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RESEARCH ARTICLE

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Xiaoli Zhou and Anya Hess contributed equally to this work.

Simultaneous Determination of I/Ca and Other Elemental Ratios in Foraminifera: Comparing Results From Acidic and Basic Solutions

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Key Points:

- Analysis of foraminiferal I/Ca in acidic solutions under controlled conditions offers reliable redox proxy estimates
- Variable sample preparations may affect I/Ca data, but the difference between oxygen-enriched and oxygen-depleted waters is maintained

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract The iodine to calcium ratio in carbonate (I/Ca) has been widely used to indicate ocean oxygenation level in the past. Given the volatility of iodine, I/Ca has been measured in alkaline solutions in previous studies. However, this limits the application of I/Ca with other element/Ca (El/Ca) proxies at the same time and in the same foraminifera because other El/Ca data are preferably analyzed in acidic solutions. This study assesses the reliability of I/Ca measurements in acidic solutions measured with other El/Ca as well as the effects of different sample pre-treatments on measured foraminiferal I/Ca. Our results show that when samples are measured within hours of preparation, the pH of the final solution has an insignificant effect on I/Ca measurements of a carbonate reference material JcP-1 and a multi-element standard solution, consistent with the slow kinetics of iodine volatilization. We find, however, that low pH possibly reduces the measured I/Ca in foraminiferal tests in some samples. Our experiments also suggest a resolvable effect of reductive cleaning, yielding lower foraminiferal I/Ca compared to without reductive cleaning. The HNO₃ concentration used to dissolve foraminiferal shells has a negligible effect. Despite the different solution pHs and cleaning and dissolving methods, our core top planktic I/Ca data are able to differentiate well-oxygenated from oxygen-depleted waters in the upper ocean, and after correcting for cleaning effect, our data are generally consistent with the published studies that analyzed I/Ca without reductive cleaning and in basic solutions. This study shows that measurements of I/Ca within hours of sample dissolutions yield reliable planktic I/Ca data, while also allowing the acquisition of other El/Ca values for paleoceanographic studies.

Plain Language Summary The ratio of chemical elements iodine to calcium (I/Ca) in carbonate has been widely used to indicate the amount of oxygen in modern and ancient oceans. Because iodine is unstable in acidic solutions, I/Ca ratios have been measured in alkaline solutions. However, acquiring I/Ca ratios in this way limits the usage of other element to calcium ratios (El/Ca) that can reflect other physical and chemical properties of the ocean such as temperature and acidity, because these El/Ca ratios are commonly measured in acidic solutions. Here we assess the possibility of producing reliable I/Ca with other El/Ca data in acidic solutions. Our results suggest that I/Ca in foraminiferal (single-celled animal in the ocean) carbonate shells measured in acidic solutions are consistent with those published but measured in alkaline solutions. This confirms the reliability of our new analytical method, which allows measurement of other El/Ca ratios alongside I/Ca.

1. Introduction

The iodine content in biogenic carbonates (I/Ca) is increasingly being used to reconstruct the oxygenation state of the ocean during different geological periods (e.g., Glock et al., 2014, 2016; Hardisty et al., 2014, 2017; Hoogakker et al., 2018; Lu et al., 2010, 2016, 2018; Taylor et al., 2017; Zhou et al., 2014, 2015, 2016). The measurement of iodide (I⁻) as iodine species by ICP-MS is complicated because of the volatility of molecular iodine (I₂) and iodine complexes (e.g., hydriodic acid or HI) as well as adsorption of them to the glass in the spray chamber, possibly resulting in unstable signal and memory effects (e.g., Al-Ammar et al., 2001). Therefore, iodine is typically measured by ICP-MS under alkaline conditions where tetramethylammonium hydroxide (TMAH), tertiary amine (TA), or ammonia (NH₄OH) are added to form non- or less-volatile forms of iodine, such as NH₄I or iodate (IO₃⁻) (e.g., Al-Ammar et al., 2001; Lu et al., 2010; Muramatsu & Wedepohl, 1998; Vanhoe et al., 1993). TMAH is often used for extracting total iodine (combined I⁻, IO₃⁻, and organic iodine) from nutritional and biological

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materials, to ensure that there is no conversion of I^- to volatile I_2 (e.g., Brix et al., 2017). This method was adopted for measuring I/Ca in foraminifera (e.g., Glock et al., 2014; Zhou et al., 2014). I/Ca is extracted from the calcitic foraminiferal tests by dissolution of the tests with dilute nitric acid, followed by the addition of an organic alkaline buffer, typically TMAH or TA, to the acidic solution to raise the sample solution's pH, thereby minimizing iodine volatility before and during the analysis by ICP-MS (Glock et al., 2014; Lu et al., 2010; Takaku et al., 1995; Winkelbauer et al., 2021). This is different from the measurement of other element/Ca (E/Ca) ratios that are routinely used in paleoceanographic research such as Mg/Ca, B/Ca, and Cd/Ca, analyses that are usually performed in acidic solutions (pH < 2.5) because metals are more stable in acidic solutions and may precipitate in alkaline solutions where the $CaCO_3$ saturation is very high ($\Omega > 10$). Furthermore, blanks contamination is often an issue when adding organic reagents. When I/Ca and other E/Ca data from the same sample are needed but the sample is limited, it may not be possible to acquire both types of data using these methods.

The inference that foraminifera incorporate IO_3^- but not I^- into their calcitic shells is fundamental to the utility of the proxy; in oxygen-rich areas, IO_3^- is the dominant species in the water and foraminiferal I/Ca is high, whereas in regions of strong oxygen depletion, I^- dominates and foraminiferal I/Ca is very low (Lu et al., 2010). Implicit to this inference is the assumption that the dominant species released by dissolving the test, by necessity done with dilute acid, is IO_3^- . As I^- is not present in foraminifera tests and therefore in the solution, there should be minimal loss of iodine during acid digestion. Therefore, it is possible that minimizing the exposure of the dissolved calcite solutions to the open air until analysis will substantially minimize the loss, as reduction of iodic acid (HIO_3) to volatile hypoiodous acid and I_2 in acidic conditions may occur at ambient O_2 levels (Cook et al., 2022). The overarching goal of this paper is to assess the conditions that may allow for reliable measurements of I/Ca in acidic solutions. We carry out several experiments to (a) test the possibility that under controlled conditions described below, foraminiferal I/Ca can be determined in acidic solutions with the same accuracy as under alkaline solutions; and (b) compare the effects of different foraminifera cleaning methods on I/Ca.

