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I / Ca ratios in benthic foraminifera from the Peruvian oxygen minimum zone: analytical methodology and evaluation as proxy for redox conditions

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Abstract

In this study we explore the correlation of I / Ca ratios in three calcitic and one aragonitic foraminiferal species. I / Ca ratios are evaluated as possible proxies for changes in ambient redox conditions across the Peruvian oxygen minimum zone to the ambient oxygen concentrations in the habitat of the foraminiferal species studied. We test cleaning and measurement methods to determine I / Ca ratios in benthic foraminifera from the Peruvian oxygen minimum zone. All species show a positive trend in their I / Ca ratios as a function of higher oxygen concentrations and these trends are all statistically significant except for the aragonitic species *Hoeglundina elegans*. The most promising species appears to be *Uvigerina striata* which shows a highly statistically significant correlation between I / Ca ratios and bottom water (BW) oxygenation ($\mathrm{I/Ca} = 0.032(\pm 0.004)[\mathrm{O_2}]_{\mathrm{BW}} + 0.29(\pm 0.03)$, $R^2 = 0.61$, $F = 75$, $P < 0.0001$). Although I / Ca ratios in benthic foraminifera might prove to be a valuable proxy for changing redox-conditions the iodine volatility in acidic solutions, the species dependency of I / Ca–$[\mathrm{O_2}]_{\mathrm{BW}}$ correlations, and the individual variability of single tests severely interfere with the observed I / Ca–$[\mathrm{O_2}]_{\mathrm{BW}}$ relationship.

1 Introduction

Tropical oxygen minimum zones (OMZs) are the most important regions of low oxygen in the recent ocean and the nutrient cycling in these regions influences the global ocean. This is particularly important because model calculations predict that the ocean will progressively loose oxygen over the next 200 years (Bopp et al., 2002; Matear and Hirst, 2003; Joos et al., 2003) with adverse consequences for marine life and fisheries. To some extent oxygen loss is related to oceanic warming but the main reason is the decreased ocean ventilation due to circulation changes related to anthropogenic induced climate change. Indeed a 50 year time series of dissolved oxygen concentrations reveals vertical expansion of the intermediate depth OMZs in the eastern equatorial Atlantic and the equatorial Pacific during this time interval (Stramma et al., 2008). One of the most distinct OMZs is located at the Peruvian upwelling cell. Although coastal upwelling cells cover only about 0.14 % of the global ocean (Baturin, 1983; Wolf, 2002) in 2007 15.5 million tons of fish has been caught by commercial fisheries in eastern boundary upwelling ecosystems (Fréon et al., 2009) corresponding to ∼ 17 % of the global catches (91.2 million tons; source: FAO FishStat, 2013). The Peruvian upwelling cell alone, contributed about 8 % of global fish catches (7.2 million tons; source: FAO FishStat, 2013). Therefore, if the oxygen depletion in this area would expand, habitats currently rich in pelagic fish would be endangered in the future.

Reconstruction of geographic extent and the magnitude of OMZs in the past might help us to estimate future changes in oxygenation and to estimate the anthropogenic role in the recent OMZ expansions. For such long term predictions a geochemical proxy for quantitative oxygen reconstruction in OMZs would be highly desirable. The aim of this study is to evaluate I / Ca ratios in benthic foraminifera from the Peruvian OMZ as a possible oxygenation-proxy. Element/Ca ratios in foraminiferal calcite have already been extensively used for reconstruction of physical and chemical properties. One of the most widespread and well established methods is the temperature reconstruction via the Mg/Ca ratio (Nürnberg et al., 1996; Rosenthal et al., 1997; Hastings et al., 1998; Lea et al., 1999; Elderfield and Ganssen, 2000; Lear et al., 2002). Some elemental ratios in foraminiferal calcite have already been evaluated as proxies for redox-conditions (V/Ca: Hastings et al., 1996a, b, c; U/Ca: Russel et al., 1994). However, the U/Ca ratio seems to be strongly affected by the carbonate ion concentration (Russel et al., 2004; Yu et al., 2008). Furthermore, Mn/Ca ratios have widely been used to trace for diagenetic alteration of the samples but there is still a disagreement of the acceptable Mn/Ca ratio (Boyle, 1983; Boyle and Keigwin, 1985, 1986; Delaney, 1990; Ohkouchi et al., 1994; Lea, 2003). Nevertheless, in the absence of diagenetic alteration the Mn/Ca ratio might also be a valuable redox proxy (Fhlaitheartha et al., 2010; Glock et al., 2012). This is supported by culture experiments on *Ammonia tepida* which showed that Mn is incorporated into the test calcite proportional to the concentration in the ambient water (Munsel et al., 2010).

Iodine is highly redox-sensitive and easily reduced to Iodite (I^-) which is easily oxidized (see the "200 years of iodine research" review by Küpper et al., 2011). From the two most thermodynamically stable inorganic forms of dissolved iodine, (iodide, e.g. I^-; iodate, e.g. IO_3^-) (Wong and Brewer, 1977) only IO_3^- seems to be incorporated into carbonates (Lu et al., 2010). Precipitation experiments by Lu et al. (2010) showed that the I / Ca ratios in synthetic calcite are a linear function of the IO_3^- concentrations in the ambient water, while I^- concentrations did not affect the I / Ca ratios at all. Thus, it was proposed that iodate is partially substituting the carbonate ions in the calcite lattice. Since the I^-/IO_3^- system has a reduction potential which is close to that of O_2/H_2O it should be highly sensitive to oxygen depletion in the oceans (Rue et al., 1997; Harris, 2006; Brewer and Peltzer, 2009; Lu et al., 2010). In the Arabian Sea OMZ, I^- concentration peaks in the core OMZ where oxygen is most depleted (Farrenkopf and Luther, 2002). The latitudinal distribution of IO_3^- in the Atlantic shows a trend to higher concentrations in high latitudes and generally lower concentrations closer to the equator (Truesdale et al., 2000). Lu et al. (2010) suggested that these trends are correlated with the different oxygen solubility at different temperatures and thus, that the IO_3^- concentrations in the Atlantic are directly correlated to the oxygen concentrations. Indeed at higher latitudes in the Atlantic IO_3^- can reach the concentration of the total iodine at high latitudes, while IO_3^- concentrations may drop during an extreme hypoxic event in the Benguela Upwelling system (Truesdale et al., 2000; Truesdale and Bailey, 2000). The I^- peaks in the core of the Arabian Sea OMZ can reach the total iodine concentrations suggesting a quantitative reduction of IO_3^- to I^- (Farrenkopf and Luther, 2002). Furthermore, the I / Ca ratios decrease in bulk carbonates and belemnites from the early Toarcian- and Cenemonian–Turonian oceanic anoxic events (OAEs), interpreted as a depletion of IO_3^- due to the strongly reducing conditions during those time intervals (Lu et al., 2010). All these results imply that I / Ca ratios in marine carbonates might be a valuable proxy for oxygen concentrations in the ancient ocean.

In our study we determined the I / Ca ratios in four different benthic foraminiferal species from the Peruvian OMZ with inductively-coupled-plasma-mass-spectrometry (ICP-MS). The samples included two shallow infaunal and two epifaunal living species of which three form calcitic (*Uvigerina striata*, *Uvigerina peregrina*, *Planulina limbata)* and one aragonitic (*Hoeglundina elegans*) tests. Cleaning protocols were modified after Barker et al. (2003) and Lu et al. (2010) to customize the I / Ca analyses to small amounts of foraminiferal carbonate. Main changes to standard cleaning protocols for foraminifera were the use of PFA instead of PE microcentrifuge vials and the application of more rigorous oxidative cleaning to avoid contamination by organically bound iodine. The measured I / Ca ratios are then correlated to bottom water oxygen concentrations $[O_2]_{BW}$ for the calibration of I / Ca ratios in benthic foraminiferal calcite as a possible paleo-oxygen-proxy. Bottom water oxygenation usually has a strong influence on the oxygen gradient and penetration depth into the pore waters (Morford et al., 2005), which justifies also use also infaunal foramnifera for this study, although this might complicate a quantitative O_2 reconstruction. In an eutrophic environment like the Peruvian OMZ where organic matter at the seafloor is available in excess (Mallon et al., 2012) an overprint by the organic flux is not to be expected.

2 Material and methods

2.1 Sampling procedure

During R.V. *Meteor* Cruises M77/1 and M77/2 (October and November 2008) nine sediment cores from the Peruvian OMZ were recovered with a video-guided multiple corer for foraminiferal analyses in the present study (Table 1). The coring tubes were of 100 mm inner diameter. Immediately after retrieval, one multicorer tube was transferred to a constant temperature (4 °C) laboratory. Supernatant water of the core was carefully removed. Then the core was gently pushed out of the multicorer tube and cut into 10-mm-thick slices for benthic foraminiferal analysis. The samples were transferred either to Whirl-Pak™ plastic bags or plastic bottles, transported at a temperature of 4 °C and finally stored at 4 °C at GEOMAR, Kiel, Germany.

2.2 Foraminiferal studies

The foraminiferal samples were washed through stacked sieves with mesh sizes of 63 µm. The > 63 µm size fractions were collected in ethanol to prevent samples from dissolution and dried at 50 °C. They were further subdivided into the grain-size fractions of 63–125, 125–250, 250–315, 315–355, 355–400, and > 400 µm. Specimens of *Uvigerina striata*, *Uvigerina pergrina*, *Planulina limbata* and *Hoeglundina elegans* were picked from the > 400 µm size fractions. Light micrographs of the different species were recorded with a MiniPixie MPX2051UC CCD-Camera (AOS Technologies™) through the objectives 1-6233 and 1-6010 of the company Navitar™. Because all individuals of *Uvigerina peregrina* from the core-top have been consumed during chemical digestion for later analyses of I / Ca ratios the individual for the light micrograph was picked from a random deeper sample (27–28 cm) of core M77/2 St. 47-3. Pictures of all species are shown in Fig. 1. The species *U. striata* and *U. pergrina* live shallow infaunal within the sediments in a pore water dominated environment while *P. limbata* and *H. elegans* live epifaunal on top of the sediments in a bottom water dominated environment.

