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High resolution I/Ca ratios of benthic foraminifera from the Peruvian oxygen-minimum-zone: A SIMS derived assessment of a potential redox proxy

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ABSTRACT

Oceanic oxygen decline due to anthropogenic climate change is a matter of growing concern. Tropical oxygen minimum zones (OMZs) are the most important areas of oxygen depletion in the modern oceans. A quantitative oxygen proxy in OMZs is highly desirable in order to identify and monitor recent dynamics as well as to reconstruct pre-Anthropocene changes in amplitude and extension of oxygen depletion.

A previous study revealed that there are significant correlations between I/Ca ratios of foraminiferal bulk samples for different benthic foraminiferal species from the Peruvian OMZ. Nevertheless, species for which less specimens were available showed a higher variability between I/Ca ratios in different badges. To test if this might be related to intra- or inter-shell heterogeneity we focused on microanalyses of I/Ca ratios within these species in our present study. We developed a method for measuring benthic foraminiferal I/Ca ratios, a potential proxy for the reconstruction of marine oxygen concentrations. We applied 92 spot analyses in individual foraminiferal specimens from the Peruvian OMZ using secondary ion mass-spectrometry (SIMS). The I/Ca ratios on 8 of 11 cleaned *Uvigerina striata* and *Planulina limbata* specimens determined with SIMS showed no significant difference to previous ICP-MS measurements on bulk samples from the same species. This indicates that both techniques are suited to the analysis and that the applied cleaning protocols efficiently removed the strong iodine contaminations.

Nevertheless, despite the highly significant correlation between bulk ICP-MS I/Ca ratios and bottom water oxygen concentrations for *U. striata*, no significant correlation was observed for the SIMS derived individual I/Ca ratios. This indicates that ICP-MS bulk analyses on pooled bulk samples might be more suitable for reliable oxygen reconstructions using I/Ca ratios. On the contrary, the strong intra-test (e.g. -shell) variations could be induced by the oxygen variability in the habitats of foraminifera. Therefore, the high resolution findings provide the perspective for tracking relative short term oxygen fluctuations by measuring ontogenetic changes in I/Ca ratios within individual foraminiferal tests.

Measurements on cross-sections of uncleaned *U. striata* specimens revealed a strong contaminant iodine phase within the massive centre of the foraminiferal test walls which usually would be considered to be free of contamination. The contaminant iodine is probably associated to organic matter and located inside a microporous framework within the foraminiferal calcite. This might be related to microtubular structures which have been revealed in previous studies during early dissolution states of foraminiferal test walls.

1. Introduction

Tropical oxygen minimum zones (OMZs) are important areas of oxygen depletion in the modern oceans. Oxygen-dependent nutrient recycling within these regions has a large socio-economic impact because they account for ~17% of global commercial fish catches (source: FAO FishStat, 2013). Potential increases in the area and magnitude of seawater oxygen depletion in these regions might, in the future, endanger rich fisheries, threatening global marine food supply. Through use of a quantitative geochemical proxy for seawater oxygen in OMZs it should be possible to reconstruct temporal variation in OMZ extent to provide information about past changes in seawater oxygenation. This is of high interest considering the recent trend of expanding OMZs (Stramma et al., 2008).

Abbreviations: ICP-MS, inductively coupled plasma mass spectrometry; $[O_2]_{BW}$, bottom water oxygen concentration; OMZ, oxygen minimum zone; SIMS, secondary ion mass spectrometry.

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For such paleoceanographic perspectives a geochemical proxy for quantitative reconstruction of oxygen concentrations ($[O_2]$) in OMZs is highly desirable. The tests (e.g. shells) of benthic foraminifera are important geochemical proxy archives for reconstructing past chemical and physical seawater properties. Benthic foraminifera inhabit the seafloor. While epifaunal foraminiferal species live on the sediment surface, infaunal species exist, which are able to migrate vertically in the sediment column to where food availability and the oxygen level meets their individual requirements up to a depth of ~10 cm ((Jorissen et al., 1995; Duijnstee, 2003). Due to the overexcess in food and the low oxygen concentrations at the Peruvian OMZ most of the living benthic foraminifera can be found in the first few millimeters of the sediment column (Mallon et al., 2012; Glock et al., 2013). Most suitable for geochemical paleoreconstructions are foraminiferal species which build their tests out of calcium carbonate. Several elemental ratios have been studied as possible proxies for past seawater oxygenation. These proxies include V/Ca and U/Ca ratios (V/Ca: Hastings et al., 1996a, b, c; U/Ca: Russell et al., 1994) as well as Mn/Ca ratios that have become of more and more interest in several recent studies (Fhlaithearta et al., 2010; Munsel et al., 2010; Glock et al., 2012; Groeneveld and Filipsson, 2013; McKay et al., 2015; Koho et al., 2015).

The most common microanalytical techniques to study foraminiferal element and isotope ratios amongst secondary ion mass spectrometry (SIMS) are laser ablation ICP-MS (Wu and Hillaire-Marcel, 1995; Hathorne et al., 2003; Reichart et al., 2003; Pena, 2005; Munsel et al., 2010; Raitzsch et al., 2011; Jonkers et al., 2012; Vetter et al., 2013a; Mewes et al., 2014; Fehrenbacher et al., 2015; Kaczmarek et al., 2015; Koho et al., 2015; Mewes et al., 2015; Spero et al., 2015) and electron-microprobe (EMP) (Nürnberg, 1995; Nürnberg et al., 1996; Eggins et al., 2003, 2004; Sadekov, 2005; Toyofuko and Kitazato, 2005; Pena et al., 2007; Kozdon et al., 2013; Fehrenbacher and Martin, 2014). Secondary ion mass spectrometry itself has also become more widespread within the last years with the advantages of a lower spot size than laser ablation techniques and a higher sensitivity than EMP (Allison and Austin, 2003; Sano et al., 2005; Bice et al., 2005; Kunioka et al., 2006; Rollion-Bard et al., 2008; Kasemann et al., 2009; Rollion-Bard and Erez, 2010; Glock et al., 2012; Nehrke et al., 2013; Kozdon et al., 2013; Vetter et al., 2013b; Vetter et al., 2014; McKay et al., 2015). Nevertheless, the effort of sample preparation and measurement for SIMS typically exceeds other techniques, which prevents it becoming widely-applicable.

Iodine is a redox sensitive element, such that the iodide (I^-) to iodate (IO_3^-) system has a reduction potential close to O_2/H_2O. Thus, the speciation of iodine is very sensitive to seawater $[O_2]$ (Rue et al., 1997; Brewer and Peltzer, 2009, Lu et al., 2010). The anions I^- and IO_3^- are the two most thermodynamically stable inorganic forms of dissolved iodine (Küpper et al., 2011). From these two forms of dissolved inorganic iodine, (Wong and Brewer, 1977) only IO_3^- (not I^-) is incorporated into carbonate materials (Lu et al., 2010). Only few studies have been focused on iodine speciation in pore waters but it has been shown that iodate reduction occurs during early diagenisis before MnO_2 reduction but after denitrification (Kennedy and Elderfield, 1987). An iodate reducing *Pseudomonas* species has been isolated from marine sediments at Sagami Bay, Japan (Amachi et al., 2007).

Inorganic precipitation experiments show that I/Ca ratios in synthetic calcite are a linear function of IO_3^- concentrations in the ambient water, while variable I^- concentrations did not affect the I/Ca ratios (Lu et al., 2010). Thus, it has been proposed that the IO_3^- anion partially substitutes for carbonate anions within the calcite lattice. More dissolved IO_3^- occurs at higher $[O_2]$ and thus higher I/Ca ratios in foraminiferal tests are supposed to be precipitated within those waters. Several modern benthic foraminiferal species show a positive covariation of test calcite I/Ca ratios with bottom water oxygen concentrations ($[O_2]_{BW}$) (Glock et al., 2014). Similarly, fossil planktonic foraminiferal I/Ca ratios decrease during mid-Cretaceous Oceanic Anoxic Events (OAE), times in the geological record when global oceans experienced stagnation and low $[O_2]$, as evidenced by the preservation of organic-rich sediments (Zhou et al., 2015).

Monospecific bulk analyses with ICP-MS revealed a lower reproducibility on I/Ca ratios in benthic foraminiferal species of which only a limited amount of specimens are available (Glock et al., 2014). In the present study we test the inter- and intra-test variability of benthic foraminiferal I/Ca ratios from the Peruvian OMZ to assess if indeed strong heterogeneity is causing this low reproducibility. Furthermore, it will be tested if I/Ca ratios from single foraminiferal specimens are already sufficient to reconstruct past oxygenation or if indeed bulk analyses are necessary to get a significant statistical average. Finally, I/Ca ratios of cleaned and uncleaned foraminiferal specimens are compared to study the impact of cleaning on SIMS derived I/Ca ratios. We focus on the shallow infaunal species *Uvigerina striata* because it showed the most significant correlation between I/Ca ratios and $[O_2]_{BW}$ (Glock et al., 2014). Due to its infaunal living environment *U. striata* is exposed to the chemical environment of the sediment pore waters.