2. Materials and Methods

2.1. Stability of I/Ca in Standard Solutions

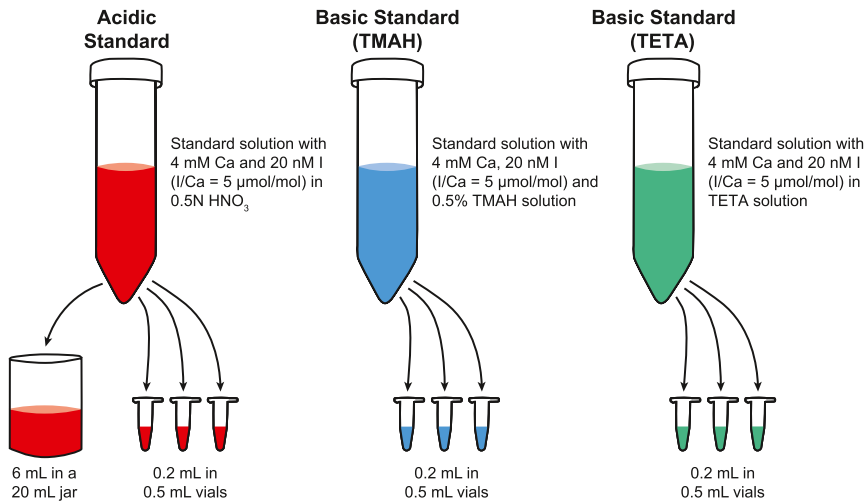
Spiked gravimetric standard solutions: To evaluate the stability of iodine during a sample run, we measured iodine and calcium concentrations in a modified multi-element spiked gravimetric standard (SGS) routinely used in our lab. It is iodine-free and contains known quantities of other elements (e.g., B, Mg, and Cd) in Ca solution. For each of the experiments, the SGS solutions were freshly spiked with dilute KIO_3 solution. The experimental design of the SGS measurements is illustrated in Figure 1a.

For acidic standards (pH ≤ 1), the KIO_3 solution was prepared by dissolving pure KIO_3 powders (Sigma-Aldrich®) in 0.5N HNO_3 solution and diluting with 0.5N HNO_3 solution to reach a target KIO_3 concentration of 60 nM. This solution was then mixed with the iodine-free primary SGS solution with 24 mM Ca to make the final solution for I/Ca analysis, which contains 4 mM Ca and 20 nM KIO_3 (I/Ca = 5 $\mu\text{mol/mol}$). Acidic blank solutions were made of 0.065N and 0.5N HNO_3 solutions at a ratio of 1:3.

For basic solutions, we tested both TMAH (1 M, Sigma Aldrich®) and triethylenetetramine (TETA) ($\geq 97.0\%$, Sigma Aldrich®) as the alkaline buffers yielding pH of ~ 12 and 8, respectively. The former is commonly used by other labs. The KIO_3 powder was dissolved and diluted in Milli-Q deionized water (DI) to make a solution with 60 nM KIO_3 , which was subsequently mixed with the iodine-free primary SGS solution and TMAH to make a basic solution that contains 4 mM Ca, 20 nM KIO_3 and 0.5% v/v TMAH, as reported by other labs (Glock et al., 2014; Taylor et al., 2017). Since TETA was used as the buffer in our experiments on foraminiferal I/Ca, here we also prepared a final solution with 4 mM Ca, 20 nM KIO_3 and 0.5% TETA (I/Ca = 5 $\mu\text{mol/mol}$). Basic blank solutions were 0.5% TMAH solutions.

In our typical runs, the SGS and blank solutions are stored in 20 mL open-topped teflon jars and all other samples are stored in 0.5 mL Eppendorf Safe-Lock vials, which are kept closed until their turn for elemental analysis. In this experiment we have compared I/Ca of standard solutions with the same initial iodine and calcium concentrations, analyzed in open jars and in closed vials. Iodine-containing SGS solutions were prepared in 9–18 mL batches in acidic, TMAH, and TETA solutions as described above, then 0.2 mL of each solution was distributed into a series of 0.5 mL closed vials, and an additional aliquot of acidic solution was also kept in an open-topped jar (Figure 1a). Solutions in closed vials and in the open-topped jar were analyzed repeatedly over the course of

A. Experiment 1 on SGS



B. Experiment 2 on JcP-1

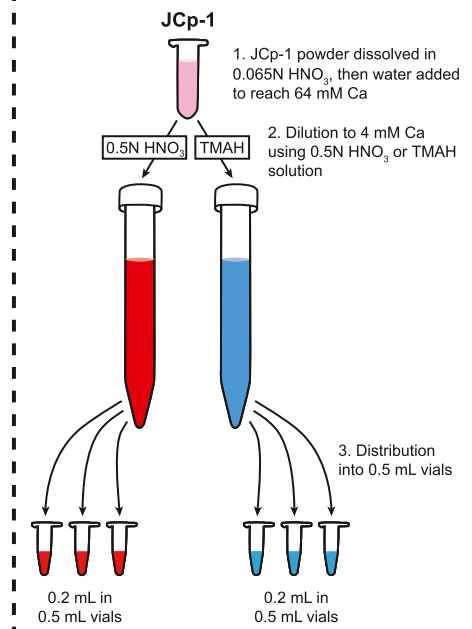


Figure 1. Schematic showing experimental design for experiments testing the effect of pH and exposure to the atmosphere on iodine and calcium in spiked gravimetric standard (SGS) (a) and the effect of pH on iodine and calcium in JcP-1 calcite (b) over the course of an 8-hr analyses. For experiment 1, vials were opened <20 min prior to measurement. Data from experiment 1 are shown in Figure 3. For experiment 2 on JcP-1, an acidic SGS and a basic SGS (with TMAH) were prepared as shown in part (a), distributed into vials, and their I/Ca values were used to correct for instrument drift and convert I/Ca intensity ratios in JcP-1 to $\mu\text{mol/mol}$. All vials in experiment 2 were opened <1 min prior to measurement. Data from this experiment are shown in Figure 4.

8 hr and vials were opened systematically within 20 min of analysis. Each set of SGS solutions was bracketed by acidic and TMAH blanks and an additional SGS prepared in TMAH solution that was used to correct for instrument drift.