2.3 Cleaning methods

The number of specimens used for the analyses varied from 6 to 25 as a function of the species and the availability of specimens in the sample (see Table 2). The tests were gently crushed between two glass plates. The test fragments were transferred into PFA microcentrifuge-vials and rinsed three times with reverse osmosis water (ROW) having a conductivity of 0.055 µS cm^{-1} (Elga™ PURELAB Ultra). After each rinsing step the vials were put into a ultrasonic bath for 20 s. Afterwards the vials were rinsed three times with ethanol and put into the supersonic bath for 1 min after each rinsing step. The vials were rinsed again two times with ROW 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 put into a waterbath at 92 °C for 15 min. During the oxidative cleaning samples were taken out of the waterbath in 5 min intervals and gas bubbles were removed by snapping against the bottom of the vials. After three 5 min intervals the vials were rinsed with ROW and another 350 µL of the fresh oxidative reagent were added. The oxidative cleaning step was repeated for another 15 min (including the removal of air bubbles at 5 min intervals). After another 20 s in the ultrasonic bath the vials were rinsed two times with ROW to remove residues of the oxidative reagent. The test fragments were transferred into clean vials with a pipette. Into each vial 250 µL 0.001 M HNO_3 (suprapure, Roth™) were added. The vials were put into the ultrasonic bath for 20 s. The extremely dilute acid solution was removed and the vials were rinsed three times with ROW. The samples were dissolved in 0.075 M HNO_3 (suprapure, Roth™), centrifuged and supernatant transferred into clean vials leaving a residue of 50 µL in the centrifuge vial. Afterwards tetramethylamoniumhydroxide (TMAH, 25 % in H_2O, Trace-SELECT, impurities: $\leq 10\,\mu g\,kg^{-1}$ total iodine, Sigma Aldrich™) solution was added to each sample to reduce loss of volatile I. The volume of 0.075 M HNO_3 for dissolution and TMAH varied due to the different sample sizes (see Table 2).

2.4 Matrix matching carbonate standards

Three different carbonate standards were used to assure reproducibility between different analytical sessions. These standards included the external aragonitic coral reference material JCp-1 (I / Ca ratios reported by Lu et al., 2010 and Chai and Muramatsu, 2007), a lab internal pure aragonite and a lab internal pure calcite standard. These three references were chosen to test the reproducibility of relative differences in the I / Ca ratios for each measurement session. Furthermore they cover a broad ranges of I / Ca ratios (e.g. high in the JCp-1 and very low in the reference calcite). Before analyses on each measurement day, fresh reference standard solutions were prepared from the solid powders to minimize loss of volatile iodine. Usually 20 mL of 50 ppm Ca-solutions were mixed by 2.5 mg carbonate, 400 µL of 25 % TMAH, 150 µL concentrated HNO_3 and 19.45 mL ROW. In some cases 100 mL solutions were prepared using 5 times of these amounts.

2.5 Quadrupole ICP-MS analyses

The analyses were performed on an Agilent 7500cx Quadrupole ICP-MS. Operation conditions are listed in Table 3. Instrument sensitivity was optimised by using a 1 ppb Li-Y-Tl-Ce-Mg-Co standard solution before the measurements. For sample introduction a micro-autosampler (Cetac ASX 100) coupled to a PFA self-aspiration nebulizer fitted to a glass spray chamber was used. Due to the small available sample volume (typically < 500 µL) the low sample uptake rate of the self-aspirating system was an important feature during the analyses. The integration times were 0.3 s for ^{43}Ca, 0.3 s for ^{44}Ca and 6.0 s for ^{127}I with 5 repetition runs.

For the preparation of the standards 170 mg solid KIO_3 (suprapur, Sigma Aldrich™) were dissolved in 97.25 mL ROW, 2 mL of 25 % TMAH and 0.75 mL conc. HNO_3 (1000 ppm of Iodine). Furthermore a 1000 ppm Ca solution was prepared by dissolving 250 mg solid $CaCO_3$ (suprapur, Sigma Aldrich™) in 99.25 mL ROW and 0.75 mL conc. HNO_3. Solid $CaCO_3$ was used for closest matching of the sample matrix. These solutions were used to prepare a succession of working standards via three steps of pre-dilution. Concentrations for standards and pre-dilutions are given in Table 4. Again, on each day all these solutions were prepared freshly before the analyses. The working standards were prepared directly in the vials which were later used for sample injection. Samples were analysed directly after the cleaning procedure to prevent loss of volatile Iodine even after trapping with TMAH. For the analyses samples were diluted to ~ 50 ppm Ca to keep the matrix consistent. Samples were diluted with a matrix matching solution prepared from 19.45 mL ROW, 400 µL of 25 % TMAH and 150 µL conc. HNO_3. (e.g. 0.5 % TMAH/0.5 % HNO_3). The standard row was measured at least after every 10 samples to correct for instrumental drift. The I / Ca ratio of the internal calcite reference standard was below the detection limit in every measurement session ($n = 70$). This indicates that the procedural blank for preparation of the standard solutions was also below the detection limit.

3 Results

3.1 Reproducibility

All determined I / Ca ratios are reported in the appendix (Tables A1 and A2). Summaries of mean values for the different reference standards and foraminiferal samples of the same species and sampling site are listed in Table 5. Figure 2 shows a comparison of I / Ca ratios measured in an aliquot of untreated JCp-1 and an aliquot of the same JCp-1 standard homogenized in a mortar. The reproducibility of the homogenized JCp-1 (3.82 ± 0.08 μmol mol^{-1}; $n = 60$; $1\sigma = 2.0\,\%$) was one order of magnitude higher than in the untreated aliquot (I/Ca = 4.05 ± 0.96 μmol mol^{-1}; $n = 100$; $1\sigma = 24\,\%$). These results strongly indicate inhomogenities within the JCp-1 in respect to the I / Ca ratios. As a consequence of these results only homogenized aliquots are used as reference standards in this study.

During each measurement session I / Ca ratios of freshly prepared solutions of the reference standards (the external JCp-1 and the internal aragonite and the calcite) were repeatedly measured to assure the reproducibility of the method between different days. Additionally, every day I / Ca ratios of one (in one case two) sample(s) of 25 *U. striata* specimens from the same sampling location (M77-1 565/MUC-60) were measured (Fig. 3). The I / Ca ratios were 3.82 ± 0.08 μmol mol^{-1} ($n = 60$; $1\sigma = 2.0\,\%$) for the JCp-1, 2.59 ± 0.09 μmol mol^{-1} ($n = 52$; $1\sigma = 3.5\,\%$) for the aragonite and 0.54 ± 0.04 μmol mol^{-1} ($n = 28$; 5 different assemblages of 25 specimens each; $1\sigma = 6.6\,\%$) for the internal *U. striata* reference samples. The mean precision for single I / Ca determinations for these standards (including the standard deviations of I and Ca counts between the different measurement cycles and the error of the calibration function) ranged from ~1.29 % ($N = 60$) for the JCp-1 to ~2.15 % ($N = 28$) for the *U. striata* samples.

3.2 Volatility of iodine

Six different foraminiferal samples from 3 different species were measured directly after the cleaning procedure and one day after dissolution to test the effects of iodine volatility on the measured I / Ca ratios (Fig. 4). For this the samples were stored in PFA microcentrifuge vials after dissolution. All samples show lower I / Ca ratios one day after dissolution except for one measurement of sample A1 where the I / Ca ratio was slightly higher than the directly measured samples. The exceptionally high standard deviation of this value (18 %) and the Grubb's outlier test indicate this data point is an outlier. The mean iodine loss after one day varied between ~6 % and ~22 % (excluding the outlier).

3.3 Correlation between foraminiferal I / Ca ratios and oxygenation

The correlation between the I / Ca ratios in tests of four different benthic foraminiferal species and $[O_2]_{BW}$ are shown in Fig. 5. The I / Ca in all species tend to be positively correlated with $[O_2]_{BW}$. The correlation is highly significant ($P < 0.0001$; ANOVA) for *U. striata*, significant for *P. limbata* ($P = 0.009$; ANOVA) but not significant for *H. elegans* ($P = 0.1000$; ANOVA). The epifaunal species *P. limbata* shows the highest I / Ca ratios (1.03–2.20 μmol mol^{-1}) followed by the shallow infaunal species *U. striata* (0.28–0.91 μmol mol^{-1}). The epifaunal aragonitic species *H. elegans* has the lowest I / Ca ratios (0.12–0.31 μmol mol^{-1}). The I / Ca ratio of *U. peregrina* is much lower than the I / Ca ratio of *U. striata* from the same sampling site (0.39 μmol mol^{-1} compared to 0.91 μmol mol^{-1}; M77/1-459/MUC-25; 697 m). Neither regression nor ANOVA were calculated for *U. peregrina* due to the low amount of data points ($n = 2$).