2. Material and methods

2.1. Sampling procedure

Six sediment cores from the Peruvian OMZ were recovered using a video-guided multiple corer in October and November 2008 during the R.V. Meteor Cruises M77/1 and M77/2 (Table 1). The water depth at the sampling locations ranged from 465 m to 878 m with a range of bottom water oxygen concentrations ($[O_2]_{BW}$) from 2 to 34 μmol/kg). This transition zone from hypoxic to suboxic conditions suites perfectly to study the switch from microxic to anaerobic processes (like the reduction of IO_3^- to I^-). The inner diameter of the coring tubes was 100 mm. The multicorer tubes were transferred to a constant temperature (4 °C) laboratory immediately after retrieval. Supernatant water of the core was carefully removed. The core was then gently pushed out of the multicorer tube and cut into 10-mm-thick slices. Finally, the sediment samples were transferred either to plastic bottles or Whirl-Pak™ plastic bags, transported to and stored at GEOMAR, Kiel, Germany at a temperature of 4 °C.

2.2. Foraminiferal studies

The sediment samples were washed through a 63 μm mesh sieve. Water was removed from the residue >63 μm through a 63 μm filter stone using a waterjet pump. The residue was taken up in a small amount of ethanol to prevent sample-dissolution and dried overnight at 50 °C. The dried residues were further subdivided into 63–125, 125–250, 250–315, 315–355, 355–400, and >400 μm fractions. All specimens from the species *Uvigerina striata*, *Planulina limbata* and *Hoeglundina elegans* were sampled from the size fraction >400-μm. Light micrographs of chosen specimens from the different species can be found in Glock et al. (2014). While foraminifera from

Table 1
Sampling sites. $[O_2]_{BW}$ are taken from Glock et al. (2011 & 2014).

Site	Longitude (W)	Latitude (S)	Water depth (m)	$[O_2]_{BW}$ (μmol/kg)
M77/1-455/MUC-21	78°19.23′	11°00.00′	465	2.4
M77/1-487/MUC-38	78°23.17′	11°00.00′	579	3.7
M77/1-565/MUC-60	78°21.40′	11°08.00′	640	8.2
M77/1-604/MUC-74	78°22.42′	11°17.96′	878	34.2
M77/1-459/MUC-25	78°25.60′	11°00.03′	697	12.6
M77/1 553/MUC-54	78°54.70′	10°26.38′	521	3.0

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the genus *Uvigerina* are typically found to live infaunal (Fontanier et al., 2006), *U. striata* most probably can migrate within the upper sediment column and lives within the sediment. Species from the genus *Planulina* have been found to live epifaunal to elevated epifaunal (Lutze & Thiel, 1989). Thus, *P. limbata* is supposed to live on the sediments surface. The aragonitc species *H. elegans* has been both found to live epifaunal to shallow infaunal (Tachikawa and Elderfield, 2004; Fontanier et al., 2006). At the studied locations within the Peruvian OMZ most of the living infaunal species are found within the first few millimeters of the sediment (Mallon et al., 2012; Glock et al., 2013). The studied specimens were not stained with rose bengal but collected from core replicates from the studies by Mallon et al. (2012) and Glock et al. (2013), which analysed the distribution of living benthic foraminifera in the Peruvian OMZ. Only the most pristine individuals were used for the analyses and since the population densities in the Peruvian OMZ can be very high (until 500–1000 individuals/cm^3), it is highly probable that the used specimens were alive during sampling. We would definitely advise against using rose bengal staining on I/Ca studies, due to the high iodine content in this dye (chemical equation: 4,5,6,7-tetrachloro-2′,4′,5′,7′-tetraiodofluorescein).

2.3. Cleaning methods

Complete single foraminiferal specimens were transferred into PFA vials and rinsed with ethanol three times to remove clay particles from within the test chambers and test pores. After each rinsing step the vials were placed in an ultrasonic bath for 1 min. The vials were rinsed again twice with reverse osmosis water (ROW; Elga™ PURELAB Ultra; conductivity ~0.055 μS cm^{-1}) to remove residual ethanol. An oxidative reagent was freshly mixed by adding 100 μl 30% H_2O_2 to 10 ml of a 0.1 M NaOH (p.a., Roth™) solution. Subsequently 350 μl of this reagent were added to each vial. The vials were transferred into a 92 °C water-bath for 15 min to remove contamination by organic matter. During this oxidative cleaning step, samples were removed from the water-bath in 5 min intervals to remove gas bubbles by tapping the bottom of the vials. After 15 min the foraminiferal specimens were rinsed with ROW and another 350 μl of fresh oxidative reagent were added. This step was repeated followed by a further 20 s in the ultrasonic bath. The vials were then rinsed twice with ROW to remove residues of the reagent. Finally, the specimens were individually collected over a 125 μm mesh stainless steel sieve rinsed with ethanol and dried.

2.4. Preparation of cross-sections for SIMS

The foraminiferal cross-sections for the SIMS analyses were prepared at GEOMAR in Kiel. The foraminiferal specimens were embedded in Araldite(™) epoxy resin under vacuum using the CitoVac(™) vacuum embedding system by Struers(™). The resin was ground down with grinding paper made out of alumo-silica using the Tegra-Pol-21 system by Struehrs(™) until the centre of the specimens were fully exposed. In cases where the chambers were not filled with resin, small amounts of resin were dropped into the inner part of the chambers, which was then ground down until the specimens were completely exposed. After the grinding step the cross-sections were polished with alumo-silica and diamond paste of various grain sizes down to 1 μm. After each polishing step, the surface of the sample mount was cleaned in an ultrasonic bath for several seconds. Cross-sections were prepared for cleaned as well as uncleaned foraminiferal specimens. Several fragments of a coral used as an internal aragonite standard and as a matrix matching carbonate standard for I/Ca ratios. The fragments were embedded either in individual epoxy pellets or together with the foraminiferal specimens. The solution based ICP-MS I/Ca ratio for this coral is 2.59 ± 0.09 μmol/mol (n = 52; sd = 3.5%; Glock et al., 2014). Cleaned and uncleaned specimens from the same sampling location were typically embedded within the same cross-section. Examples for cross-sections of *H. elegans* and *U. striata* are shown in Fig. 1.

2.5. SIMS analyses

The I/Ca ratios were determined using a Cameca 1280-HR instrument at the Helmholtz Zentrum Potsdam. Samples were prepared as 25 mm diameter, round epoxy mounts. Prior to SIMS analyses the samples were cleaned for five minutes using a high-purity ethanol ultrasonic bath, after which they were argon sputter coated with carbon. We did not apply gold coating as it was shown that the sputtered gold contained significant amounts of iodine. During measurement runs the iodine signal strongly decreased over time while using the gold coating. Volatile iodine contaminations might be introduced to gold by purification processes (Baghalha, 2012). The samples were imaged using a flat bed scanner and were then placed in sample holders using tension springs. The scanned images were used to assist navigation during the SIMS session.

The SIMS analyses employed a ~ 5 nA, $^{133}Cs^+$ primary ion beam using a Gaussian distribution with a total impact energy of 20 keV which was rastered over a 25 μm^2 area with the dynamic transfer activated. The egate was set at 6%. The egate is an electronic window/electronic shut off of the counting system, it was set to 6% so that 94% of the ions reach the detector while 6% of the remaining ions, coming from the edges of the crater are deviated in the secondary column of the mass spectrometer and not measured by the system. Negative secondary ions were extracted using a −10 kV potential as applied to the sample holder, to which no offset voltage was applied, in conjunction with a 50 eV wide energy window, the position of which was mechanically centered at the beginning of the analytical session. Each analysis was preceded by a 90 s pre-sputtering of the target domain with a 25 μm raster. Total pressure in the source chamber was typically around $3 \pm 0.3 \times 10^{-8}$ mbar. Sample degassing appeared to be the primary contributor to the residual gas in the chamber.

After completing the pre-sputtering and before starting an analysis, automatic centering routines were applied to the secondary beam in both X and Y directions on the field aperture, followed by an automatic centering of the secondary beam in Y on the contrast aperture using the ^{127}I mass station. The instrument was operated in electron multiplier mono-collection mode. A single analysis consisted of 15 cycles of the peak stepping sequence mass 71 (dummy mass which is needed for the magnet to be settled) followed by mass 72 ($^{40}Ca^{16}O_2$), 80 ($^{40}Ca_2$) and 127 (^{127}I), with 1, 2, 3, and 8 s integration time for the respective isotope. An entire analysis, including pre-sputtering and automatic centering, lasted around 11 min. Sampling of the sputtered 25 × 25 μm area was restricted to the innermost 8 × 8 μm by applying a combination of electronic window (8%) and mechanical confinement by setting the field aperture at 3000 μm and the field of view at 80 μm. This setup prevents contamination from the edges and assures that only the innermost 8 × 8 μm of the measurement spot are analysed. All measurement spots on the foraminiferal samples were adjusted by hand, mapping the $^{40}Ca_2$ counts within the 8 × 8 μm window to assure that only pure calcium carbonate is measured and the centre of the test walls is hit. Measurements which still showed low $^{40}Ca_2$ count rates at the end were not considered for the evaluation of the results. The mass resolution of the instrument was set at $M/\Delta M \approx 6000$. Since $^{40}Ca_2$ showed a better stability than the $^{40}Ca^{16}O_2$ signal, $^{40}Ca_2$ was used for all evaluations within this paper. Typical count rates for $^{40}Ca_2$ were around 1600 cps and around 200,000 cps for $^{40}Ca^{16}O_2$. The dead time was 46.2 ns.