Natural coral solution: In a separate experiment (experiment 2, Figure 1b), we analyzed JcP-1, a coral reference material commonly analyzed for I/Ca (e.g., Glock et al., 2014; Lu et al., 2010), in acidic and basic solutions, along with the SGS. Unlike the SGS solutions, corals contain organic matrix in their aragonite skeleton, which might affect the I/Ca analysis. JcP-1 powder was dissolved with 0.5N HNO_3 , then diluted with DI to reach a concentration of 64 mM Ca. An aliquot of that solution was further diluted with 0.5N HNO_3 to create an acidic solution ($\text{pH} \leq 1$) with 4 mM Ca, and another aliquot was diluted with DI and buffered with TMAH to make a solution ($\text{pH} > 12$) with 0.5% TMAH and 4 mM Ca (Figure 1b). Each set of samples included JcP-1, SGS solution, and a blank prepared as described above, forming sets of SGS-blank-JcP-1 in either acidic or basic solution. All solutions were distributed into vials and opened <1 min prior to measurement. When switching between acidic and basic (or vice versa) sets, the system was flushed with an additional basic blank to remove any lingering iodine from the instrument, a concern only during experiments such as this where acidic and basic solutions are analyzed alternately.

2.2. Analysis of I/Ca in Foraminifera

We tested the effects of cleaning methods, concentrations of the acid used for dissolving foraminifera tests, and solution pH on measured I/Ca using core top and down core foraminifera tests from various locations. Previously, foraminifera for I/Ca analysis were cleaned without using reductive solutions (Lu et al., 2010; Zhou et al., 2014). This is different from the cleaning protocol for the measurement of other E/Ca ratios such as Mg/Ca and Cd/Ca (Boyle & Keigwin, 1985; Rosenthal et al., 1997). Therefore, it is not clear whether reductive cleaning has an effect on measured I/Ca; in solution, hydrazine (N_2H_4) used in the reductive cleaning reduces iodate to iodide (e.g., Hasty, 1973; Holak, 1987). In published I/Ca studies, foraminiferal tests are dissolved with HNO_3 of concentrations from 0.075N to 0.5N and diluted to achieve a Ca concentration of $\sim 50 \pm 30$ ppm (or $\sim 1.25 \pm 0.75$ mM) (e.g., Glock et al., 2014; Zhou et al., 2014). For the measurement of other E/Ca ratios in our

Table 1
Site Information for Core Top and Down Core Sediments

| Type | Location | Site | Core | Latitude (N) | Longitude (E) | Water depth (m) |
|-----------|----------------------|----------|-------|--------------|---------------|-----------------|
| core top | Ontong Java Plateau | MW97-20 | MC9 | 0.00 | 159.87 | 2015 |
| core top | Ontong Java Plateau | MW97-20 | MC20 | 0.00 | 159.87 | 2958 |
| core top | Hawaii | MW98-13 | 26GGC | 20.84 | -157.2 | 1200 |
| core top | Peru Margin | KNR195-5 | 12MC | -3.75 | -81.13 | 378 |
| core top | Peru Margin | KNR195-5 | 38MC | -1.27 | -89.70 | 597 |
| core top | Peru Margin | KNR195-5 | 33MC | -3.22 | -82.91 | 2949 |
| core top | Peru Margin | KNR195-5 | 34MC | -3.60 | -83.96 | 3224 |
| core top | North Atlantic Ocean | M39059-2 | - | 39.07 | -10.54 | 1605 |
| core top | Caribbean Sea | OC205-2 | BC60 | 26.14 | -77.74 | 1312 |
| core top | Walvis Ridge | V29-120 | - | -29.83 | 2.63 | 1805 |
| core top | Walvis Ridge | V22-154 | - | -31.20 | 2.77 | 1618 |
| core top | Walvis Ridge | V27-214 | - | -31.12 | 2.68 | 1752 |
| down core | Sea of Japan | YK10-07 | PC4 | 38.21 | 136.92 | 693 |

lab, foraminiferal tests are initially dissolved using 0.065N HNO₃ and diluted to achieve a Ca concentration of 4 ± 2 mM, comparable to that in the SGS, to minimize matrix effects (the effect of Ca concentration on sensitivities of other elements) (Rosenthal et al., 1999). It is not clear whether the concentration of HNO₃ used to dissolve foraminiferal tests has an impact on I/Ca and to what extent the matrix effect plays a role on the measured I/Ca.

Samples: We analyzed I/Ca in 5 planktic foraminifera species (*Globigerinoides ruber*, *Trilobatus sacculifer* (with sac), *Globigerina bulloides*, *Pulleniatina obliquiloculata*, and *Neogloboquadrina dutertrei*) in 12 core top samples from multiple locations and in *G. bulloides* in 14 down core samples from the Sea of Japan (Table 1 and Data Set S1, Figure S1) with sample ages ranging between 10.4 and 26.5 kyr. The age model is based on three radiocarbon data of planktonic foraminifera that were calibrated using Calib7.0.4 with Marine13. Sample depths that go beyond the age model are extrapolated.

Preparation of solutions: Planktic foraminiferal specimens were hand-picked from the >250 μm (for core top samples) or 180–250 μm (for down core samples) size fraction so that the final weight of the specimen for I/Ca analysis falls in the range of ~100–400 μg, which is generally ~20–30 foraminifera. Foraminifera specimens were crushed, split into aliquots, and treated with one of five methodologies, as outlined in Figure 2. To compare the effects of different cleaning procedures on measured I/Ca, foraminifera fragments were cleaned either following the full reductive-oxidative (labeled “R + O”) protocol of Boyle and Keigwin (1985) modified by Rosenthal et al. (1997) and Zhou et al. (2021), or following the same protocol without reductive cleaning (labeled “O”). Notably, all samples underwent a 10 min hot water bath with DI water three times and a methane rinse twice at the beginning of the cleaning and a weak acid leach with 0.001N HNO₃ as the last cleaning step to remove authigenic calcite, which were not always done in other labs. The fully cleaned foraminifera tests were then split into several groups, each of which was dissolved either the night before or the day of I/Ca analysis with 50–150 μL (as needed to achieve full dissolution) of either 0.065N or 0.5N HNO₃ solution. Following dissolution of foraminifera specimens, the solutions were centrifuged for 10 min at 10,000 rpm to concentrate any undissolved solids at the bottom of the vials. Approximately 90–95 μL supernatant was transferred to new 0.5 mL vials and diluted with 300 μL of either 0.5N HNO₃ solution or a mixture of 0.5N HNO₃, 1% TETA, and DI water. This resulted in final solutions with a 1:3 ratio of sample solution to 0.5N HNO₃ solution and a pH of ~1 (groups 1, 3, and 4; Figure 2) or with a 1:2:1 ratio of sample to 1% TETA to DI water and a pH of ~9 (groups 2 and 5).