4 Discussion

4.1 Methodical issues: reproducibility and iodine volatility

The significant differences in reproducibility of the I / Ca ratio of untreated vs. homogenized JCp-1 aliquots (Fig. 2) indicate that heterogeneities may have a huge impact on the precision of the iodine measurements. Even within one session by measuring the same solution out of the same beaker, the I / Ca ratio of the untreated JCp-1 is reproducible only within 24 %. The I / Ca-reproducibility of the homogenized JCp-1 ($n = 60$; $1\sigma = 2.0\,\%$) is in the same order of magnitude as reported earlier by (Lu et al., 2010: $n = 8$; $1\sigma = 1.4\,\%$; Chai and Muramatsu, 2007: $n = 5$; $1\sigma = 3.7\,\%$). Apart from that there are problems with the accuracy of the standards because the I / Ca ratio of the homogenized JCp-1 reported here ($3.82 \pm 0.08\,\mu\text{mol mol}^{-1}$) is lower than the I / Ca ratios of the JCp-1 reported in the literature (Lu et al., 2010: $4.27 \pm 0.06\,\mu\text{mol mol}^{-1}$; Chai and Muramatsu, 2007: $4.33 \pm 0.16\,\mu\text{mol mol}^{-1}$). A possible explanation might be that volatile Iodine adsorbed to the surface of the JCp-1 powder has been mobilized and removed during the grinding process since the mean I / Ca ratio of the untreated JCp-1 aliquot is closer to the values reported in the literature. Another possibility is that different aliquots of the JCp-1 which show a difference in the I / Ca ratios have been used in the different labs. Nevertheless, the reproducibility of all our carbonate-reference standards (except the JCp-1 before homogenization) indicate that drift effects are negligible between the different measurement sessions.

Iodine is a volatile element which could be stabilized by adding TMAH, which also reduces the memory effect during ICP-MS measurement (Muramatsu and Wedepohl, 1998; Tagami and Uchida, 2005; Lu et al., 2010). The fact that we observe a strong decrease of the I / Ca ratios after one day of sample dissolution supports the requirement of an immediate measurement directly after sample dissolution. Although a similar matrix was used for the samples after dissolution (e.g. 0.5 % TMAH) the results presented here differ from the observations of Lu et al. (2010). The author tested the iodine volatility in such a matrix over 2 months, did not observe a strong loss in iodine after 30 days and concluded that iodine loss within two days should negligible. Despite the volatility problem the well reproducible I / Ca ratio in 5 different samples of 25 *U. striata* specimens (I/Ca = 0.54 ± 0.04 µmol mol^{-1}; 1σ = 6.6 %) from the same location (M77-1 565/MUC-60) which were cleaned, dissolved and measured in four different sessions (on four different days) shows that the results are robust providing that samples are measured within two hours after dissolution.

4.2 Foraminiferal I / Ca ratios as redox-proxy

Our results indicate that I / Ca ratios in benthic foraminifera might prove to be a valuable proxy for oxygen in the adjacent waters. This is supported by the observation that all analysed species show a positive correlation for the I / Ca–$[O_2]_{BW}$ relationship. For two of three species the correlations are significant (one even highly significant). Only the aragonitic species *H. elegans* shows no significant correlation. The fact that *P. limbata*, which lives epifaunal, shows much higher I / Ca ratios than the other two calcitic infaunal species also supports the trend of higher I / Ca ratios under elevated oxygenation: oxygen concentrations are typically higher in the bottom waters compared to the pore waters. In general, our results support and confirm the earlier observations and conclusions of Lu et al. (2010). Furthermore, the variability of foraminiferal I / Ca ratios by location (e.g. $[O_2]_{BW}$) or species is much higher than the uncertainties discussed in Sect. 4.1, which indicates that the trends in the I / Ca–$[O_2]_{BW}$ relationships are robust in respect to the technical issues.

Nevertheless, there are some pitfalls which must be considered in this discussion. The importance of methodological issues has been discussed separately above. Another important point is the high variability of I / Ca ratios between different samples of the same location in some species which are further amplified by analytical uncertainties. The amount of foraminifera available for analysis is often limited in geological samples. Thus, if monospecific samples are analysed the amount is often limited to one sample. Additionally, the amount of measurements of such a sample is limited by the volume of sample solution consumed by the mass spectrometer and the circumstance that a constant concentration of 50 ppm Ca is needed to minimize matrix related drifts and consider enough iodine for the analyses. Consequently, some samples are limited to one analysis.

Furthermore, the fact that we observe a strong species dependency of the I / Ca ratio accentuates this problem, because the use of bulk species samples which would provide enough material for a sufficient number of analyses might influence the results. The I / Ca ratio of *U. striata* is twice as high when compared to *U. peregrina* from the same location. Both species are living shallow infaunal, belong to the same genus and have in general similar morphologies. This difference might either be related to a strong vital effect or to a slight species dependant difference in calcification depths, since the oxygen gradients in the pore waters are quite steep. These results suggest that a careful distinction of the analysed species is essential for the application of this proxy. Nevertheless, since the species dependency of I / Ca ratios appears to be higher than oxygenation dependency, bulk analyses might provide information about oxygenation in a different way: the species composition of a foraminiferal assemblage often is oxygen dependent (Bernhard, 1986; Sen Gupta and Machain-Castello, 1993; Bernhard and Sen Gupta, 1999; Mallon et al., 2012). Thus, bulk I / Ca ratios might be dominated by the species composition, which is affected by oxygen availability.

Furthermore, the variability of samples from the same location seems also to be strongly species dependent. The epifaunal species *P. limbata* has a much higher variability in the I / Ca ratio (22.80 %) than the infaunal species *U. striata* (6.68 %) from the same location (M77-1 487/MUC-38; see Table 5). This is unexpected because infaunal species are supposed to migrate vertically in the sediment column following the chemical gradients (especially oxygen penetration) in the surrounding pore waters strongly varying within a few millimetres. Due to the TROX model the living depth of infaunal benthic foraminifera is controlled by the availability of food (e.g. organic matter) and the oxygen penetration depth (Jorisson et al., 1995). In an eutrophic environment like the Peruvian OMZ the living depth is mostly controlled by oxygen availability (Mallon et al., 2012). On the contrary the epifaunal species do not have the possibility to migrate in the pore waters and are directly exposed to changing bottom water conditions while the infaunal species might compensate changing conditions by migration. It is also possible that the smaller numbers of specimens in the analysed assembleges (6 for *P. limbata*; 10–20 for *U. striata*) might explain the difference. The inter-test variability of Mg/Ca ratios for example can be very high within one sample (Sadekov et al., 2008). Thus, the uncertainty of paleotemperature estimates using Mg/Ca ratios can be decreased by using a higher number of specimens for each analysis (Anand and Elderfield, 2005). In general due to the steep chemical gradients in the pore waters mentioned above epifaunal species might be more suitable for oxygen reconstructions because they should directly represent bottom water conditions not influenced by the microhabitat in the pore waters. Nevertheless, this might require the use of a higher amount of specimens for the I / Ca analyses to reduce uncertainties due to inter-test variability, which again would require more sampling material. The strong inter-test variability might indeed be related to real changes in oxygenation of the habitat, since there are strong seasonal fluctuations in the magnitude of the OMZ.

Finally the aragonitic epifaunal species *H. elegans* shows no significant I / Ca–$[O_2]_{BW}$ correlation. Additionally this species has the lowest I / Ca ratios, although it lives epifaunal and has aragonitic tests (all our aragonite standards showed much higher I / Ca ratios than all calcite samples analysed). Dissolution and recrystallization of metastable aragonite can already occur during the earliest sedimentation-stages as shown by studies in the Bahama Banks (Hover et al., 2001; Rosenthal et al., 2006). Thus, although the analysed *H. elegans* specimens originate from recent core top samples they might already be influenced by diagenesis recrystallized test portionsmay have altered I / Ca ratios.

5 Summary and conclusions

We provide cleaning protocols and a method to measure I / Ca ratios in benthic foraminifera. Due to its volatility, iodine is lost in measurable amounts already one day after dissolution although TMAH was used to trap the Iodine. Nevertheless, our results show that this effect is negligible if the samples are measured within two hours after dissolution. The I / Ca ratios of different *Uvigerina striata* samples from the same location and two different aragonitic coral standards are well reproducible in different measurement sessions given the samples are measured within 2 h after dissolution (JCp-1: $n = 60$; $1\sigma = 2.0\,\%$; Lab internal aragonitc coral standard: $n = 52$; $1\sigma = 3.5\,\%$; *U. striata*: $n = 28$, $1\sigma = 6.6\,\%$). Thus, the measurement of the samples within a short time after dissolution is essential.

There is a strong inter-species variability of I / Ca ratios in two infaunal species from the same location which indicates either strong vital effect or slight species dependant differences in the calcification depth of these species. All analysed species show a trend of positive I / Ca correlations with $[O_2]_{BW}$. This correlation is significant for two calcitic species (even highly significant for *U. striata*) and not significant for the aragonitic species *Hoeglundina elegans*, which shows relatively low I / Ca ratios in general. The most promising of the analysed species is *U. striata* ($I/Ca = 0.0324(\pm 0.004)[O_2]_{BW} + 0.285(\pm 0.026)$, $R^2 = 0.608$, $F = 75.38$, $P < 0.0001$). This is surprising since *U. striata* is living infaunal and thus migrates vertically in the sediment column undergoing a variety of oxygen and thus IO_3^- concentrations over lifetime. When samples are carefully prepared and measured, accounting for the pitfalls outlined here, the resulting I / Ca ratios from benthic foraminifera analysis may be considered a robust proxy for redox conditions in the ambient water mass.

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Table 1. Sampling sites. $[O_2]_{BW}$ in bold numbers are taken from Glock et al. (2011). $[O_2]_{BW}$ for station M77/1-406/MUC-06 is taken from the CTD-profile from station M77/1-392/CTD-RO-4. $[O_2]_{BW}$ for station M77/2 St. 47-3 is taken from the CTD-profile from station M77/2 St. 47-1 – CTD-19 (Krahmann, 2012). $[O_2]_{BW}$ in italic numbers indicates that this value was intrapolated from the closest CTD-profiles available.

Site	Longitude (W)	Latitude (S)	Water depth (m)	$[O_2]_{BW}$ (μmol L^{-1})
M77/1-406/MUC-06	71°52.40′	17°28.00′	492	25.2
M77/1-455/MUC-21	78°19.23′	11°00.00′	465	**2.4**
M77/1-487/MUC-39	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**
M77/1-516/MUC-40	78°20.00′	11°00.00′	512	**2.4**
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*
M77/2 St. 47-3	80°31.36′	07°52.01′	625	8.1

Table 2. Details for analysed foraminiferal samples. Note that TMAH was added after transfer of the centrifuged dissolved sample into a clean vial. Thus, the volume of 0.0075 M HNO_3 is reduced by 50 µL when TMAH is added (see text Sect. 2.).

