiments are underway to clarify the origin of the offset, we note that the $\delta^{18}\text{O}$ offset is uniform across the population of *Uvigerina* tests analyzed in this study. The precision of the SIMS analyses is established by a rigorous approach to standardization, so the relative inter- and intra-shell $\delta^{18}\text{O}$ variability we observe (regardless of the offset in absolute values) and the previously mentioned lack of correlation to Mg/Ca suggests that factors beyond temperature contribute to the $\delta^{18}\text{O}$ of *Uvigerina* test calcite in the Santa Monica basin.

4.2.2. Mg/Ca and Sr/Ca

We found considerable variability in the Mg/Ca data within and among individual specimens of the same genus and time slice. Variability among different individual foraminifera has been clearly shown in cultured foraminifera (Dissard et al., 2010; Duenas-Bohorquez et al., 2011) including benthic species (Wit et al., 2010). Thus, in addition to analytical errors, the variability in the Mg/Ca data is due to short time-scale (diurnal, seasonal, decadal) environmental variability and biological effects related to differences among individuals even if they belong to the same genus and were collected in samples representing the same time-interval (Wit et al., 2010).

A strong correlation is observed between the 12 μm spots and bulk analyses in both Mg/Ca and Sr/Ca analyses. The agreement between the 12 μm and the bulk analyses and their lack of agreement with the larger 50 μm depth-profiling of whole foraminifera may be explained by real differences in the material included in each analysis. Specifically, the bulk analysis was done on crushed and chemically cleaned specimens using a procedure that removes a considerable amount of surface-bound organic matter and may preferentially remove high-Mg calcite (Bian and Martin, 2010). In contrast, the foraminifera samples that were analyzed by laser (both 50 μm and 12 μm spot methods) were only cleaned by sonication and rinsing with methanol and water (a

procedure that does not necessarily remove all the organic matter present on the shell). There is a critical difference between the laser methods, however, in that 50 μm depth-profiling indiscriminately includes all material between the sample surface and bottom of the laser pit whereas the 12 μm analysis of the cross section uses SEM imaging to avoid contamination that may be present on the surface or in cracks of the sample.

We suggest that the use of the 12 μm beam to analyze a shell in cross-section together with SEM imaging allows measurement of Mg/Ca in better-preserved or less-contaminated domains than the 50 μm depth-profiling technique. The correlation observed between bulk and 12 μm Mg/Ca results indicates that although the reductive cleaning may have lowered the Mg/Ca of bulk material, the relative Mg/Ca is preserved. In planktonic tests it has been suggested that Mg/Ca ratios obtained by LA-ICP-MS on whole foraminifera (50 μm spots) could record a large range of values that are not related to environmental temperatures but instead to the presence of detrital material on the test (Eggins et al., 2003 and references therein). However, it is also possible that the application of different cleaning techniques plays a significant role in determining the result of the analysis (Sadekov et al., 2005). Another possibility could be that the lack of significant correlation between the 50 μm and 12 μm in situ analyses is due to the limited number of foraminifera analyzed. We suggest that further work is warranted to compare depth-profiling analyses of element/Ca to small spot, cross-section analyses where care is taken to avoid organic-rich or porous domains. Such a study would be particularly useful if both types of analyses could be completed in a single individual (e.g. Wycech et al., 2018a).

5. Conclusion

In this study, we apply bulk and high-resolution in situ analytical methodologies to obtain $\delta^{18}\text{O}$, Mg/Ca and Sr/Ca values from the benthic foraminifera genus *Uvigerina*. We show an approach for obtaining paired, in situ measurements of element/Ca ratios by LA-ICPMS and $\delta^{18}\text{O}$ by SIMS within the same individual benthic foraminifera. For both the element/Ca and $\delta^{18}\text{O}$ proxies, the same range of values is seen in the averaged in situ measurements as in the bulk foraminifera, but there are varying degrees of correlation between the different analytical methodologies. The large intra-shell variability for each of the proxies measured by in situ methodologies (12 μm and 50 μm spots) does not follow chamber number, which implies that there are no significant size (age)-related impacts on Mg/Ca, Sr/Ca and $\delta^{18}\text{O}$ for this species. Further, the intra-shell variability is not correlated between the above geochemical proxies. We surmise that the differences between proxies for the time slices we examined and the correlations (or lack thereof) between the proxies that we reported, are due to a combination of 1) real variability in the water chemistry from which the individual foraminifera tests were precipitated, and 2) biological responses of the foraminifera to different growth conditions. The biological mechanisms behind this natural variability are still unknown (Wit et al., 2010), and most importantly they could be unique to specific setting and environmental characteristics (e.g., Santa Monica Basin in this case). Our data also demonstrate large inter-shell variability in all three geochemical proxies (Mg/Ca, Sr/Ca and $\delta^{18}\text{O}$) analyzed in *Uvigerina* where environmental conditions are expected to be less variable than in the surface ocean. This observed variability may represent some combination of: 1) real environmental conditions specific to the study site (samples from the deep ocean could verify if this is unique to coastal settings), 2) vital effects on individual specimens as seen in culture studies, or 3) variability in non-calcite phases included in the analysis (e.g. intra-crystalline organic matter or other contaminating phases) that strongly depend on cleaning and ablation conditions. This study illustrates the complexities of micro-scale geochemistry inherent to benthic *Uvigerina* foraminifera and demonstrates that inter- and intra-shell variability should be expected when constructing paleoclimate proxy records.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2019.119377>.

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