The SGS and blank solutions were analyzed every five foraminifera samples, and they were prepared in the same way as in experiment 1 (Figure 1a), except that basic blank and SGS solution were buffered using TETA instead of TMAH. At the beginning of each sample run, a set of six multi-element standards with the same EI/Ca ratio but different Ca concentrations were analyzed to constrain the matrix effect following the protocol outlined in Rosenthal et al. (1999). These standards were prepared in a way similar to that of the SGS, that is, from the

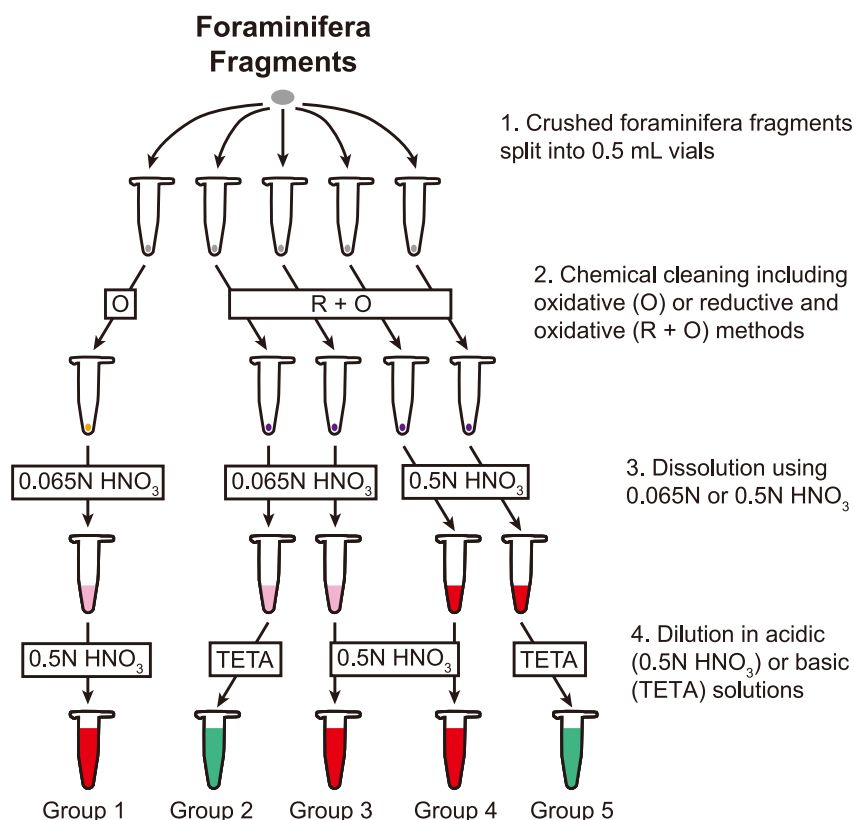


Figure 2. Schematic showing experimental design for experiments testing the effects of pH, cleaning methods, and concentration of acid used to dissolve foraminifera on foraminifera I/Ca values. Spiked gravimetric standard solutions as shown in Figure 1 were distributed into vials and used to correct for instrument drift and convert I/Ca intensity ratios in foraminifera to $\mu\text{mol/mol}$. All vials were opened <1 min prior to measurement. Data from this experiment are shown in Figure 6.

concentrated iodine-free multi-element standard and diluted KIO_3 solution. The Ca and iodate concentrations in these matrix standards range from 1.5 to 8 mM and from 7.5 to 40 nM, respectively. In most runs, JCP-1 was analyzed alongside the foraminifera samples as an extra way to monitor the stability of the instrument during the run and the long-term reproducibility of the measurements. For each batch of sample analysis, a small amount (~1–2 mg) of JCP-1 powder was dissolved and diluted, and analyzed every few samples, usually generating 3–5 measurements per analysis day. All foraminifera and JCP-1 samples were measured from 0.5 mL vials opened within <1 min of measurement.

2.3. Analytical Methods

I/Ca and other EI/Ca ratios were measured using the Element-XR sector-field ICP-MS at Rutgers University. The measurements included elemental ratios of paleoceanographic interest including Li/Ca (e.g., Lear & Rosenthal, 2006), B/Ca (e.g., Sosdian et al., 2018), Na/Ca (e.g., Zhou et al., 2021), Mg/Ca and Sr/Ca (e.g., Rosenthal et al., 2004), Cd/Ca (e.g., Oppo & Rosenthal, 1994), Ba/Ca (e.g., Weldeab et al., 2007), Nd/Ca (e.g., Liu et al., 2015), and U/Ca (e.g., Lear et al., 2016) and ratios measured to monitor contamination including Al/Ca, Ti/Ca, and Mn/Ca. These elemental ratios were measured in low resolution ($m/\Delta m = 300$) following a protocol modified from Rosenthal et al. (1999). Fe/Ca contamination was measured at medium resolution ($m/\Delta m = 3000$). To reduce the boron memory effect and improve washout efficiency, anhydrous ammonia (NH_3) gas was injected into a high purity quartz cyclonic spray chamber (Elemental Scientific, ESI), raising the pH of the injected sample (to >9) and converting boric acid to ammonium borate, which solubilizes and is removed during rinsing (Babila et al., 2014). These conditions should also help to stabilize IO_3^- in the spray chamber. Sample analyses all started within 2 hr after the final solutions were prepared, which reduces iodine loss to a minimum. The operation conditions for the ICP-MS are given in Table 2.