Sample name	Sample Location	Species	Number of specimens	Volume of 0.075 M HNO_3 for dissolution (µL)	Volume of TMAH added after dissolution (µL)
A1	566/MUC-59	*U. striata*	20	550	9
A2	566/MUC-59	*U. striata*	20	550	9
A3	566/MUC-59	*U. striata*	20	550	9
A4	566/MUC-59	*U. striata*	20	550	9
A5	566/MUC-59	*P. limbata*	6	400	7
A6	566/MUC-59	*P. limbata*	6	400	7
A7	566/MUC-59	*P. limbata*	6	400	7
A8	566/MUC-59	*P. limbata*	6	400	7
A9	566/MUC-59	*U. striata*	20	450	8
A10	566/MUC-59	*P. limbata*	10	450	8
B1	487/MUC-38	*U. striata*	15	550	9
B2	487/MUC-38	*U. striata*	15	450	8
B3	487/MUC-38	*U. striata*	15	450	8
B4	487/MUC-38	*P. limbata*	6	400	7
B5	487/MUC-38	*P. limbata*	6	400	7
B6	487/MUC-38	*P. limbata*	6	350	6
B7	487/MUC-38	*H. elegans*	11	400	7
B8	487/MUC-38	*H. elegans*	10	550	9
C1	455/MUC-21	*U. striata*	15	400	7
C2	455/MUC-21	*U. striata*	15	450	8
C3	455/MUC-21	*H. elegans*	10	550	9
C4	455/MUC-21	*H. elegans*	15	550	9
D1	553/MUC-54	*P. limbata*	6	350	6
E1	406/MUC-	*P. limbata*	6	350	6
F1	M77-2 47-3	*U. striata*	15	450	8
G1	516/MUC-40	*U. striata*	15	450	8
H1	459/MUC-25	*U. peregrina*	15	450	8
H2	459/MUC-25	*U. striata*	10	400	7
J1	604/MUC-74	*U. peregrina*	9	400	7
J2	604/MUC-74	*H. elegans*	10	450	8

Table 3. Operation conditions for Agilent 7500cx.

	value/description
RF power	1500 W
Nebulizer	PFA (100 µL/min, self aspirating)
Spray chamber	Glass (cooled to 2 °C)
Autosampler	Cetac ASX 100
Uptake rate (µL min^{-1})	100
Washout time (s) Beaker 1	60
Washout time (s) Beaker 2	120
Uptake time (s)	40
Stabilisation time (s)	40
Argon plasma gas flow rate (L min^{-1})	14
Argon auxiliary gas flow rate (L min^{-1})	0.23
Argon nebulizer gas flow rate (L min^{-1})	0.93
Sample cone	Nickel (Agilent)
Skimmer cone	Nickel
CeO/Ce and Ba^{2+}/Ba^{+} ratios	< 2.5 %

Table 4. Element concentrations and volumes of different pre-dillutions for the different standard rows used for ICP-MS.

Standard or Dilution	Ca (ppm)	Iodine	H_2O (ROW) (mL)	25 % TMAH (µL)	Conc. HNO_3 (µL)	1000 ppm Ca (µL)	Iodine-predilution (µL)	Concentration of used Iodine-predilution
5 ppm I	0	5 ppm	19.35	400	150	0	100	1000 ppm
50 ppb I	0	50 ppb	19.25	400	150	0	200	5 ppm
5 ppb I	0	5 ppb	17.50	360	135	0	2000	50 ppb
Standard 0	50	0 ppt	3.68	80	29.2	200	0	–
Standard 1	50	25 ppt	3.67	79.6	29.0	200	20	5 ppb
Standard 2	50	50 ppt	3.64	79.2	28.9	200	40	5 ppb
Standard 3	50	125 ppt	3.59	78.0	28.4	200	100	5 ppb
Standard 4	50	250 ppt	3.50	76.0	27.7	200	200	5 ppb
Standard 5	50	500 ppt	3.30	72.0	26.2	200	400	5 ppb
Standard 6	50	1000 ppt	2.91	64.0	23.2	200	800	5 ppb

Table 5. Mean I / Ca ratios, number of measurements (*n*) and errors for the reference standards and foraminiferal samples at the different sampling sites. The variability represents the standard deviation between all measurements of the sample/standard.

Standard/ Species	Sampling Site	*n*	I / Ca (µmol mol^{-1})	Variability (1σ)	Mean precision for single measurement (1 sd)	1σ of precision for single measurement
Calcite		70	n.d.	–	–	–
Aragonite		70	2.59	3.22 %	1.56 %	0.92 %
JCp-1 (no treatment)		100	4.05	23.80 %	1.51 %	0.62 %
JCp-1 (homogenized)		60	3.82	1.97 %	1.29 %	0.53 %
U. striata	M77-1 565/MUC-59	28	0.54	6.56 %	2.15 %	0.92 %
U. striata	M77-1 487/MUC-38	12	0.43	6.86 %	2.51 %	0.60 %
U. striata	M77-1 455/MUC-21	6	0.32	7.19 %	4.09 %	0.85 %
U. striata	M77-2 47-3	1	0.41	–	4.47 %	–
U. striata	M77-1 516/MUC-40	1	0.57	–	3.13 %	–
U. striata	M77-1 459/MUC-25	1	0.91	–	2.35 %	–
P. limbata	M77-1 565/MUC-59	8	1.22	6.84 %	2.07 %	0.50 %
P. limbata	M77-1 487/MUC-38	5	1.32	22.80 %	1.67 %	0.40 %
P. limbata	M77-1 553/MUC-54	1	1.34	–	1.99 %	–
P. limbata	M77-1 406/MUC-06	1	2.20	–	1.28 %	–
H. elegans	M77-1 487/MUC-38	9	0.13	4.89 %	6.34 %	1.91 %
H. elegans	M77-1 455/MUC-21	8	0.19	34.57 %	6.78 %	3.36 %
H. elegans	M77-1 604/MUC-74	1	0.29	–	5.87 %	–
U. peregrina	M77-1 604/MUC-74	1	0.40	–	4.87 %	–
U. peregrina	M77-1 459/MUC-25	1	0.48	–	3.55 %	–

Table A1. I / Ca ratios and precisions for the single measurements of the internal reference standards. All measurements for the internal calcite reference standard ($n = 70$) were below the detection limit and are not listed in this table.

Reference Standard	I / Ca (μmol mol^{-1})	Precision (1σ)	Date of measurement
Aragonite	2.42	1.63 %	19 Nov 2013
Aragonite	2.40	1.53 %	19 Nov 2013
Aragonite	2.44	2.00 %	19 Nov 2013
Aragonite	2.43	1.00 %	19 Nov 2013
Aragonite	2.45	1.38 %	19 Nov 2013
Aragonite	2.44	1.30 %	19 Nov 2013
Aragonite	2.47	1.75 %	19 Nov 2013
Aragonite	2.46	1.08 %	19 Nov 2013
Aragonite	2.64	1.02 %	20 Nov 2013
Aragonite	2.66	1.13 %	20 Nov 2013
Aragonite	2.58	1.43 %	20 Nov 2013
Aragonite	2.57	1.04 %	20 Nov 2013
Aragonite	2.54	1.61 %	20 Nov 2013
Aragonite	2.56	1.53 %	20 Nov 2013
Aragonite	2.57	1.68 %	20 Nov 2013
Aragonite	2.57	1.63 %	20 Nov 2013
Aragonite	2.54	1.36 %	20 Nov 2013
Aragonite	2.55	1.37 %	20 Nov 2013
Aragonite	2.53	1.86 %	20 Nov 2013
Aragonite	2.56	1.40 %	20 Nov 2013
Aragonite	2.60	1.23 %	20 Nov 2013
Aragonite	2.62	1.28 %	20 Nov 2013
Aragonite	2.65	1.05 %	21 Nov 2013
Aragonite	2.62	0.90 %	21 Nov 2013
Aragonite	2.52	0.91 %	21 Nov 2013
Aragonite	2.54	1.01 %	21 Nov 2013
Aragonite	2.44	1.97 %	21 Nov 2013
Aragonite	2.52	1.68 %	21 Nov 2013
Aragonite	2.58	1.59 %	21 Nov 2013
Aragonite	2.55	1.36 %	21 Nov 2013
Aragonite	2.48	1.37 %	21 Nov 2013
Aragonite	2.50	2.09 %	21 Nov 2013
Aragonite	2.56	2.28 %	21 Nov 2013
Aragonite	2.58	2.42 %	21 Nov 2013
Aragonite	2.63	2.10 %	21 Nov 2013
Aragonite	2.63	2.26 %	21 Nov 2013
Aragonite	2.60	1.33 %	21 Nov 2013
Aragonite	2.58	1.06 %	21 Nov 2013
Aragonite	2.59	1.70 %	22 Nov 2013
Aragonite	2.59	1.22 %	22 Nov 2013
Aragonite	2.60	1.15 %	22 Nov 2013
Aragonite	2.57	1.29 %	22 Nov 2013
Aragonite	2.57	1.46 %	22 Nov 2013
Aragonite	2.57	1.26 %	22 Nov 2013
Aragonite	2.51	8.35 %	22 Nov 2013
Aragonite	2.62	1.55 %	22 Nov 2013
Aragonite	2.70	1.26 %	22 Nov 2013
Aragonite	2.71	1.25 %	22 Nov 2013
Aragonite	2.65	1.51 %	22 Nov 2013
Aragonite	2.67	1.20 %	22 Nov 2013
Aragonite	2.65	1.49 %	22 Nov 2013
Aragonite	2.63	1.26 %	22 Nov 2013
Aragonite	2.63	1.35 %	22 Nov 2013
Aragonite	2.63	0.94 %	22 Nov 2013
Aragonite	2.72	1.03 %	25 Nov 2013
Aragonite	2.76	1.29 %	25 Nov 2013

Table A1. Continued.