Possible contaminations of ^{127}I and $^{40}Ca_2$ through the resin and sample preparation were checked by doing spot measurements directly on the resin. The blank of the resin was 20 cps ± 5 cps (1sd) for ^{127}I and 35 cps ± 5 cps (1sd) for $^{40}Ca_2$. This results in a detection limit of 35 cps for ^{127}I and 50 cps for $^{40}Ca_2$. Typical $^{40}Ca_2$ cps on the Ca-carbonate

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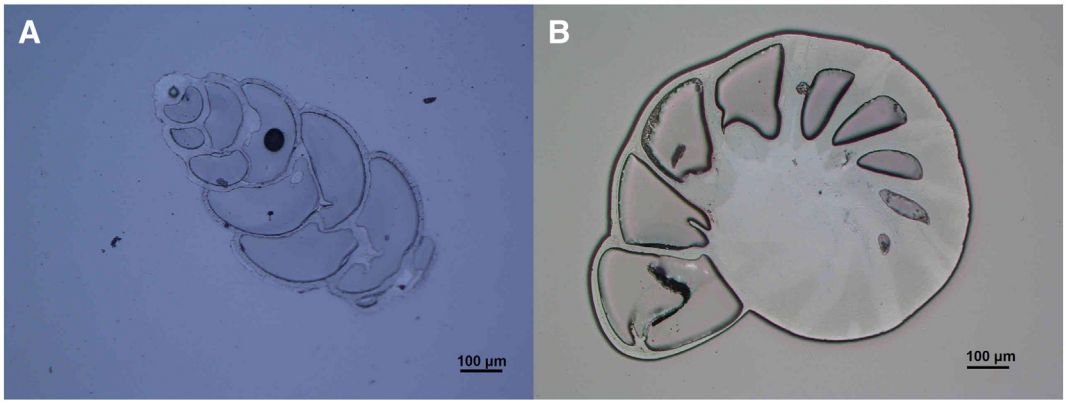

Fig. 1. Cross-sections of cleaned *Uvigerina striata* (A) and *Hoeglundina elegans* (B) specimens.

samples and standards were ~1600 while the sample with the lowest iodine concentration had count rates for ^{127}I of 73 cps and average count rates for cleaned samples were around 200 cps, everything well above the detection limit.

2.6. A note on terms "heterogeneity" and "precision"

In the following part of the manuscript we will distinguish between the terms "heterogenity" and "precision". The heterogeneity is the standard deviation (sd) or standard error of the mean (sem) between all measured spots on a sample, which are supposed to represent the heterogeneity of the sample. The precision is the sd or sem between the different counting cycles on a single measurement spot which mainly derives from the analytical method but also might indicate microscale heterogeneities of the sample (see Discussion). Only the standard deviation of the count rates during a single spot measurement were used to calculate precisions. Accuracies which also include the heterogeneity of the standard are listed in the appendix.

3. Results

3.1. Matrix matching coral standard

A lab internal aragonitic coral standard (*Pocillopora damicornis*) was used as a matrix matching standard to normalize foraminiferal I/Ca ratios. The mean I/Ca ratio on a homogenized powder of this coral has been determined previously (2.59 µmol/mol; sd = 3.2%; n = 70; Glock et al., 2014). To assess the heterogeneity of this standard for the study presented here, 108 spot measurements were made on 6 different fragments of the coral within 4 measurement sessions on different days. Due to the heterogeneity of the coral, the different fragments showed heterogeneities ranging from 13.2–22.5% sd and 2.1–6.8% sem, respectively. Typical precisions ranged from 0.6–3.0% for individual measurements. Mean $^{127}I/^{40}Ca_2$ count ratios are shown in Fig. 2 and Table 2. All individual measurements on the different coral fragments and the corresponding precisions are shown in the appendix (Table A1).

Two of the coral pieces showed slightly lower $^{127}I/^{40}Ca_2$-count-ratios than the other four. For another two of the coral fragments, $^{127}I/^{40}Ca_2$-count-ratios were determined in two different sessions three days apart. Both fragments showed the same count ratios in both sessions that were within the heterogeneity (sd), indicating that the heterogeneity of the coral has a greater influence than drift effects during different measurement sessions. Hence, for the evaluation of the foraminiferal I/Ca ratios, mean $^{127}I/^{40}Ca_2$-count-ratios from all measurements in every coral fragment were used to obtain the best average from the heterogenic standard material (see Discussion for details). The mean $^{127}I/^{40}Ca_2$-count-ratio of all measurements was 0.54 (n = 108; sd = 22.0%; sem = 2.1%).

3.2. Effect of oxidative cleaning on benthic foraminiferal I/Ca ratios

The mean I/Ca ratios from uncleaned specimens of *U. striata* were compared to cleaned specimens that have been treated with an oxidative step (Fig. 3). All individual measurements on the different foraminiferal samples and the corresponding precisions and accuracies are shown in the appendix (Table A2). The accuracies are calculated as an error propagation using the precision of the measurement and the heterogeneity of the coral standard (1sem = 2.1%). The accuracies are only marginally higher than the precisions.

Mean I/Ca ratios in the cleaned specimens ranged from 0.49 to 1.14 µmol/mol (Table 3) and thus were ~10 to 100 times lower than the mean I/Ca ratios in the uncleaned specimens (Table 4; 6.0 to 95.5 µmol/mol). Both cleaned and uncleaned specimens showed a high heterogeneity.

In total 63 spots were measured on 19 specimens of *Uvigerina striata* (11 cleaned and 8 uncleaned) from 4 different locations on a transect along the Peruvian margin. The heterogeneity for the uncleaned specimens was sd = 6 to 141% and sem = 4 to 95%, while the heterogeneity for the cleaned specimens was sd = 17 to 145% and 1sem = 10 to 59%. The precision for single measurement spots was distinctively better and typically ranged from 0.7 to 6.2% (n = 60) within the cleaned specimens. Five additional measurements were less precise (sd = 10.8 to 18.1%). In particular, 2 of 50 spots on cleaned specimens and 3 of 15 spots on uncleaned specimens

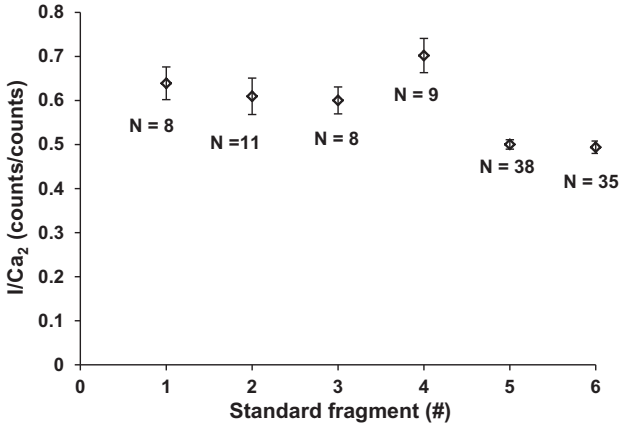

Fig. 2. Mean I/Ca_2 count-ratios for the different coral fragments which have been used as a matrix matching standard. Error bars show standard error of the mean (1σ). Typical precisions for single measurement spots ranged from 0.6–3.0%.

Table 2
Mean $^{127}I/^{80}Ca_2$ count-ratios, number of measurements (N) and errors for the different fragments of the coral used as matrix matching reference standard in this study.

Coral fragment (#)	N	$^{127}I/^{80}Ca_2$ (counts/counts)	Heterogeneity (1sd)	Heterogeneity (1 sem)
1	8	0.639	16.4%	5.8%
2	11	0.609	22.5%	6.8%
3	8	0.600	14.4%	5.1%
4	9	0.702	16.6%	5.5%
5	38	0.500	13.2%	2.1%
6	35	0.494	16.9%	2.9%

showed lowered precision. In general measurements were less precise on the uncleaned specimens (~5.3%; n = 15) compared to the cleaned specimens (~2.79%; n = 50), although the I/Ca ratios of the uncleaned specimens were much higher.

To assess the cleaning effect also on different species, one cleaned and one uncleaned specimen of *Planulina limbata* and *Hoeglundina elegans* were compared. Pairs of cleaned and uncleaned specimens were from the same sample. Again, the I/Ca ratios as well as the heterogeneity for I/Ca of the uncleaned specimens (*P. limbata*: 20.4 μmol/mol; n = 3; sd = 180.2%; sem = 104.0%; *H. elegans*: 6.9 μmol/mol; n = 7; 1sd = 127.3%; 1sem = 48.1%) were much higher than those of the cleaned specimens (*P. limbata*: 1.64 μmol/mol; n = 5; sd = 18.3%; sem = 8.2%; *H. elegans*: 1.3 μmol/mol; n = 14; sd = 56.5%; 1sem = 15.1%).

3.3. SIMS I/Ca ratios on cleaned specimens and comparison to ICP-MS bulk data

The SIMS-derived I/Ca ratios on cross-sections of cleaned *U. striata* specimens were compared to *U. striata* bulk samples measured by Q-ICP-MS (Fig. 4). The Q-ICP-MS bulk data was taken from Glock et al. (2014). The I/Ca ratios of the bulk samples (ICP-MS) varied between 0.28 and 0.91 μmol/mol and are therefore comparable to the mean normalized I/Ca ratios determined with SIMS on individual cleaned specimens (0.49 to 1.14 μmol/mol). A direct comparison of these ratios shows that the two methods actually overlapped within the range of heterogeneity (sd) due to the heterogeneity of the individual specimens (Fig. 4).