Table 2
Operation Conditions for ICP-MS

| Instrument settings | Value |
|---|--|
| RF power (W) | 1250 |
| Nebulizer uptake rate ($\mu\text{L}/\text{min}$) | 70 |
| Washout time (s) | 60 |
| Uptake time (s) | 60 |
| Ar plasma gas flow rate (L/min) | 16 |
| Ar auxiliary gas flow rate (L/min) | 0.8 |
| Ar nebulizer gas flow rate (L/min) | 0.780 |
| Additional NH_3 gas flow rate (L/min) | 0.357 |
| Optimized In sensitivity in 1 ppb tune solution (cps) | 1,200,000 |
| Optimized UO (%) | ~5% |
| Acquisition settings | Value |
| Isotopes measured | $^{43}\text{Ca}^+$, $^{87}\text{Sr}^{++}$, $^{86}\text{Sr}^+$, $^{127}\text{I}^+$ |
| Resolution | Low resolution |
| Mass window | 10% |
| Sample per peak | 100 |

3. Results and Discussion

3.1. Stability of I/Ca in Standard Solutions

A continuous analysis of the SGS solutions shows identical relative decreases in iodine intensities in both acidic and basic solutions throughout the >8 hr run (Figure 3). For samples measured in closed vials (experiment 1, Figure 1a), there is no discernible difference in the trends of decreasing iodine intensities between the acidic and basic solutions, so we attribute the decrease to loss of instrumental sensitivity. Similar decreasing trends, though with lower magnitude, are observed for calcium intensities. Notably, there is no evidence for additional iodine loss in the acidic solutions, both stored in closed vials and in large open jars, and there is no difference in relative changes in iodine and calcium intensities between the basic solutions buffered with TMAH and TETA (Figure 3). By the end of the 8.5 hr run, iodine intensities decreased by ~30% for the solutions that were kept in closed vials (Figure 3a). In the same experiment, calcium intensities decreased by ~35% by the end of the analysis, in both acidic and basic solutions kept in closed vials (Figure 1b). These trends in elemental sensitivities are corrected for in calcite samples (e.g., foraminifera) using standards such as these, measured periodically over the course of analysis.

In experiment 2, the iodine and calcium intensities of JCp-1 in acidic and basic solutions both decrease with time by about 20%–25% relative to the initial intensities (Figures 4a and 4b). These changes are similar to those in the SGS solutions, which decrease by ~25–30% of the intensities of the first measurements by the end of the run (Figures 4a and 4b). The results of these two experiments are consistent with a recently published study, which shows no significant difference in the iodine concentration measured on check standards with both acidic and basic solution for the first 7 days since the solutions were made (Figure 3 in Cook et al., 2022). The results diverged after 7 days suggesting that slow kinetics of iodine volatilization makes it possible to get reliable I measurements from dilute acidic solution within hours of preparation as we show.

In our calcite (e.g., foraminifera and coral) runs, the I/Ca ratio in the SGS solution is spiked to 5 $\mu\text{mol}/\text{mol}$ and is used to calculate I/Ca ratios in $\mu\text{mol}/\text{mol}$ of foraminifera and JCp-1 samples and correct for instrument drift. After correcting for the drifts, the results of experiment 2 (Figure 4) show that the I/Ca values of JCp-1 in both acidic and basic solutions fall within 2 standard deviations (<3% for both) of the average value of each type during the run (Figure 4c), suggesting that I/Ca values of JCp-1 measured with either method are relatively stable through a sample run. As long as the standard and unknown samples are prepared in the same way (i.e., both are either acidic or basic), the drift in I/Ca throughout the run can be corrected for effectively.

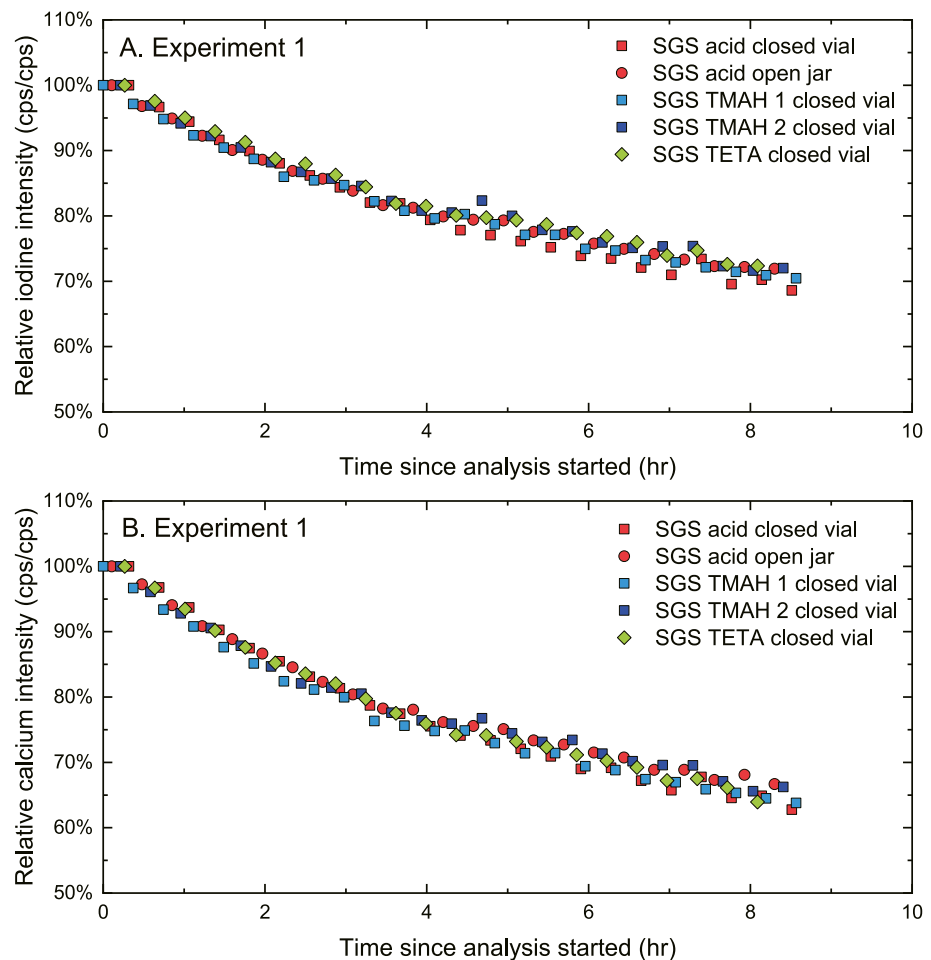


Figure 3. Relative iodine (a) and calcium (b) intensities in acidic (warm colors) and basic (cool colors) spiked gravimetric standard (SGS), in counts per second (cps) normalized to the first measurement of each type. Most solutions were measured in closed vials except where specified.