Reference Standard	I / Ca (µmol mol^{-1})	Precision (1σ)	Date of measurement
Aragonite	2.70	1.75 %	25 Nov 2013
Aragonite	2.69	1.20 %	25 Nov 2013
Aragonite	2.71	1.67 %	25 Nov 2013
Aragonite	2.61	1.41 %	25 Nov 2013
Aragonite	2.65	1.26 %	25 Nov 2013
Aragonite	2.68	0.76 %	25 Nov 2013
Aragonite	2.64	1.13 %	25 Nov 2013
Aragonite	2.73	1.72 %	25 Nov 2013
Aragonite	2.65	1.09 %	25 Nov 2013
Aragonite	2.67	1.18 %	25 Nov 2013
Aragonite	2.66	2.26 %	25 Nov 2013
Aragonite	2.70	2.28 %	25 Nov 2013
Aragonite	2.63	2.63 %	25 Nov 2013
Aragonite	2.66	1.53 %	25 Nov 2013
JCp-1 (no treatment)	2.42	0.80 %	15 Nov 2013
JCp-1 (no treatment)	2.40	3.25 %	15 Nov 2013
JCp-1 (no treatment)	2.44	0.69 %	15 Nov 2013
JCp-1 (no treatment)	2.43	1.90 %	15 Nov 2013
JCp-1 (no treatment)	2.45	1.81 %	15 Nov 2013
JCp-1 (no treatment)	2.44	0.70 %	15 Nov 2013
JCp-1 (no treatment)	2.47	1.24 %	15 Nov 2013
JCp-1 (no treatment)	2.46	1.01 %	15 Nov 2013
JCp-1 (no treatment)	2.64	1.77 %	15 Nov 2013
JCp-1 (no treatment)	2.66	3.51 %	15 Nov 2013
JCp-1 (no treatment)	2.58	1.69 %	15 Nov 2013
JCp-1 (no treatment)	2.57	1.46 %	15 Nov 2013
JCp-1 (no treatment)	2.54	1.54 %	15 Nov 2013
JCp-1 (no treatment)	2.56	1.38 %	15 Nov 2013
JCp-1 (no treatment)	2.57	1.52 %	15 Nov 2013
JCp-1 (no treatment)	2.57	1.74 %	15 Nov 2013
JCp-1 (no treatment)	2.54	1.46 %	15 Nov 2013
JCp-1 (no treatment)	2.55	1.16 %	15 Nov 2013
JCp-1 (no treatment)	2.53	0.82 %	15 Nov 2013
JCp-1 (no treatment)	2.56	1.04 %	15 Nov 2013
JCp-1 (no treatment)	2.60	1.41 %	15 Nov 2013
JCp-1 (no treatment)	2.62	1.03 %	15 Nov 2013
JCp-1 (no treatment)	2.65	1.70 %	15 Nov 2013
JCp-1 (no treatment)	2.62	1.03 %	15 Nov 2013
JCp-1 (no treatment)	2.52	1.35 %	15 Nov 2013
JCp-1 (no treatment)	2.54	1.59 %	15 Nov 2013
JCp-1 (no treatment)	2.44	1.60 %	15 Nov 2013
JCp-1 (no treatment)	2.52	1.61 %	15 Nov 2013
JCp-1 (no treatment)	2.58	1.77 %	15 Nov 2013
JCp-1 (no treatment)	2.55	2.82 %	15 Nov 2013
JCp-1 (no treatment)	2.48	1.46 %	18 Nov 2013
JCp-1 (no treatment)	2.50	0.81 %	18 Nov 2013
JCp-1 (no treatment)	2.56	1.39 %	18 Nov 2013
JCp-1 (no treatment)	2.58	1.31 %	18 Nov 2013
JCp-1 (no treatment)	2.63	1.43 %	18 Nov 2013
JCp-1 (no treatment)	2.63	1.34 %	18 Nov 2013
JCp-1 (no treatment)	2.60	1.76 %	18 Nov 2013
JCp-1 (no treatment)	2.58	1.36 %	18 Nov 2013
JCp-1 (no treatment)	2.59	1.97 %	18 Nov 2013
JCp-1 (no treatment)	2.59	1.68 %	18 Nov 2013
JCp-1 (no treatment)	2.60	1.64 %	18 Nov 2013
JCp-1 (no treatment)	2.57	1.52 %	18 Nov 2013
JCp-1 (no treatment)	2.57	2.07 %	18 Nov 2013
JCp-1 (no treatment)	2.57	1.13 %	18 Nov 2013
JCp-1 (no treatment)	2.51	1.44 %	18 Nov 2013
JCp-1 (no treatment)	2.62	1.29 %	18 Nov 2013

Table A1. Continued.

Reference Standard	I / Ca (µmol mol^{-1})	Precision (1σ)	Date of measurement
JCp-1 (no treatment)	2.70	2.16 %	18 Nov 2013
JCp-1 (no treatment)	2.71	2.38 %	18 Nov 2013
JCp-1 (no treatment)	2.65	0.74 %	19 Nov 2013
JCp-1 (no treatment)	2.67	1.54 %	19 Nov 2013
JCp-1 (no treatment)	2.65	3.46 %	19 Nov 2013
JCp-1 (no treatment)	2.63	1.52 %	19 Nov 2013
JCp-1 (no treatment)	2.63	1.06 %	19 Nov 2013
JCp-1 (no treatment)	2.63	1.45 %	19 Nov 2013
JCp-1 (no treatment)	2.72	1.14 %	19 Nov 2013
JCp-1 (no treatment)	2.76	1.21 %	19 Nov 2013
JCp-1 (no treatment)	2.70	1.75 %	19 Nov 2013
JCp-1 (no treatment)	2.69	1.59 %	19 Nov 2013
JCp-1 (no treatment)	2.71	0.99 %	19 Nov 2013
JCp-1 (no treatment)	2.61	0.87 %	19 Nov 2013
JCp-1 (no treatment)	2.65	1.34 %	19 Nov 2013
JCp-1 (no treatment)	2.68	1.36 %	19 Nov 2013
JCp-1 (no treatment)	2.64	0.95 %	19 Nov 2013
JCp-1 (no treatment)	2.73	1.96 %	19 Nov 2013
JCp-1 (no treatment)	2.65	1.33 %	19 Nov 2013
JCp-1 (no treatment)	2.67	1.61 %	19 Nov 2013
JCp-1 (no treatment)	2.66	1.14 %	20 Nov 2013
JCp-1 (no treatment)	2.70	0.79 %	20 Nov 2013
JCp-1 (no treatment)	2.63	1.25 %	20 Nov 2013
JCp-1 (no treatment)	2.66	1.84 %	20 Nov 2013
JCp-1 (no treatment)	4.29	1.47 %	20 Nov 2013
JCp-1 (no treatment)	12.67	1.10 %	20 Nov 2013
JCp-1 (no treatment)	5.32	1.09 %	20 Nov 2013
JCp-1 (no treatment)	5.17	1.75 %	20 Nov 2013
JCp-1 (no treatment)	5.18	1.40 %	20 Nov 2013
JCp-1 (no treatment)	4.20	1.04 %	20 Nov 2013
JCp-1 (no treatment)	4.41	1.35 %	20 Nov 2013
JCp-1 (no treatment)	4.43	1.61 %	20 Nov 2013
JCp-1 (no treatment)	5.23	1.16 %	20 Nov 2013
JCp-1 (no treatment)	4.87	1.36 %	20 Nov 2013
JCp-1 (no treatment)	4.15	0.70 %	20 Nov 2013
JCp-1 (no treatment)	4.06	2.03 %	20 Nov 2013
JCp-1 (no treatment)	4.13	1.94 %	20 Nov 2013
JCp-1 (no treatment)	4.53	1.40 %	20 Nov 2013
JCp-1 (no treatment)	4.34	1.04 %	20 Nov 2013
JCp-1 (no treatment)	4.10	1.17 %	20 Nov 2013
JCp-1 (no treatment)	4.01	2.15 %	20 Nov 2013
JCp-1 (no treatment)	4.12	2.20 %	20 Nov 2013
JCp-1 (no treatment)	4.20	1.09 %	20 Nov 2013
JCp-1 (no treatment)	4.07	1.22 %	20 Nov 2013
JCp-1 (no treatment)	4.10	0.62 %	21 Nov 2013
JCp-1 (no treatment)	4.13	4.96 %	21 Nov 2013
JCp-1 (no treatment)	4.07	1.16 %	21 Nov 2013
JCp-1 (no treatment)	3.99	0.85 %	21 Nov 2013
JCp-1 (no treatment)	3.97	1.72 %	21 Nov 2013
JCp-1 (no treatment)	4.09	0.98 %	21 Nov 2013
JCp-1 (no treatment)	4.05	1.57 %	21 Nov 2013
JCp-1 (no treatment)	4.08	1.65 %	21 Nov 2013
JCp-1 (no treatment)	3.84	1.28 %	21 Nov 2013
JCp-1 (no treatment)	3.79	1.56 %	21 Nov 2013
JCp-1 (no treatment)	5.02	2.17 %	21 Nov 2013
JCp-1 (no treatment)	4.31	1.85 %	21 Nov 2013
JCp-1 (no treatment)	4.24	1.93 %	21 Nov 2013
JCp-1 (no treatment)	5.02	1.93 %	21 Nov 2013
JCp-1 (no treatment)	4.36	1.18 %	21 Nov 2013
JCp-1 (no treatment)	4.30	0.89 %	21 Nov 2013

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Table A1. Continued.