Despite the highly significant correlation between the bulk I/Ca ratios to $[O_2]_{BW}$ ($P < 0.0001$; ANOVA; Glock et al., 2014), no correlation to $[O_2]_{BW}$ was found for the SIMS data on individual cross-sections of *U. striata* ($P = 0.11$; ANOVA). The SIMS I/Ca ratios for the individual specimens have been compared to all bulk ICP-MS analyses from the same sampling locations using 2-sided, heteroscedastic student's *t*-tests, to assess if there is a significant difference between the results of the two methods. A statistical comparison for the 697 m was not possible since only one measurement was available from the bulk analyses. The individual from the 521 m station analysed with SIMS (M77/1 553/MUC-54) was compared to the bulk analyses from a station with similar water depth and redox conditions (M77/1-487/MUC-39; 579 m), since there was no bulk data available from the same location. In total 7 out of 10 *U. striata* individuals showed no significant difference in their SIMS I/Ca ratios compared to the corresponding ICP-MS bulk data ($P = 0.06–0.66$). Three individuals showed significantly elevated I/Ca compared to the corresponding bulk data ($P = 0.02–0.04$).

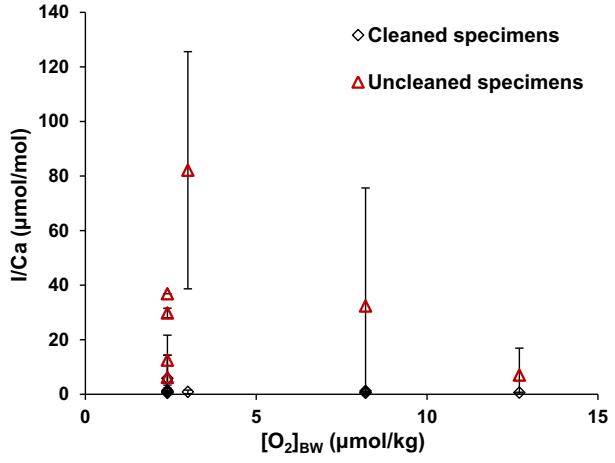

Fig. 3. Comparison of mean I/Ca ratios for cleaned and uncleaned specimens of *U. striata* plotted against $[O_2]_{BW}$. The number of measurements per specimen (N) varied between 2 and 7 (Table 3 & 4). Error bars show standard deviation (1sd). Note that the I/Ca ratios in the uncleaned specimens are 10–100 times higher than in the cleaned specimens.

The mean SIMS I/Ca ratio on the individual cleaned *P. limbata* specimen from M77-1 487/MUC-38 (1.64 ± 0.30 μmol/mol; sd) was also not significantly different from the *P. limbata* bulk data (1.32 ± 0.30 μmol/mol; sd; Glock et al., 2014) from the same sampling location ($P = 0.12$). The mean SIMS I/Ca ratio on the individual cleaned *H. elegans* specimen from M77-1 604/MUC-74 (1.34 ± 0.76 μmol/mol; sd) was much higher, than the I/Ca from the corresponding *H. elegans* bulk data (0.29 μmol/mol; sd; Glock et al., 2014). However, a statistical comparison was not possible with the *H. elegans* specimen since only one measurement was available from the bulk analyses.

An analysis of the I/Ca variation between different chambers in single cleaned specimens of *U. striata* is shown in the appendix (Fig. A1). There is no obvious trend in the intra-test evolution of I/Ca ratios.

4. Discussion

4.1. Heterogeneity of the coral standard

A general challenge in applying a new microanalytical protocol on a new element system (e.g. SIMS derived I/Ca ratios on calcium carbonate) is the identification of a suitable matrix matching calibration standard that is well characterised and shows the best possible homogeneity. Only few calcium carbonate reference materials are well characterised, since I/Ca ratios are a relatively new developed proxy (Lu et al., 2010). The only characterised reference materials available are the JCP-1 (Chai and Muramatsu, 2007; Lu et al., 2010 and Glock et al., 2014) and a laboratory internal aragonitic coral standard (Glock et al., 2014). We focused on our laboratory internal coral standard since no pieces of the JCP-1 of a suitable size were available. As shown in Section 3.1 this standard is relatively heterogeneous. Due to the heterogeneity a maximal error of around 22.5% (1sd) of the different spots on the coral standard can be assumed. The application of 108 measurements on different spots of the coral standard reduced this uncertainty to 2.1% (1sem) related to the bulk average of the homogenized powder of the same coral analysed in Glock et al. 2014. The accuracies for the different measurements on the foraminiferal samples, which include the heterogeneity of the standard as well as the precision of the individual measurement is shown in the appendix (Table A2). The accuracies range from 2.2% to 18.2%. The general observations discussed within this paper lie in a completely different order of magnitude making the error introduced to the heterogeneity of the standard negligible. The fact that the SIMS derived I/Ca ratios on cleaned foraminiferal specimens are comparable to the bulk ICP-MS data additionally support the quality of the data in general. Nonetheless, a standard reference material of higher homogeneity and a lower I/Ca ratio that is closer to the ratio in the sample is highly desirable to improve the reproducibility of this method for future applications.

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Table 3
Mean I/Ca ratios, number of measurements (N) and errors for the cleaned foraminiferal specimens at the different sampling sites. The number of the specimen (#) is used to distinguish between different specimens from the same sample. The heterogeneity is defined in Section 2.6.

Species	Sampling site	Specimen (#)	N	I/Ca (μmol/mol)	Heterogeneity (1sd)	Heterogeneity (1 sem)
U. striata	M77-1 455/MUC-21	1	3	0.49	49.7%	28.7%
U. striata	M77-1 455/MUC-21	2	3	0.85	38.3%	22.1%
U. striata	M77-1 455/MUC-21	3	5	2.36	72.6%	32.5%
U. striata	M77-1 455/MUC-21	4	4	1.30	73.0%	36.5%
U. striata	M77-1 455/MUC-21	5	3	0.66	17.0%	9.8%
U. striata	M77-1 455/MUC-21	6	4	0.86	36.9%	18.5%
U. striata	M77-1 565/MUC-60	1	6	0.55	52.2%	21.3%
U. striata	M77-1 565/MUC-60	2	5	1.14	31.0%	13.9%
U. striata	M77-1 565/MUC-60	3	5	0.60	46.8%	20.9%
U. striata	M77-1 553/MUC-54	1	7	1.02	75.4%	28.5%
U. striata	M77-1 459/MUC-25	1	4	1.22	21.4%	10.7%
P. limbata	M77-1 487/MUC-38	1	5	1.64	18.3%	9.1%
H. elegans	M77-1 604/MUC-74	1	14	1.34	56.5%	15.1%

4.2. Organic iodine contaminations within a (sub)microporous system in foraminiferal tests

The standard cleaning procedures for measurements of most trace elements in foraminiferal calcite include the removal of adhesive clays by rinsing ultrasonically with (m-)ethanol and ultrapure water and reductive removal of diagenetic coatings (Boyle, 1983) and the dissolution of organic contaminants by oxidative cleaning (Boyle and Keigwin, 1985). Some diagenetic contaminant phases have been identified as Mn carbonates as well as Mn and Fe rich (oxyhydr)oxides using laser-ablation-ICP-MS (LA-ICPMS) and EMP mapping (Pena et al., 2005, 2007). Since it has been shown that recent benthic foraminifera from the Peruvian OMZ are free of diagenetic coatings, probably due to the low $[O_2]_{BW}$ (Glock et al., 2012), reductive cleaning in this study was not necessary.

Our comparison between cleaned and uncleaned specimens of *Uvigerina striata* revealed iodine concentrations to be 10–100 times lower in the cleaned tests (Fig. 2). The SIMS analyses are applied within the massive centre of the foraminiferal test walls, which are usually supposed to be free of contaminants. This observation is best explained by removal of iodine-containing contaminants from within a microporous framework in the foraminiferal calcite. Because the chemical (oxidative) cleaning would have oxidised, thus removed, any organic components, it is possible that elevated iodine concentrations are associated with organic compounds (either a test matrix or contaminants), rather than bound within the test calcite as iodate. The fact that a comparison of cleaned and an uncleaned specimens of *P. limbata* and *H. elegans* showed similar results implies that this feature is not species dependent.

Similar observations have been made on the distributions of Fe in benthic foraminifera from the Peruvian OMZ (Glock et al., 2012). Elemental mapping with EMP revealed Fe hotspots in the massive centre of the test walls within cross-sections of uncleaned *Bolivina spissa* specimens. These hotspots were absent in specimens that were treated with the same oxidative cleaning we used within this study. Furthermore, high Fe concentrations in *B. spissa* and *U. striata* were often associated with high concentrations of S, which also hints at association with organic matter. A study on natural and experimental induced progressive dissolution and ultrastructural breakdown on tests of planktonik foraminifera revealed microtubules within the tests in jigsaw puzzle like patterns during early stages of dissolution (Bé et al., 1975). Similar jigsaw puzzle like microtubules have been observed on cross-sections of *Bolivina spissa* specimens, which have been treated by the same oxidative cleaning procedure we used for the present study (Glock et al., 2012). A study on the impact of cleaning procedures on trace elemental distributions in the planktonic foraminiferal species *Globigerina bulloides*, using LA-ICP-MS was made by Marr et al. (2013). They observed micro-fractures in the tests of all specimens with SEM after chemical cleaning with ultrasonication. Such microtubules or cracks might very well be present in the cleaned specimens from our study, allowing the cleaning solution to intrude up to the centre of the test walls. Future studies on the influence of different cleaning steps on the ultrastructure, I/Ca ratios and other with organics associated element/Ca ratios (e.g. S/Ca) of foraminiferal tests might reveal if there are indeed organic enrichments present within these jigsaw patterned microtubules themself. However, it might be possible that the iodine contamination is not associated with organic matter but related to residual porewater iodide accumulated in micropores. Future studies comparing different cleaning methods might bring a deeper insight about the origin of the contaminant iodine.