3.2. Long-Term Reproducibility of I/Ca : I/Ca in JCP-1

We compiled I/Ca data of JCP-1 from 6 foraminifera runs in which JCP-1 was prepared in both acidic and basic solutions to compare the long-term variability of I/Ca between the two methods (Figure 5a). I/Ca values for JCP-1 prepared and measured on the same day in acidic and basic solutions do not show a systematic difference. The relative changes in I/Ca data in acidic and basic solutions between different runs are maintained, suggesting that the variations in I/Ca on different days are likely related to the varying instrument condition on different days rather than a pH effect (Figure 5a).

We also summarize the I/Ca data of JCP-1 over a longer time interval of 4 years (Figure 5b). The results show that the average I/Ca values in acidic and basic solutions are the same within error, that is, 4.20 ± 0.43 (1 SD, $n = 141$) and 4.12 ± 0.26 (1 SD, $n = 41$), respectively (Figure 5b). The average I/Ca value in basic solutions from this study is consistent with the previously reported average I/Ca values of 4.33 ± 0.16 (1 SD, $n = 5$) (Gakushuin University, Japan) (Chai & Muramatsu, 2007) and 4.27 ± 0.06 ($n = 8$) (Lu et al., 2010) that were also analyzed in basic solutions. Our I/Ca data from acidic solutions seem to be more variable, likely because the number of data in that study is also much larger than those in the other two. Although all analyzed in basic solutions, later work by other labs reported lower values, that is, 3.82 ± 0.39 $\mu\text{mol/mol}$ ($n = 60$) (GEOMAR, Kiel, Germany) (Glock et al., 2014) and 3.70 ± 0.27 $\mu\text{mol/mol}$ (1 SD, $n = 2,280$) (Lu, Lu, et al., 2020). These lower values may be derived from different settings of instruments in these institutions, different sample preparation procedures, and/or heterogeneity of JCP-1 powders. In comparison, the difference between the average I/Ca values of JCP-1 prepared in acidic and basic solutions from this study is statistically insignificant.

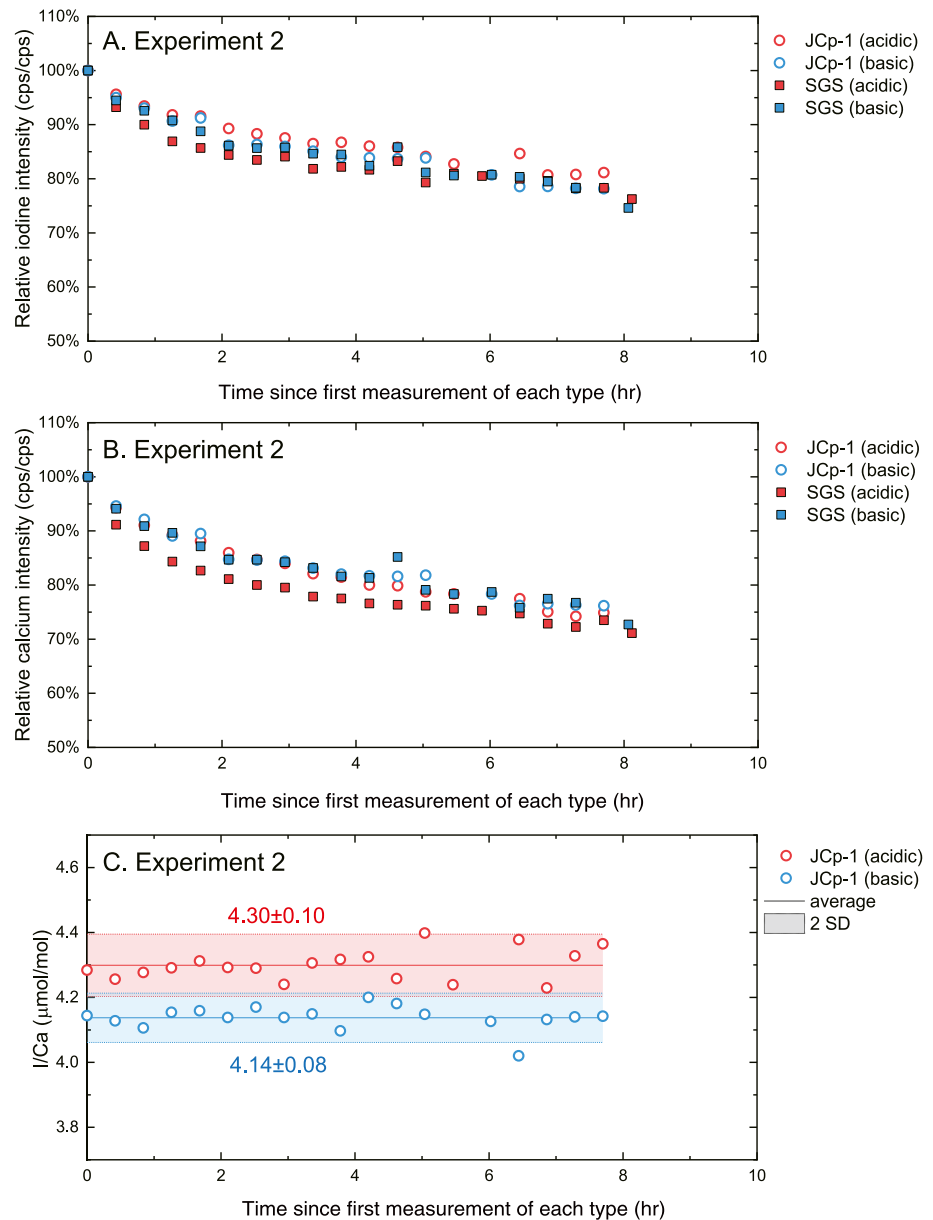


Figure 4. JcP-1 and spiked gravimetric standard (SGS) in acidic and basic (buffered with TMAH) solutions measured over the course of 8 hr. All solutions measured in closed vials opened within <1 min of measurement. Relative iodine (a) and calcium (b) intensities in JcP-1 and SGS, in counts per second (cps) normalized to the first measurement of each type. (c) I/Ca ratios in $\mu\text{mol/mol}$ of JcP-1 measured in acidic (red) and basic (blue) solutions, with the average value and 2 SD shaded and shown with text. SGS data were used to correct data in JcP-1 in parts (a) and (b) to arrive at values shown in part (c).