Reference Standard	I / Ca (µmol mol^{-1})	Precision (1σ)	Date of measurement
JCp-1 (homogenized)	4.74	1.50 %	21 Nov 2013
JCp-1 (homogenized)	4.14	0.83 %	21 Nov 2013
JCp-1 (homogenized)	4.23	1.28 %	21 Nov 2013
JCp-1 (homogenized)	4.97	1.46 %	21 Nov 2013
JCp-1 (homogenized)	4.19	1.39 %	21 Nov 2013
JCp-1 (homogenized)	4.20	1.20 %	21 Nov 2013
JCp-1 (homogenized)	4.98	2.34 %	21 Nov 2013
JCp-1 (homogenized)	4.23	2.28 %	21 Nov 2013
JCp-1 (homogenized)	4.22	1.91 %	21 Nov 2013
JCp-1 (homogenized)	4.99	1.96 %	21 Nov 2013
JCp-1 (homogenized)	4.35	0.73 %	21 Nov 2013
JCp-1 (homogenized)	4.42	0.76 %	21 Nov 2013
JCp-1 (homogenized)	3.74	1.29 %	22 Nov 2013
JCp-1 (homogenized)	3.63	1.02 %	22 Nov 2013
JCp-1 (homogenized)	3.55	1.52 %	22 Nov 2013
JCp-1 (homogenized)	3.64	1.07 %	22 Nov 2013
JCp-1 (homogenized)	3.56	1.55 %	22 Nov 2013
JCp-1 (homogenized)	3.53	1.33 %	22 Nov 2013
JCp-1 (homogenized)	3.53	1.17 %	22 Nov 2013
JCp-1 (homogenized)	3.49	1.35 %	22 Nov 2013
JCp-1 (homogenized)	3.58	1.90 %	22 Nov 2013
JCp-1 (homogenized)	3.50	2.36 %	22 Nov 2013
JCp-1 (homogenized)	3.52	1.39 %	22 Nov 2013
JCp-1 (homogenized)	3.54	0.60 %	22 Nov 2013
JCp-1 (homogenized)	3.49	0.89 %	22 Nov 2013
JCp-1 (homogenized)	3.51	1.10 %	22 Nov 2013
JCp-1 (homogenized)	3.48	1.05 %	22 Nov 2013
JCp-1 (homogenized)	3.51	0.60 %	22 Nov 2013
JCp-1 (homogenized)	3.56	1.33 %	22 Nov 2013
JCp-1 (homogenized)	3.57	1.57 %	22 Nov 2013
JCp-1 (homogenized)	3.86	0.88 %	22 Nov 2013
JCp-1 (homogenized)	3.73	0.97 %	22 Nov 2013
JCp-1 (homogenized)	3.80	0.78 %	22 Nov 2013
JCp-1 (homogenized)	3.59	3.65 %	22 Nov 2013
JCp-1 (homogenized)	3.56	1.33 %	22 Nov 2013
JCp-1 (homogenized)	3.58	1.31 %	22 Nov 2013
JCp-1 (homogenized)	3.51	0.79 %	25 Nov 2013
JCp-1 (homogenized)	3.51	0.81 %	25 Nov 2013
JCp-1 (homogenized)	3.47	1.74 %	25 Nov 2013
JCp-1 (homogenized)	3.59	1.35 %	25 Nov 2013
JCp-1 (homogenized)	3.51	0.89 %	25 Nov 2013
JCp-1 (homogenized)	3.50	0.97 %	25 Nov 2013
JCp-1 (homogenized)	3.57	1.21 %	25 Nov 2013
JCp-1 (homogenized)	3.52	1.01 %	25 Nov 2013
JCp-1 (homogenized)	3.63	1.16 %	25 Nov 2013
JCp-1 (homogenized)	3.54	0.49 %	25 Nov 2013
JCp-1 (homogenized)	3.63	1.54 %	25 Nov 2013
JCp-1 (homogenized)	3.58	0.75 %	25 Nov 2013
JCp-1 (homogenized)	3.56	1.92 %	25 Nov 2013
JCp-1 (homogenized)	3.53	0.63 %	25 Nov 2013
JCp-1 (homogenized)	3.54	1.01 %	25 Nov 2013
JCp-1 (homogenized)	3.66	1.14 %	25 Nov 2013
JCp-1 (homogenized)	3.67	1.12 %	25 Nov 2013
JCp-1 (homogenized)	3.60	0.98 %	25 Nov 2013
JCp-1 (homogenized)	3.98	1.62 %	25 Nov 2013
JCp-1 (homogenized)	4.02	1.40 %	25 Nov 2013
JCp-1 (homogenized)	3.85	1.63 %	25 Nov 2013
JCp-1 (homogenized)	3.72	1.18 %	25 Nov 2013
JCp-1 (homogenized)	3.68	1.26 %	25 Nov 2013
JCp-1 (homogenized)	3.63	1.09 %	25 Nov 2013

Table A2. I / Ca ratios and precision for the single measurements of the foraminiferal samples. Bold and italic numbers represent measurements which were done one day after the dissolution of the sample.

Sample	Species	Sampling Site	I / Ca (mmol mol^{-1})	Precision (1σ)	Date of measurement
A1	*U. striata*	M77-1 565/MUC-59	0.58	1.69 %	19 Nov 2013
A1	*U. striata*	M77-1 565/MUC-59	0.56	0.98 %	19 Nov 2013
A1	*U. striata*	M77-1 565/MUC-59	0.56	1.59 %	19 Nov 2013
A1	*U. striata*	M77-1 565/MUC-59	0.53	1.90 %	19 Nov 2013
A1	*U. striata*	M77-1 565/MUC-59	0.50	1.31 %	19 Nov 2013
A1	*U. striata*	M77-1 565/MUC-59	0.52	1.24 %	19 Nov 2013
A1	*U. striata*	M77-1 565/MUC-59	***0.47***	***3.39 %***	20 Nov 2013
A1	*U. striata*	M77-1 565/MUC-59	***0.49***	***3.68 %***	20 Nov 2013
A1	*U. striata*	M77-1 565/MUC-59	***0.51***	***3.97 %***	20 Nov 2013
A1	*U. striata*	M77-1 565/MUC-59	***0.51***	***3.85 %***	20 Nov 2013
A1	*U. striata*	M77-1 565/MUC-59	***0.49***	***7.45 %***	20 Nov 2013
A1	*U. striata*	M77-1 565/MUC-59	***0.60***	***17.95 %***	20 Nov 2013
A2	*U. striata*	M77-1 565/MUC-59	0.62	1.35 %	19 Nov 2013
A2	*U. striata*	M77-1 565/MUC-59	0.61	0.96 %	19 Nov 2013
A2	*U. striata*	M77-1 565/MUC-59	0.60	1.32 %	19 Nov 2013
A2	*U. striata*	M77-1 565/MUC-59	0.59	1.42 %	19 Nov 2013
A2	*U. striata*	M77-1 565/MUC-59	0.56	1.39 %	19 Nov 2013
A2	*U. striata*	M77-1 565/MUC-59	0.55	1.32 %	19 Nov 2013
A2	*U. striata*	M77-1 565/MUC-59	***0.54***	***2.80 %***	20 Nov 2013
A2	*U. striata*	M77-1 565/MUC-59	***0.53***	***3.13 %***	20 Nov 2013
A2	*U. striata*	M77-1 565/MUC-59	***0.55***	***3.47 %***	20 Nov 2013
A2	*U. striata*	M77-1 565/MUC-59	***0.52***	***3.46 %***	20 Nov 2013
A3	*U. striata*	M77-1 565/MUC-59	0.53	1.96 %	21 Nov 2013
A3	*U. striata*	M77-1 565/MUC-59	0.51	2.40 %	21 Nov 2013
A3	*U. striata*	M77-1 565/MUC-59	0.50	3.08 %	21 Nov 2013
A3	*U. striata*	M77-1 565/MUC-59	0.48	2.96 %	21 Nov 2013
A3	*U. striata*	M77-1 565/MUC-59	0.52	2.42 %	21 Nov 2013
A3	*U. striata*	M77-1 565/MUC-59	0.52	2.17 %	21 Nov 2013
A3	*U. striata*	M77-1 565/MUC-59	0.51	2.05 %	21 Nov 2013
A4	*U. striata*	M77-1 565/MUC-59	0.53	1.85 %	22 Nov 2013
A4	*U. striata*	M77-1 565/MUC-59	0.52	2.43 %	22 Nov 2013
A4	*U. striata*	M77-1 565/MUC-59	0.53	3.90 %	22 Nov 2013
A4	*U. striata*	M77-1 565/MUC-59	0.52	3.74 %	22 Nov 2013
A4	*U. striata*	M77-1 565/MUC-59	0.53	2.25 %	22 Nov 2013
A4	*U. striata*	M77-1 565/MUC-59	0.52	1.74 %	22 Nov 2013
A4	*U. striata*	M77-1 565/MUC-59	0.52	3.19 %	22 Nov 2013
A4	*U. striata*	M77-1 565/MUC-59	0.54	3.12 %	22 Nov 2013
A9	*U. striata*	M77-1 565/MUC-59	0.51	4.38 %	25 Nov 2013
B1	*U. striata*	M77-1 487/MUC-38	0.47	1.86 %	19 Nov 2013
B1	*U. striata*	M77-1 487/MUC-38	0.44	2.15 %	19 Nov 2013
B1	*U. striata*	M77-1 487/MUC-38	0.40	3.06 %	19 Nov 2013
B1	*U. striata*	M77-1 487/MUC-38	0.41	2.98 %	19 Nov 2013
B1	*U. striata*	M77-1 487/MUC-38	***0.35***	***4.70 %***	20 Nov 2013
B1	*U. striata*	M77-1 487/MUC-38	***0.32***	***4.37 %***	20 Nov 2013
B1	*U. striata*	M77-1 487/MUC-38	***0.38***	***5.24 %***	20 Nov 2013
B1	*U. striata*	M77-1 487/MUC-38	***0.36***	***4.91 %***	20 Nov 2013
B1	*U. striata*	M77-1 487/MUC-38	***0.36***	***4.71 %***	20 Nov 2013
B1	*U. striata*	M77-1 487/MUC-38	***0.33***	***5.24 %***	20 Nov 2013
B2	*U. striata*	M77-1 487/MUC-38	0.37	2.43 %	21 Nov 2013
B2	*U. striata*	M77-1 487/MUC-38	0.35	3.71 %	21 Nov 2013
B2	*U. striata*	M77-1 487/MUC-38	0.35	2.78 %	21 Nov 2013
B2	*U. striata*	M77-1 487/MUC-38	0.33	2.29 %	21 Nov 2013
B3	*U. striata*	M77-1 487/MUC-38	0.51	2.24 %	22 Nov 2013
B3	*U. striata*	M77-1 487/MUC-38	0.51	3.78 %	22 Nov 2013
B3	*U. striata*	M77-1 487/MUC-38	0.47	3.36 %	22 Nov 2013

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Table A2. Continued.