Although the mean I/Ca ratios in the uncleaned specimens are much higher, the analytical sensitivities for single measurement spots are generally worse than within the cleaned specimens ($sd_{uncleaned}$ = ~5.3%; $sd_{cleaned}$ = ~2.8%). A comparison between the 15 cycles of two SIMS measurements on a cleaned and an uncleaned specimen of *U. striata* from the same sample is shown in Fig. 5. Both measurements have an average precision for their

Table 4
Mean I/Ca ratios, number of measurements (N) and errors for the uncleaned foraminiferal specimens at the different sampling sites. The number of the specimen (#) is used to distinguish between different specimens from the same sample. The heterogeneity is defined in Section 2.6.

Species	Sampling site	Specimen (#)	N	I/Ca (μmol/mol)	Heterogeneity (1sd)	Heterogeneity (1 sem)
U. striata	M77-1 455/MUC-21	7	2	28.90	5.9%	4.2%
U. striata	M77-1 455/MUC-21	8	2	5.98	133.2%	94.2%
U. striata	M77-1 455/MUC-21	9	1	35.72	–	–
U. striata	M77-1 455/MUC-21	10	2	12.13	73.2%	51.8%
U. striata	M77-1 565/MUC-60	4	2	30.73	133.9%	94.7%
U. striata	M77-1 553/MUC-54	2	2	8.17	140.7%	81.3%
U. striata	M77-1 459/MUC-25	2	3	95.45	52.9%	37.4%
P. limbata	M77-1 487/MUC-38	2	3	1.64	180.2%	104.0%
H. elegans	M77-1 604/MUC-74	2	7	6.87	127.3%	48.1%

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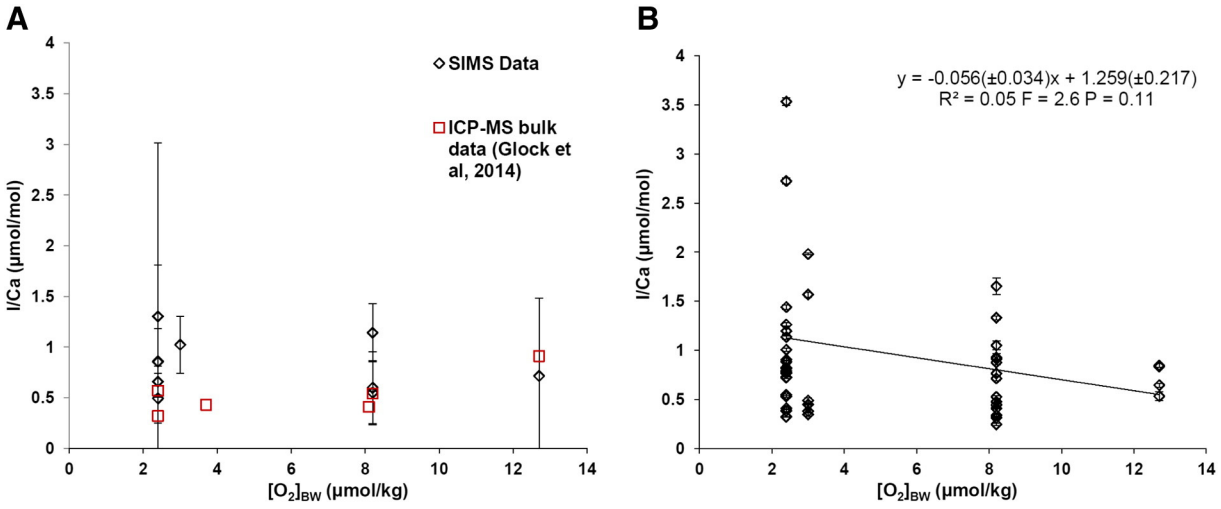

Fig. 4. A: Correlation between mean I/Ca ratios in cleaned *U. striata* specimens with $[O_2]_{BW}$. Hollow black diamonds show the SIMS data measured on individual specimens of *U. striata*. The number of measurements per specimen (N) varied between 3 and 7 (Table 4). Red squares show ICP-MS data of bulk *U. striata* samples (Glock et al., 2014). Error bars show heterogeneity (1sd). Mean precisions for the ICP-MS data were 3.2%. B: Correlation between I/Ca ratios in cleaned *U. striata* specimens with $[O_2]_{BW}$. All individual measured spots are shown. Error bars show precisions for the individual measurements (1sd). The correlation is not significant ($P = 0.11$; ANOVA). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

treatment (2.9% for the cleaned specimen and 5.5% for the uncleaned specimen). While the ^{127}I signal is relatively stable on the cleaned specimen it shows distinct variations over time on the uncleaned specimen. This probably indicates indeed iodine contaminations on a submicrometer scale which are successfully removed by oxidative cleaning. It remains speculative if these contaminations are associated with organic parts of the foraminiferal test or if small organic rich particles from the surrounding sediments were enclosed during the calcification process.

4.3. SIMS I/Ca ratios on cleaned specimens - evaluation as redox proxy

The high impact of oxidative cleaning on the I/Ca ratios measured by SIMS makes it difficult to assess to what extent the observed differences between individual cleaned specimens is caused by variations in the lattice bound iodate or by organic contamination within the tests. As shown in Fig. 4, the I/Ca ratios derived by SIMS measurements on cleaned specimens of *U. striata* are of the same order of magnitude as the results of Q-ICP-MS measurements (Glock et al., 2014) made on the same foraminiferal species from the same samples. Cleaning of the bulk samples is supposed to be far more efficient since the specimens were crushed prior to cleaning. The fact that the cleaning procedure had essentially the same effect on both SIMS and bulk-ICP-MS samples indicates that the procedure sufficiently removes the iodine contamination. This is supported by the fact that in total 8 out of 11 specimens of *U. striata* or *P. limbata*, analysed with SIMS, showed no significant difference to the bulk data from the corresponding sampling locations (for details see Section 3.3).

In contrast to the Q-ICP-MS bulk measurements, the SIMS derived I/Ca ratios in *U. striata* showed no covariation with $[O_2]_{BW}$. This is probably caused by the strong inter- and intra-test heterogeneity of iodine in foraminiferal tests. The variation of I/Ca within one specimen of *U. striata* was already higher than the complete covariation of I/Ca with $[O_2]_{BW}$ measured on the bulk samples (Fig. 4) and the correlation of the SIMS I/Ca ratios with $[O_2]_{BW}$ was not significant ($P = 0.11$; ANOVA). Yet, the previous ICP-MS bulk analyses showed a highly significant correlation ($P < 0.0001$; ANOVA). These results support the assumption that a greater variability in the bulk I/Ca ratios of *P. limbata* compared to *U. striata* was caused by the lower number specimens in a single bulk sample (~6 instead of ~20; Glock et al., 2014). It might not be possible to assess enough SIMS measurements to smooth out the inter- and intra-test heterogeneity of the I/Ca ratios for a robust $[O_2]_{BW}$ reconstruction. Nonetheless, microanalytical techniques such as SIMS and laser ablation seem to work well for other benthic foraminiferal redox proxies (e.g. Mn/Ca and Fe/Ca; Glock et al., 2012; McKay et al., 2015; Koho et al., 2015). Thus, ICP-MS bulk methods are probably much more suitable for oxygen reconstructions using foraminiferal I/Ca ratios. A convenient amount of specimens (20+) should be considered for these measurements.

A spot-by spot comparison of the SIMS I/Ca ratios on individual cleaned *U. striata* specimens is given in the appendix (Fig. A1). The fact, that there is no obvious onthogenetic trend in the I/Ca ratios on single specimens indicates that there was probably strong $[O_2]_{BW}$ variability during the lifetime of the individual specimens. The sampling locations in this study are located below the core of the OMZ, which is located ~200 to 300 m. According to a study by Paulmier and Ruiz-Pino (2009) this core is supposed to be permanently anoxic. However, the authors found a strong seasonal fluctuation in the vertical extention of the OMZ by 20% between fall and winter and an intensification of the OMZ core by an oxygen depletion of 7% between spring and summer. This might have a severe seasonal influence on $[O_2]_{BW}$ at our sampling locations.