3.3. Sample Preparation Effects

We compare I/Ca in planktic foraminifera tests that were cleaned, dissolved, and diluted in different ways (Figure 2). The results demonstrate that not only are the differences in I/Ca between samples from oxygen-enriched and oxygen-depleted sites maintained regardless of which method is used but also that the relative order in I/Ca is preserved (Figure 6). This is a clear demonstration for the efficacy of the proposed method. More specifically, we find that among the three investigated factors, the choice of cleaning method has the greatest impact on measured I/Ca (Figure 6). Our data suggest that reductive cleaning reduces I/Ca in foraminifera, resulting in I/Ca values $23 \pm 5\%$ lower in samples that underwent reductive and oxidative cleaning than in samples that underwent only oxidative cleaning (Figure 6c). Similar differences between cleaning methods have been observed for other

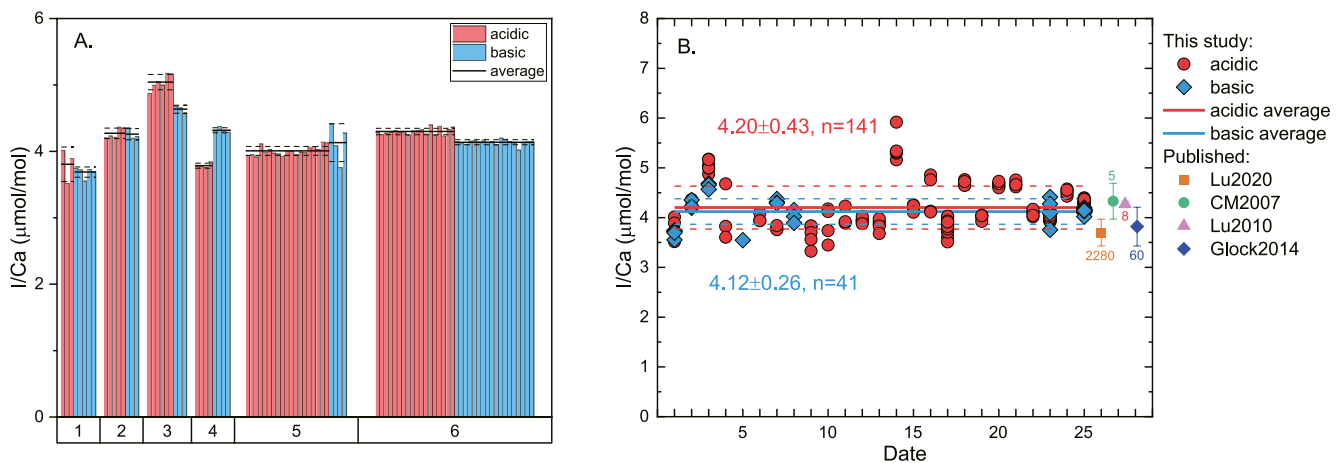


Figure 5. I/Ca in JcP-1 prepared in acidic (pH ~1) and basic (pH ~9) solutions across sample runs. (a) Individual I/Ca values (each bar) from 6 sample runs. The labels 1–6 represent the date I/Ca values were measured, with 1 being the earliest and 6 the latest. Each pair of acidic and basic solutions were prepared and measured on the same day. Basic solutions from 1 to 4 were buffered with triethylenetetramine, while those from 5 to 6 were buffered with TMAH. (b) Compilation of JcP-1 data from all sample runs over a time period of 4 years, with the long-term average I/Ca values for acidic and basic solutions (solid lines) with ± 1 SD (dashed lines). The average RSD for a single measurement of I/Ca in JcP-1 is 2% and 1% in acidic and basic solutions, respectively. The average I/Ca with ± 1 SD of JcP-1 in published studies (Chai & Muramatsu, 2007; Glock et al., 2014; Lu, Dickson, et al., 2020; Lu et al., 2010) are plotted to the right of our data, with the number of data from each study beside their corresponding symbols.

elements such as Mg/Ca (Rosenthal et al., 2004) and are attributed to partial dissolution of the tests during reductive cleaning, which are enriched with Mg and Na (Mezger et al., 2018), and apparently also iodine. We conclude that a correction is needed when comparing results generated by different cleaning methods.

Comparing data from basic and acidic solutions suggests a possible bias at high I/Ca values. Samples from low oxygen sites with I/Ca between 0 and 2.5 $\mu\text{mol/mol}$, generated by both methods, fall within errors on the 1:1 line. At higher oxygen levels (I/Ca > 3 $\mu\text{mol/mol}$) basic solutions display higher I/Ca values than in acidic solutions (Figure 6a). The experiments show insignificant effect due to the choice of acid concentration for dissolving foraminifera tests (Figure 6b). Our observations could be explained by the results of a recently published study suggesting higher iodine volatility at pH < 1, relative to basic solutions (Cook et al., 2022). This would have the largest effect for high I/Ca samples. The results are, however, apparently at odds with the experiments on SGS and