Sample	Species	Sampling Site	I / Ca (mmol mol^{-1})	Precision (1σ)	Date of measurement
B3	*U. striata*	M77-1 487/MUC-38	0.48	3.70 %	22 Nov 2013
C1	*U. striata*	M77-1 455/MUC-21	0.28	3.14 %	21 Nov 2013
C1	*U. striata*	M77-1 455/MUC-21	0.34	4.29 %	21 Nov 2013
C2	*U. striata*	M77-1 455/MUC-21	0.33	3.23 %	22 Nov 2013
C2	*U. striata*	M77-1 455/MUC-21	0.34	5.14 %	22 Nov 2013
C2	*U. striata*	M77-1 455/MUC-21	0.31	3.79 %	22 Nov 2013
C2	*U. striata*	M77-1 455/MUC-21	0.33	4.93 %	22 Nov 2013
F1	*U. striata*	M77-2 47-3	0.41	4.47 %	25 Nov 2013
G1	*U. striata*	M77-1 516/MUC-40	0.57	3.13 %	25 Nov 2013
H2	*U. striata*	M77-1 459/MUC-25	0.91	2.35 %	25 Nov 2013
A5	*P. limbata*	M77-1 565/MUC-59	1.38	2.57 %	19 Nov 2013
A5	*P. limbata*	M77-1 565/MUC-59	1.19	2.56 %	19 Nov 2013
A5	*P. limbata*	M77-1 565/MUC-59	***1.00***	***1.74 %***	20 Nov 2013
A6	*P. limbata*	M77-1 565/MUC-59	1.21	1.55 %	19 Nov 2013
A6	*P. limbata*	M77-1 565/MUC-59	1.16	1.36 %	19 Nov 2013
A6	*P. limbata*	M77-1 565/MUC-59	***0.94***	***2.10 %***	20 Nov 2013
A7	*P. limbata*	M77-1 565/MUC-59	1.19	1.99 %	21 Nov 2013
A7	*P. limbata*	M77-1 565/MUC-59	1.20	1.69 %	21 Nov 2013
A8	*P. limbata*	M77-1 565/MUC-59	1.32	2.61 %	22 Nov 2013
A10	*P. limbata*	M77-1 565/MUC-59	1.13	2.20 %	25 Nov 2013
B4	*P. limbata*	M77-1 487/MUC-38	1.07	1.54 %	19 Nov 2013
B4	*P. limbata*	M77-1 487/MUC-38	1.03	2.18 %	19 Nov 2013
B4	*P. limbata*	M77-1 487/MUC-38	***0.88***	***3.08 %***	20 Nov 2013
B5	*P. limbata*	M77-1 487/MUC-38	1.43	1.40 %	22 Nov 2013
B5	*P. limbata*	M77-1 487/MUC-38	1.31	2.01 %	22 Nov 2013
B6	*P. limbata*	M77-1 487/MUC-38	1.77	1.25 %	22 Nov 2013
D1	*P. limbata*	M77-1 553/MUC-54	1.34	1.99 %	25 Nov 2013
E1	*P. limbata*	M77-1 406/MUC-06	2.20	1.28 %	25 Nov 2013
B7	*H. elegans*	M77-1 487/MUC-38	0.13	4.49 %	19 Nov 2013
B7	*H. elegans*	M77-1 487/MUC-38	0.12	9.13 %	19 Nov 2013
B7	*H. elegans*	M77-1 487/MUC-38	***0.11***	***13.40 %***	20 Nov 2013
B7	*H. elegans*	M77-1 487/MUC-38	***0.13***	***13.13 %***	20 Nov 2013
B7	*H. elegans*	M77-1 487/MUC-38	***0.10***	***17.23 %***	20 Nov 2013
B8	*H. elegans*	M77-1 487/MUC-38	0.13	7.06 %	21 Nov 2013
B8	*H. elegans*	M77-1 487/MUC-38	0.12	6.79 %	21 Nov 2013
B8	*H. elegans*	M77-1 487/MUC-38	0.14	9.42 %	21 Nov 2013
B8	*H. elegans*	M77-1 487/MUC-38	0.13	5.62 %	21 Nov 2013
B8	*H. elegans*	M77-1 487/MUC-38	0.12	5.51 %	21 Nov 2013
B8	*H. elegans*	M77-1 487/MUC-38	0.14	4.44 %	21 Nov 2013
B8	*H. elegans*	M77-1 487/MUC-38	0.13	4.64 %	21 Nov 2013
C3	*H. elegans*	M77-1 455/MUC-21	0.31	7.27 %	22 Nov 2013
C3	*H. elegans*	M77-1 455/MUC-21	0.23	4.55 %	22 Nov 2013
C3	*H. elegans*	M77-1 455/MUC-21	0.24	5.37 %	22 Nov 2013
C3	*H. elegans*	M77-1 455/MUC-21	0.22	6.46 %	22 Nov 2013
C3	*H. elegans*	M77-1 455/MUC-21	0.27	5.58 %	22 Nov 2013
C3	*H. elegans*	M77-1 455/MUC-21	0.23	3.57 %	22 Nov 2013
C3	*H. elegans*	M77-1 455/MUC-21	0.26	3.18 %	22 Nov 2013
C3	*H. elegans*	M77-1 455/MUC-21	0.24	3.24 %	22 Nov 2013
C4	*H. elegans*	M77-1 455/MUC-21	0.14	4.57 %	22 Nov 2013
C4	*H. elegans*	M77-1 455/MUC-21	0.12	3.80 %	22 Nov 2013
C4	*H. elegans*	M77-1 455/MUC-21	0.14	12.25 %	22 Nov 2013
C4	*H. elegans*	M77-1 455/MUC-21	0.13	12.97 %	22 Nov 2013
C4	*H. elegans*	M77-1 455/MUC-21	0.13	6.72 %	22 Nov 2013
C4	*H. elegans*	M77-1 455/MUC-21	0.13	6.24 %	22 Nov 2013
C4	*H. elegans*	M77-1 455/MUC-21	0.13	10.51 %	22 Nov 2013
C4	*H. elegans*	M77-1 455/MUC-21	0.12	12.16 %	22 Nov 2013
J1	*H. elegans*	M77-1 604/MUC-74	0.29	5.87 %	25 Nov 2013
H1	*U. peregrina*	M77-1 459/MUC-25	0.40	4.87 %	25 Nov 2013
J2	*U. peregrina*	M77-1 604/MUC-74	0.48	3.55 %	25 Nov 2013

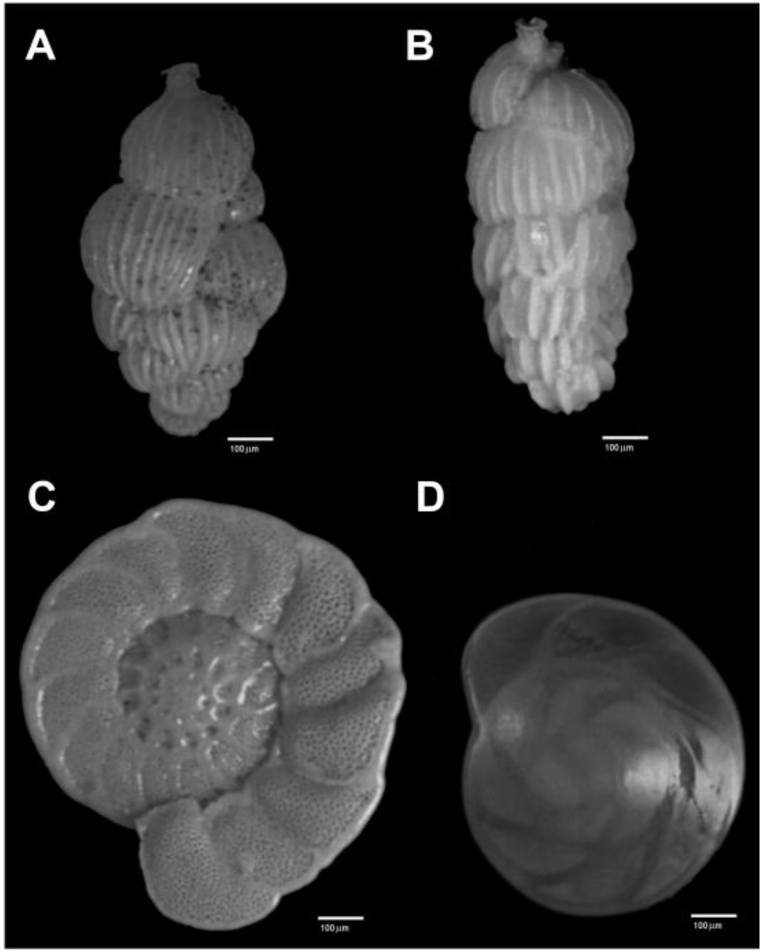

Figure 1. Photographs of the foraminiferal species used in this study. **(A)** *Uvigerina striata*, **(B)** *Uvigerina peregrina*, **(C)** *Planulina limbata*, **(D)** *Hoeglundina elegans*.