Since *U. striata* is a shallow infaunal species it is possible that the high intra-test variability was caused by migration within the sediment column. Analysis of the onthogenetic variation at the depth where *Bolivina spissa* live within the sediments at the Peruvian OMZ showed that juvenile specimens live at shallower sediment depths whereas bigger specimens migrate deeper into the sediment column (Glock et al., 2011). If this trend would also pertain to *U. striata* and the living depth in the sediment column dominates the I/Ca ratios, there should be an obvious onthogenetic trend within the intra-test I/Ca variations. Since this is not the case, it may be possible that the strong intra-test variability is indeed caused by fluctuations in $[O_2]_{BW}$. In some specimens we observed also strong heterogeneities within different spots on a single test chamber. Chamber formation is a quite fast process which happens within 24–48 h (de Nooijer et al., 2014). Nevertheless, during each chamber formation all older chambers are also overgrown with a new layer of calcite (Erez, 2003). A distinct layering of low magnesium and high magnesium layers has been shown for *Uvigerina* species from the Peruvian

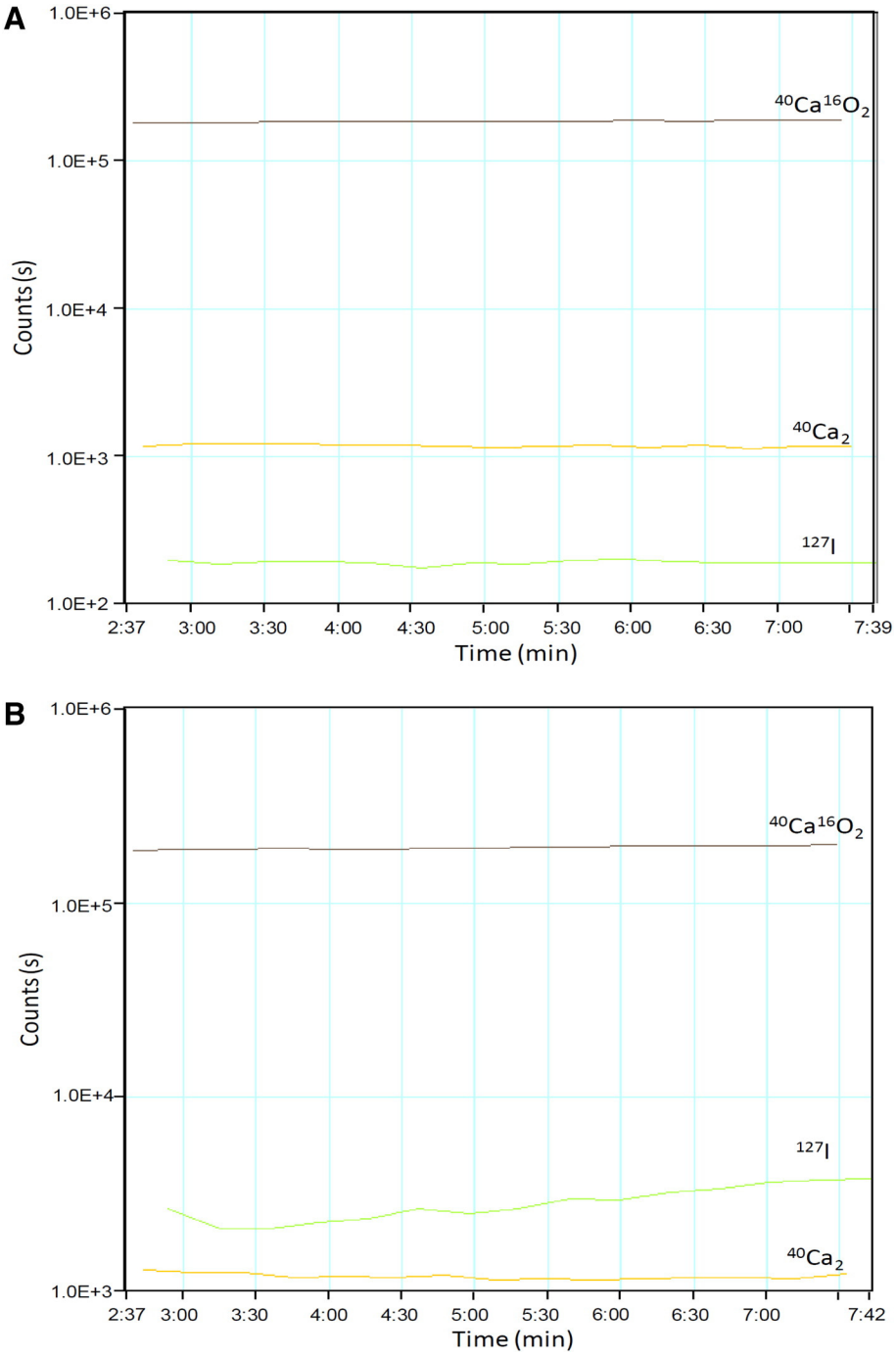

Fig. 5. A comparison between the 15 cycles of two SIMS measurements on a cleaned (A) and an uncleaned (B) specimen of *U. striata* from the same sample (M77-1455/MUC-21). Both measurements have an average precision for their treatment (2.9% for the cleaned specimen and 5.5% for the uncleaned specimen). Note: while the ^{127}I signal is relatively stable on the cleaned specimen it shows distinct variations over time on the uncleaned specimen.

OMZ. Since it was not possible to distinguish between these different layers by choosing the spot for the SIMS analyses it might be possible that the ratio of initial calcite to younger overgrown calcite was different between the different spots within the same chamber. Other effects during the biomineralisation process might as well contribute to the heterogeneities. At least a proportion of the calcium carbonate during a new chamber formation is precipitated from a cell internal vacuolized seawater reservoir (Erez, 2003), although it is highly possible that another part of the ions to form a new chamber derive from transmembrane transport and extracellular seawater (Nehrke et al., 2013). Rayleigh fractionation of the internal reservoir causes intra test heterogeneities during chamber formation. Also it might be that kinetic effects due to changes in precipitation rate influence the distribution of iodine within the test walls. Nevertheless, similar heterogeneities have been observed also for other elements in planktonic foraminiferal tests (Hathorne et al., 2009). Neither changes in precipitation rate nor changes in the cell internal reservoir alone were sufficient enough to explain these heterogeneities, which indicates, that all these processes probably contribute to the observed heterogeneities. Finally, since the effect of cleaning on the I/Ca ratios was so strong we cannot exclude that this scattering is a cause by rests of contaminations within the walls, although the results that there is no significant difference to the ICP-MS data indicate that the cleaning worked sufficiently.

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4.4. Comparison to other foraminiferal geochemical redox proxies and future implications

Since studies on foraminiferal I/Ca ratios as redox proxy are only very scarce until today (Zhou et al., 2015; Glock et al., 2014; Lu et al., 2016), other element/Ca ratios received more and more attention as redox proxies within the recent years. Probably the highest attention has been paid to Mn/Ca ratios. Studies have been done on Mn/Ca ratios of recent or cultured specimens (Reichart et al., 2003; Hathorne et al., 2009; Munsel et al., 2010; Glock et al., 2012; Groeneveld and Filipsson, 2013; Koho et al., 2015) and very promising results are available from several downcore records (Fhlaithearta et al., 2010; McKay et al., 2015). Also several other element ratios like U/Ca, Fe/Ca and V/Ca have been considered as potential redox proxies (references see Introduction). All these elements have their own advantages and disadvantages due to their different redox potentials and chemical characteristics. Solid MnO_2 in the modern Peruvian OMZ for example is already reduced within the water column due to the strongly anoxic conditions within the water column (Glock et al., 2012). Elevated Mn/Ca ratios in benthic foraminiferal tests might thus not just be limited to remobilization of reduced Mn^{2+} in the pore waters but also to the supply of Mn to the seafloor. Then again, foraminiferal V/Ca ratios might be suitable to reconstruct global extensions of oxygen depleted areas on the seafloor (Hastings et al., 1996a, b, c).

Furthermore, the different elements have their own analytical advantages/disadvantages and limitations. Elements like Mn, Fe, V or U are often associated by diagenetic coatings covering benthic formainiferal tests. Actually elevated Mn/Ca and Fe/Ca ratios are often used as an indicator for such diagenetic contaminations (Boyle, 1983; Boyle and Keigwin, 1985; Delaney, 1990; Ohkouchi et al., 1994; Lea, 2003). In regions where high concentrations of Mn^{2+} are remobilized under anoxic bottom-/pore-water conditions authigenic $MnCO_3$ might precipitate on the foraminiferal tests (Boyle, 1983; Pena et al., 2007). Since these contaminant coatings tend to form under either oxic or completely anoxic conditions Mn/Ca probably might find their most robust application under suboxic to hypoxic conditions (McKay et al., 2015). An advantage of I/Ca is that it is not influenced by such coatings (Lu et al., 2016) and might already record changes in oxygenation from oxic to suboxic conditions, due to the reduction potential of the I^-/IO_3^- system being very close to the one of O_2 in seawater. A multiproxy approach, combining all these potential proxies on the same individuals might bear a strong potential for detailed redox reconstructions from the foraminiferal microenvironment until the water column or global extention of oxygen depleted bottom waters. Nevertheless, this approach might be hampered by the volatility of iodine and thus, the special analytical treatment, compared to the other named elements, which is necessary for the I/Ca analyses (Lu et al., 2010, Glock et al., 2014).

The strong heterogeneity regarding the I/Ca ratios within the individual foraminiferal tests shown within in this study might appear discouraging but concentrations of other elements like Mn, Mg, Li, B and Ba in individual tests of planktic forams analysed by LA-ICP-MS also showed variations by a factor of 10 (Hathorne et al., 2009). This variability could not be explained by individually modeling either calcite precipitation rate, Rayleigh distillation of the calcifying reservoir or crystal structure. Nevertheless, the average Mg/Ca for each chamber generally reconstructed a Mg/Ca temperature that matched the actual temperature in the water column. This probably applies also to I/Ca ratios, considering that the bulk analyses on *U. striata* showed a significant correlation to $[O_2]_{BW}$ (Glock et al., 2014), whereas the SIMS I/Ca ratios from the study presented here did not. These facts emphasize again the advantage to use bulk samples to get a significant mean signal which averages all the individual heterogeneities. None of these element to Ca ratios is yet in the stage for robust quantitative oxygen reconstructions and a lot of work still has to be done on calibrations for the different proxies.

5. Conclusions

We developed a protocol to measure I/Ca ratios on cross-sections of individual benthic foraminiferal specimens using SIMS. In contrast to most SIMS applications it is important to work with a carbon coating instead of a gold, since the sputtered gold contains high enough concentrations of iodine to compromise the results. We tested a lab internal aragonitic coral standard as a matrix matching standard to calibrate foraminiferal I/Ca ratios. Although this coral shows a relatively high heterogeneity for a SIMS standard, the general variations within and between the foraminiferal specimens analysed within this study are orders of magnitude higher. Furthermore, we applied 108 measurements on the different fragments to statistically reduce the uncertainty due to heterogeneity of the standard (1sem = 2.1%).

I/Ca ratios were measured in individual cleaned and uncleaned benthic foraminiferal specimens. The cleaning procedure included an oxidative cleaning step. Even within the massive centre of the foraminiferal test walls, which is supposed to be free of contamination, the cleaning substantially affected the measured I/Ca ratios. In the uncleaned specimens, I/Ca ratios were ~10 to 100 times higher than in the cleaned specimens. This can most likely be explained by contaminations inside a microporous framework within the foraminiferal calcite. These contaminations are probably associated with organic matter.

Although the I/Ca ratios of the cleaned *U. striata* specimens measured by SIMS are comparable to the Q-ICP-MS measurements on *U. striata* bulk samples (Glock et al., 2014) from the same sampling sites, the intra test heterogeneity is already higher than the complete covariation to $[O_2]_{BW}$. Thus, a high number of specimens is needed to smooth these heterogeneities in order to assess robust $[O_2]_{BW}$-reconstructions. Whereas the bulk solution techniques like ICP-MS seem to work well, microanalytical techniques like SIMS or laser ablation are probably not ideal for quantitative $[O_2]_{BW}$-reconstructions using benthic foraminiferal I/Ca ratios but more to study biomineralisation and element distributions in foraminiferal tests. Due to the strong heterogeneity of the individual foraminifera a very high number of measurements would be necessary to get a comprehensive proxy calibration or for paleo applications. It may be possible, however, that the intra-test heterogeneities are indeed caused by variations in the redox-conditions over the lifetime of a single foraminiferal specimen, making it possible to reconstruct relative $[O_2]_{BW}$ changes on sub-annual time scales.

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Appendix

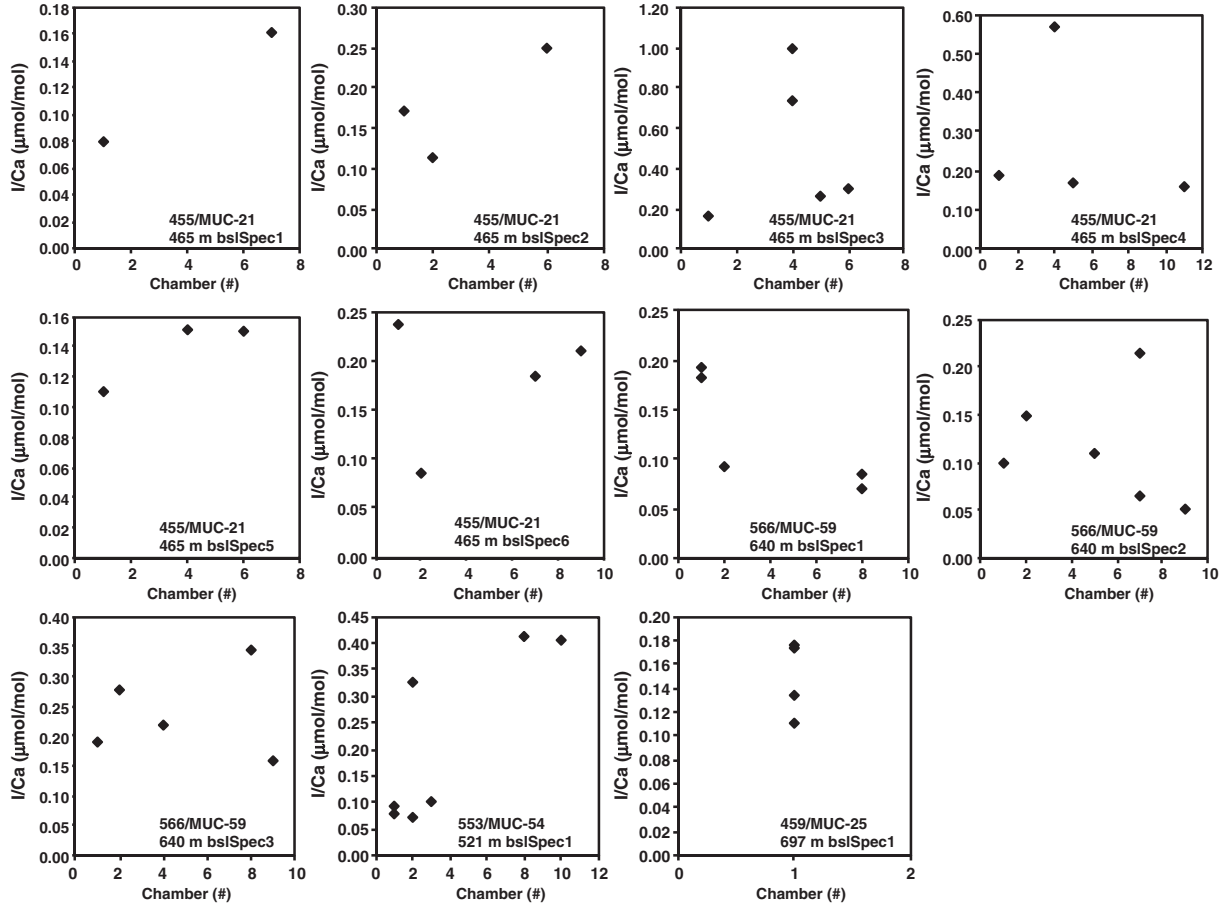

Fig. A1. Differences of I/Ca ratios between the individual chambers in cleaned *U. striata* specimens measured by SIMS. Chamber no. 1 represents the oldest chamber (the proloculus). Note that there is no clear onthogenetic trend.

Table A1
$^{127}I/^{80}Ca_2$ count-ratios for individual measurements on the different fragments of the coral used as matrix matching reference standard in this study.

Coral fragment (#)	$^{127}I/^{80}Ca_2$ (counts/counts)	Precision (1sd)
1	0.61	0.69%
1	0.86	0.87%
1	0.66	0.82%
1	0.52	0.79%
1	0.53	0.49%
1	0.63	0.50%
1	0.67	1.08%
1	0.62	1.46%
2	0.54	1.39%
2	0.56	1.11%
2	0.59	0.86%
2	0.55	1.31%
2	0.52	1.43%
2	0.66	0.58%
2	1.00	0.75%
2	0.48	1.22%
2	0.60	1.38%
2	0.60	1.52%
2	0.61	0.72%
3	0.55	0.81%
3	0.65	1.12%
3	0.57	1.14%
3	0.60	1.67%
3	0.49	0.76%
3	0.59	1.47%
3	0.78	1.56%
3	0.56	1.12%
4	0.68	0.52%
4	0.59	1.32%
4	0.51	0.74%
4	0.88	1.02%
4	0.75	0.98%
4	0.85	1.93%
4	0.72	1.54%
4	0.63	1.20%
4	0.69	2.14%
5	0.53	2.25%
5	0.49	1.17%
5	0.48	1.84%
5	0.64	3.82%
5	0.50	0.98%
5	0.50	0.98%
5	0.51	0.95%
5	0.56	1.77%
5	0.44	1.65%
5	0.60	2.95%
5	0.41	1.03%
5	0.47	1.23%
5	0.46	1.01%
5	0.41	2.17%
5	0.52	1.38%
5	0.51	2.64%

Table A1 (*continued*)

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Table A1 (*continued*)

Coral fragment (#)	$^{127}I/^{80}Ca_2$ (counts/counts)	Precision (1sd)
5	0.50	1.36%
5	0.56	1.50%
5	0.45	1.95%
5	0.43	2.33%
5	0.47	2.93%
5	0.62	1.22%
5	0.41	0.76%
5	0.48	1.64%
5	0.48	1.65%
5	0.49	1.54%
5	0.42	2.16%
5	0.49	1.38%
5	0.44	1.72%
5	0.64	1.38%
5	0.44	1.84%
5	0.55	2.39%
5	0.52	2.30%
5	0.44	1.95%
5	0.66	1.77%
5	0.45	1.48%
5	0.52	1.05%
6	0.66	1.50%
6	0.47	1.70%
6	0.48	1.76%
6	0.41	1.51%
6	0.42	2.29%
6	0.50	2.02%
6	0.48	2.30%
6	0.44	2.03%
6	0.54	1.45%
6	0.46	1.88%
6	0.49	1.53%
6	0.42	1.20%
6	0.55	1.99%
6	0.51	1.62%
6	0.37	1.96%
6	0.36	2.40%
6	0.41	2.71%
6	0.40	1.23%
6	0.48	1.35%
6	0.51	0.81%
6	0.43	1.31%
6	0.49	2.24%
6	0.50	2.00%
6	0.49	1.82%
6	0.70	2.05%
6	0.68	1.99%
6	0.50	0.96%
6	0.44	1.67%
6	0.52	2.63%
6	0.69	2.09%
6	0.44	1.83%
6	0.44	1.86%
6	0.53	1.20%
6	0.52	1.45%
6	0.55	1.37%

Table A2
All I/Ca ratios from the individual SIMS measurements, precisions and accuracies for all foraminiferal specimens at the different sampling sites. Precisions just include the standard deviation from the determination of the count rates, while the accuracies were calculated with an error propagation using the heterogeneity of the standard (1sem) and standard deviation of the count rates on this measurement spot. The number (#) of the specimen is used to distinguish between different specimens from the same sample.