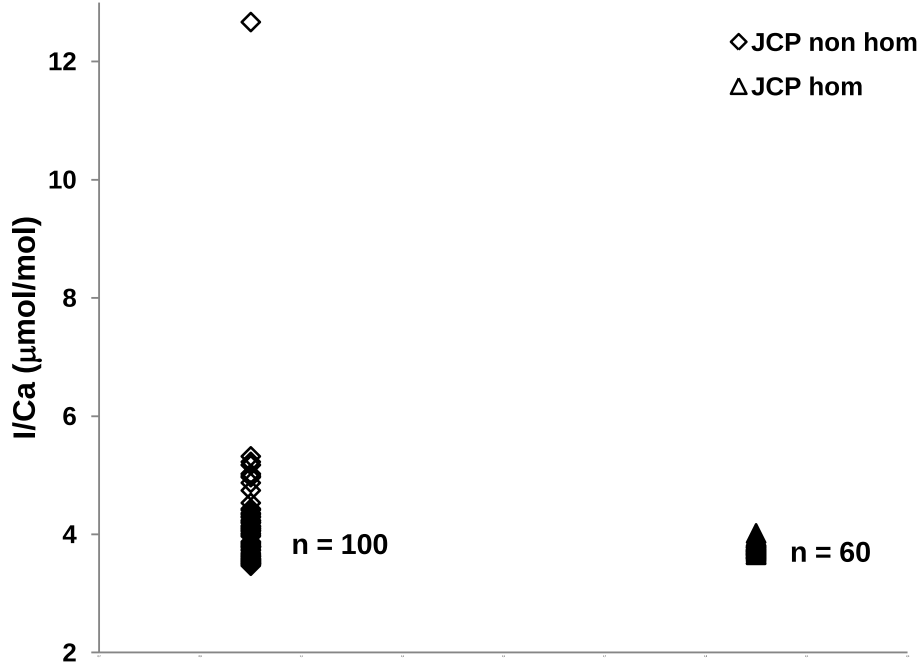

Figure 2. Comparison of all I / Ca measurements on the untreated JCp-1 and an aliquot of the same standard homogenized using a mortar. The mean precision for a single analysis for the aragonitic reference standards in this study was $1\sigma_{\text{mean}} = 1.5\,\%$ ($n = 236$).

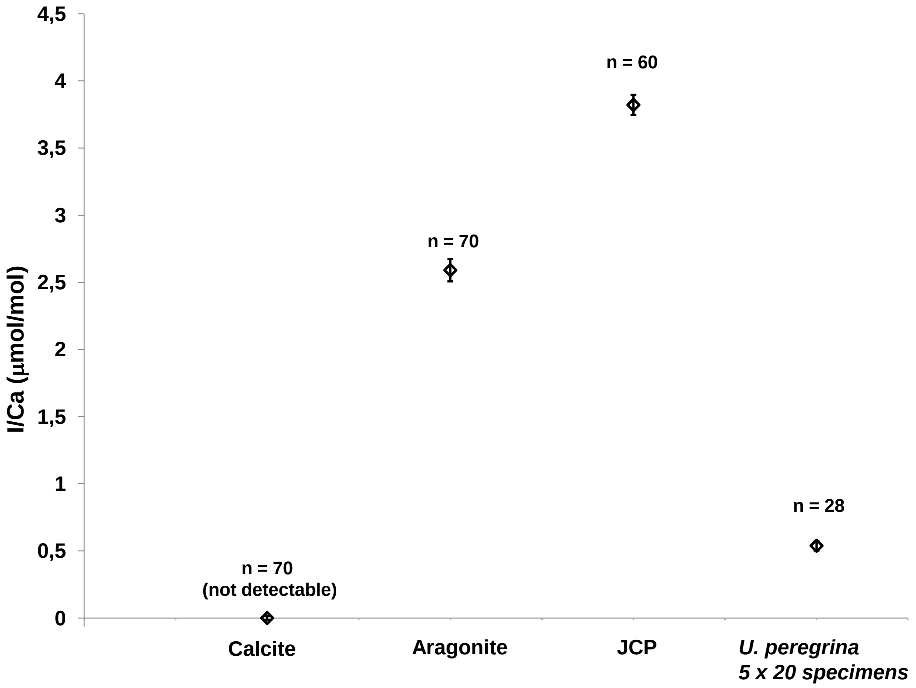

Figure 3. Mean I / Ca ratios, number of measurements (*n*) and errors (1 sd) for the carbonate reference standards and 5 different samples of 20 *U. striata* specimens from the same location (M77-1 565/MUC-60).

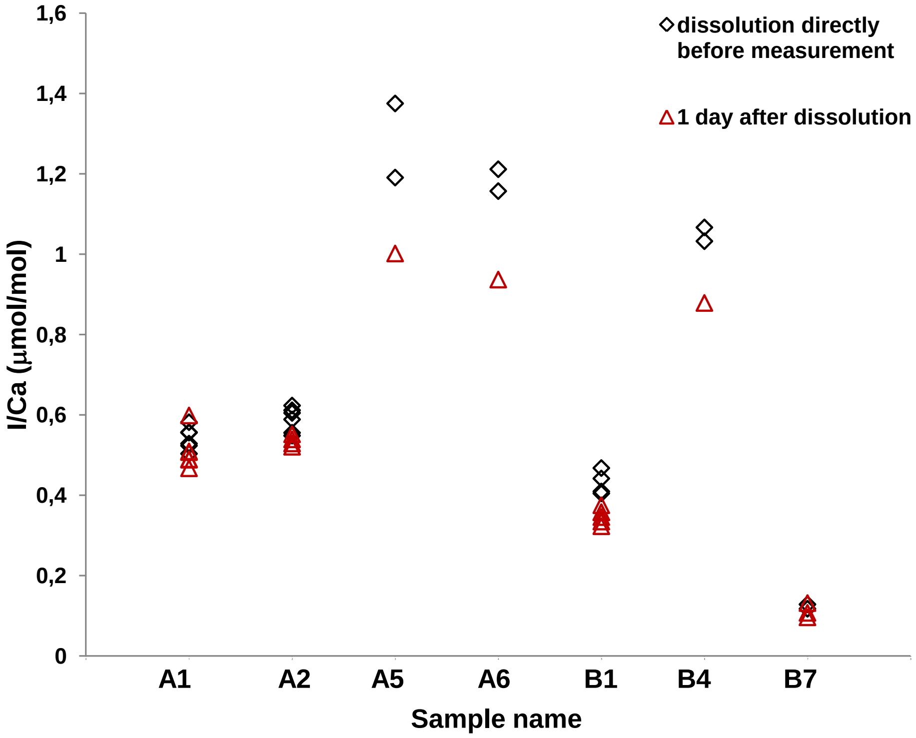

Figure 4. Comparison of I / Ca ratios measured in seven different samples directly after dissolution (diamonds) and one day after dissolution (triangles). Iodine volatility appears to have a strong influence on the samples within one day. For sample specification see Table 2. The mean precision for the foraminiferal analyses in this study was species dependant $1\sigma_{\text{mean}} = 3.2\,\%$ (*U. striata* $n = 65$); 4.21 % (*U. peregrina* $n = 2$); 2.0 % (*P. limbata* $n = 18$) and 7.4 % (*H. elegans* $n = 29$).

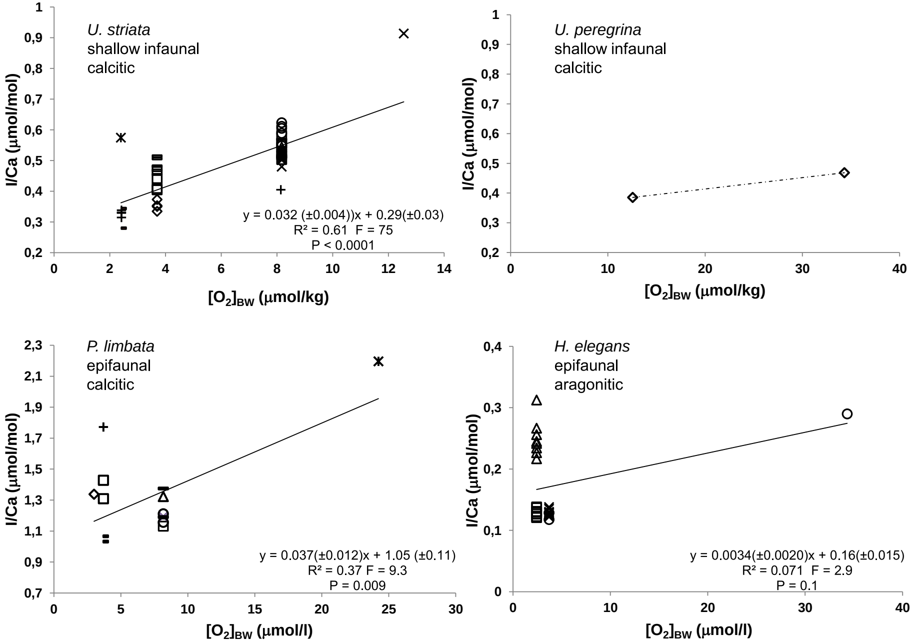

Figure 5. Correlation of I / Ca ratios with bottom water oxygen concentrations $[O_2]_{BW}$ for the four analysed benthic foraminiferal species. Different symbols at the same locations indicate that measurements were done on different sample assembleges from the same sampling site. Significances were calculated with an ANOVA. The dashed line is just for orientation because no correlation could be calculated with only 2 data points. The mean precision for the foraminiferal analyses in this study was species dependant $1\sigma_{mean} = 3.2\,\%$ (*U. striata* $n = 65$); 4.21 % (*U. peregrina* $n = 2$); 2.0 % (*P. limbata* $n = 18$) and 7.4 % (*H. elegans* $n = 29$).