Species	Sampling site	Specimen (#)	Cleaned?	I/Ca (μmol/mol)	Precision (1sd)	Accuracy (1sd)
U. striata	M77-1 455/MUC-21	1	yes	0.38	3.7%	4.3%
U. striata	M77-1 455/MUC-21	1	yes	0.77	1.0%	2.3%
U. striata	M77-1 455/MUC-21	1	yes	0.32	1.4%	2.5%

Table A2 (*continued*)

Species	Sampling site	Specimen (#)	Cleaned?	I/Ca (μmol/mol)	Precision (1sd)	Accuracy (1sd)
U. striata	M77-1 455/MUC-21	2	yes	1.20	4.1%	4.6%
U. striata	M77-1 455/MUC-21	2	yes	0.82	2.9%	3.6%
U. striata	M77-1 455/MUC-21	2	yes	0.54	1.3%	2.5%
U. striata	M77-1 455/MUC-21	3	yes	0.79	1.8%	2.8%
U. striata	M77-1 455/MUC-21	3	yes	3.53	1.2%	2.4%
U. striata	M77-1 455/MUC-21	3	yes	4.77	1.4%	2.5%
U. striata	M77-1 455/MUC-21	3	yes	1.26	1.3%	2.5%
U. striata	M77-1 455/MUC-21	3	yes	1.44	1.5%	2.6%
U. striata	M77-1 455/MUC-21	4	yes	0.90	1.5%	2.6%
U. striata	M77-1 455/MUC-21	4	yes	2.73	1.2%	2.4%
U. striata	M77-1 455/MUC-21	4	yes	0.77	1.2%	2.4%
U. striata	M77-1 455/MUC-21	4	yes	0.81	1.7%	2.7%
U. striata	M77-1 455/MUC-21	5	yes	0.53	1.3%	2.5%
U. striata	M77-1 455/MUC-21	5	yes	0.72	1.1%	2.4%
U. striata	M77-1 455/MUC-21	5	yes	0.73	2.1%	3.0%
U. striata	M77-1 455/MUC-21	6	yes	1.01	1.6%	2.6%
U. striata	M77-1 455/MUC-21	6	yes	0.88	1.6%	2.6%
U. striata	M77-1 455/MUC-21	6	yes	0.41	2.1%	3.0%
U. striata	M77-1 455/MUC-21	6	yes	1.14	2.2%	3.0%
U. striata	M77-1 565/MUC-60	1	yes	0.48	4.8%	5.2%
U. striata	M77-1 565/MUC-60	1	yes	0.31	2.2%	3.0%
U. striata	M77-1 565/MUC-60	1	yes	1.03	13.1%	13.3%
U. striata	M77-1 565/MUC-60	1	yes	0.71	3.2%	3.8%
U. striata	M77-1 565/MUC-60	1	yes	0.52	2.5%	3.3%
U. striata	M77-1 565/MUC-60	1	yes	0.25	3.8%	4.3%
U. striata	M77-1 565/MUC-60	2	yes	0.91	2.0%	2.9%
U. striata	M77-1 565/MUC-60	2	yes	1.33	1.5%	2.6%
U. striata	M77-1 565/MUC-60	2	yes	1.65	5.1%	5.5%
U. striata	M77-1 565/MUC-60	2	yes	0.76	4.4%	4.9%
U. striata	M77-1 565/MUC-60	2	yes	1.05	4.4%	4.9%
U. striata	M77-1 565/MUC-60	3	yes	0.93	4.4%	4.9%
U. striata	M77-1 565/MUC-60	3	yes	0.88	2.8%	3.5%
U. striata	M77-1 565/MUC-60	3	yes	0.44	4.1%	4.6%
U. striata	M77-1 565/MUC-60	3	yes	0.41	1.7%	2.7%
U. striata	M77-1 565/MUC-60	3	yes	0.34	2.7%	3.4%
U. striata	M77-1 553/MUC-54	1	yes	1.95	1.9%	2.8%
U. striata	M77-1 553/MUC-54	1	yes	0.45	1.7%	2.7%
U. striata	M77-1	1	yes	0.38	1.7%	2.7%

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Table A2 (*continued*)

Species	Sampling site	Specimen (#)	Cleaned?	I/Ca (μmol/mol)	Precision (1sd)	Accuracy (1sd)
	553/MUC-54					
U. striata	M77-1 553/MUC-54	1	yes	0.49	2.5%	3.3%
U. striata	M77-1 553/MUC-54	1	yes	1.57	1.6%	2.6%
U. striata	M77-1 553/MUC-54	1	yes	1.98	1.3%	2.5%
U. striata	M77-1 553/MUC-54	1	yes	0.35	2.0%	2.9%
U. striata	M77-1 459/MUC-25	1	yes	0.53	2.8%	3.5%
U. striata	M77-1 459/MUC-25	1	yes	0.85	5.3%	5.7%
U. striata	M77-1 459/MUC-25	1	yes	0.64	2.8%	3.5%
U. striata	M77-1 459/MUC-25	1	yes	0.83	2.4%	3.2%
P. limbata	M77-1 487/MUC-38	1	yes	1.91	0.6%	2.2%
P. limbata	M77-1 487/MUC-38	1	yes	1.39	0.9%	2.3%
P. limbata	M77-1 487/MUC-38	1	yes	1.87	0.9%	2.3%
P. limbata	M77-1 487/MUC-38	1	yes	1.80	0.8%	2.3%
P. limbata	M77-1 487/MUC-38	1	yes	1.25	1.0%	2.3%
H. elegans	M77-1 604/MUC-74	1	yes	2.58	0.5%	2.2%
H. elegans	M77-1 604/MUC-74	1	yes	1.93	0.5%	2.2%
H. elegans	M77-1 604/MUC-74	1	yes	1.69	1.7%	2.7%
H. elegans	M77-1 604/MUC-74	1	yes	1.60	1.1%	2.4%
H. elegans	M77-1 604/MUC-74	1	yes	0.69	1.0%	2.3%
H. elegans	M77-1 604/MUC-74	1	yes	1.34	0.9%	2.3%
H. elegans	M77-1 604/MUC-74	1	yes	1.88	1.1%	2.4%
H. elegans	M77-1 604/MUC-74	1	yes	0.14	3.8%	4.3%
H. elegans	M77-1 604/MUC-74	1	yes	2.47	3.9%	4.4%
H. elegans	M77-1 604/MUC-74	1	yes	1.01	3.4%	4.0%
H. elegans	M77-1 604/MUC-74	1	yes	1.61	1.2%	2.4%
H. elegans	M77-1 604/MUC-74	1	yes	0.39	2.5%	3.3%
H. elegans	M77-1 604/MUC-74	1	yes	0.44	1.3%	2.5%
H. elegans	M77-1 604/MUC-74	1	yes	1.04	2.3%	3.1%
U. striata	M77-1 455/MUC-21	7	no	27.69	1.2%	2.4%
U. striata	M77-1 455/MUC-21	7	no	30.10	0.6%	2.2%
U. striata	M77-1 455/MUC-21	8	no	0.35	2.8%	3.5%
U. striata	M77-1 455/MUC-21	8	no	11.61	5.6%	6.0%
U. striata	M77-1 455/MUC-21	9	no	35.72	18.1%	18.2%
U. striata	M77-1 455/MUC-21	10	no	18.41	2.2%	3.0%
U. striata	M77-1 455/MUC-21	10	no	5.85	2.9%	3.6%
U. striata	M77-1 565/MUC-60	4	no	59.84	14.1%	14.3%
U. striata	M77-1 565/MUC-60	4	no	1.63	1.5%	2.6%
U. striata	M77-1 553/MUC-54	2	no	131.18	3.1%	3.7%

Table A2 (*continued*)

Species	Sampling site	Specimen (#)	Cleaned?	I/Ca (μmol/mol)	Precision (1sd)	Accuracy (1sd)
U. striata	M77-1 553/MUC-54	2	no	59.73	4.6%	5.1%
U. striata	M77-1 459/MUC-25	2	no	2.21	10.8%	11.0%
U. striata	M77-1 459/MUC-25	2	no	21.43	6.2%	6.6%
U. striata	M77-1 459/MUC-25	2	no	0.87	4.2%	4.7%
P. limbata	M77-1 487/MUC-38	2	no	3.08	1.6%	2.6%
P. limbata	M77-1 487/MUC-38	2	no	55.16	1.8%	2.8%
P. limbata	M77-1 487/MUC-38	2	no	3.08	0.9%	2.3%
H. elegans	M77-1 604/MUC-74	2	no	6.03	0.8%	2.3%
H. elegans	M77-1 604/MUC-74	2	no	2.95	1.0%	2.3%
H. elegans	M77-1 604/MUC-74	2	no	2.61	2.1%	3.0%
H. elegans	M77-1 604/MUC-74	2	no	26.54	2.9%	3.6%
H. elegans	M77-1 604/MUC-74	2	no	3.78	1.7%	2.7%
H. elegans	M77-1 604/MUC-74	2	no	3.10	0.8%	2.3%
H. elegans	M77-1 604/MUC-74	2	no	3.10	0.8%	2.3%

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