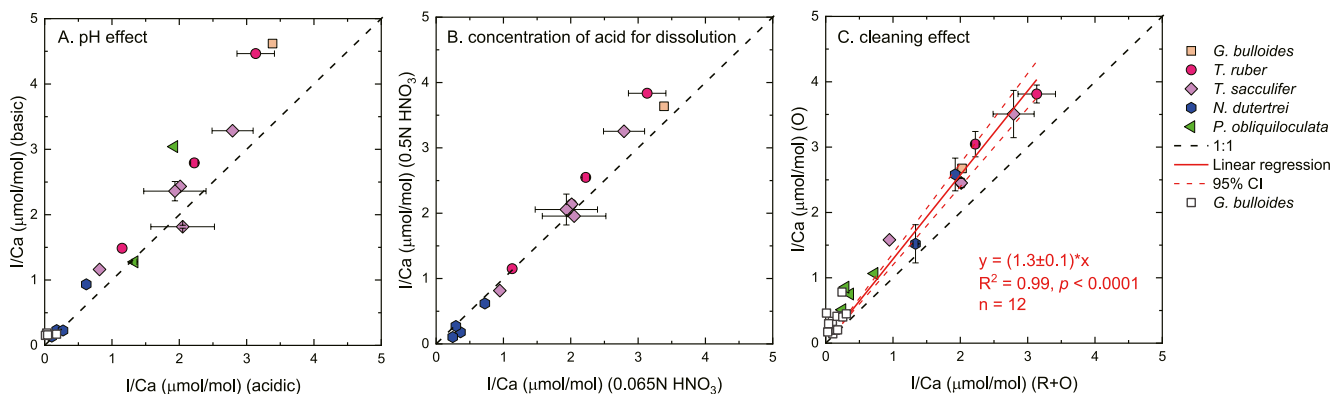


Figure 6. The effects of the pH of solutions (a), acid concentrations used to dissolve samples (b), and different cleaning procedures (c) on I/Ca in multiple planktic foraminifera species from core top sediments in several sites (solid symbols) and in *G. bulloides* from down core sediments in the oxygen depleted Sea of Japan (open squares). For data points with replicates, the average value with 1 SD is plotted. Error bars for single analyses are not plotted because the RSD is generally < 5% and smaller than the symbol size. Samples were treated following the experimental design in Figure 2. In each plot, the effect of a single variable is tested. (a) The x and y axes are I/Ca analyzed in acidic and basic (buffered with triethylenetetramine) solutions (group 3 vs. group 2 and group 4 vs. group 5 in Figure 2), respectively. (b) The x and y axes are I/Ca in foraminifera dissolved by 0.065N (group 3) and 0.5N HNO₃ (group 4), respectively. (c) The x and y axes are I/Ca in foraminifera cleaned with (group 3) and without (group 1) reductive solution, respectively. “R” and “O” in the axis titles represent reductive and oxidative cleaning, respectively. The data from core top samples are fitted with linear regression forced to the origin (red solid line), with 95% confidence intervals (red dashed lines) and the regression equation (slope with 2 SD) shown. Down core data are plotted with the core top data for comparison purposes only, and they are not included in the regression.

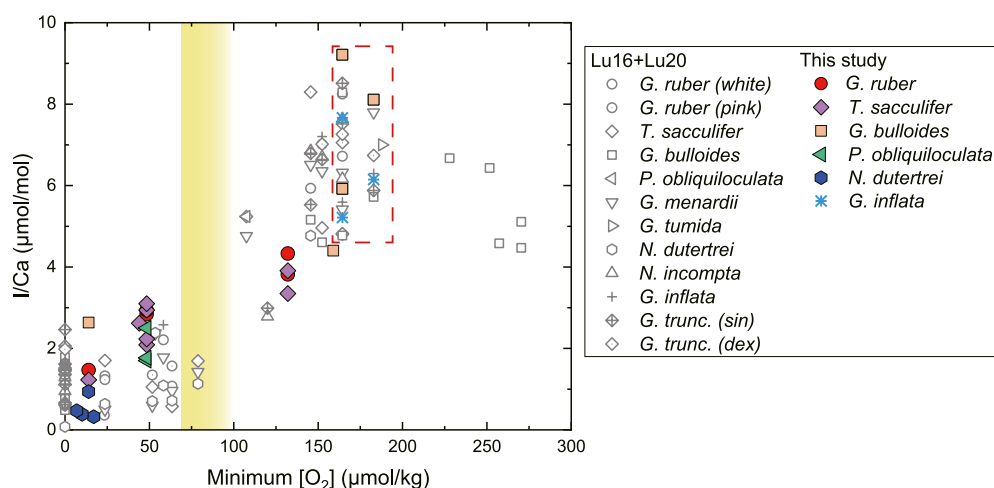


Figure 7. Comparison of I/Ca data from core top planktic foraminifera in this study, corrected for cleaning effect (colored symbols) with published I/Ca data (Lu, Dickson, et al., 2020) (black and white symbols) relative to the minimum oxygen concentration ($[O_2]_{min}$) in the upper ocean at each site. Note that from Lu, Dickson, et al. (2020), only I/Ca data from samples from the uppermost 10 cm of sediment were included. Yellow shading indicates the threshold $[O_2]$ for iodate reduction in the upper ocean (Lu, Dickson, et al., 2020). The planktic I/Ca values from this study are from samples that underwent reductive cleaning and were analyzed in acidic solutions (group 3 as shown in Figure 2), while those from published literature are from samples that were not reductively cleaned and were analyzed in basic solutions. For inter-lab comparison, the I/Ca data from this study have been corrected for cleaning effect by multiplying our I/Ca data by 1.3, the relationship derived from Figure 6c. The $[O_2]_{min}$ data from this study are from the surrounding $0.25^\circ \times 0.25^\circ$ area of each sampling site in WOD18 (Boyer et al., 2018), while the others are from WOD13 as used by Lu, Dickson, et al. (2020). The red dashed box highlights identical samples (colored symbols) analyzed in this study and in Lu, Dickson, et al. (2020).

JCp-1, where a pH effect is not observed consistently (Figures 3 and 4). We also note that at this point we cannot be sure that the results obtained on QP-ICPMS using collision cell mode are directly comparable with results from SF-ICPMS. Therefore, at this point we are not inclined to correct the measured I/Ca data for the difference between acidic and basic solutions until further experiments on samples from more oxygenated areas provide further evidence on a pH effect in foraminiferal I/Ca .

3.4. Comparison With Published Studies

To further assess the reliability of our methods, we have compared our foraminiferal I/Ca data with those from published papers (Figure 7). Because foraminifera samples in previous studies did not undergo reductive cleaning (e.g., Lu et al., 2016; Lu, Dickson, et al., 2020; Zhou et al., 2014, 2016) we applied a +30% correction to our data based on the experiments above (Figure 6c). A direct comparison shows that core top planktic I/Ca values from this study are consistent with data in published literature from the same areas (Lu, Dickson, et al., 2020). In the Peru margin, where the $[O_2]_{min}$ within the oxygen minimum zone is below $20 \mu\text{mol/kg}$, planktic I/Ca values are all below $3 \mu\text{mol/mol}$, consistent with the results from other studies (Lu et al., 2016, Lu, Dickson, et al., 2020) (Figure 7). Our I/Ca data at $[O_2]_{min}$ of $\sim 160\text{--}180 \mu\text{mol/kg}$ are from the same Walvis Ridge sites analyzed by Lu, Dickson, et al. (2020), and I/Ca values are similar to theirs, with I/Ca in *G. bulloides* and *G. inflata* of 5.96 ± 1.29 (7.69 ± 1.66 after correcting for cleaning effect, $n = 3$) and 4.88 ± 0.95 (6.29 ± 1.23 after correcting for cleaning effect, $n = 3$), respectively, in this study, and 6.26 ± 1.82 ($n = 3$) and 6.51 ± 1.04 ($n = 3$), respectively, in Lu, Dickson, et al. (2020) (Figure 7 and Data Set S1). We also provide I/Ca data from areas with minimum oxygen concentrations for which I/Ca has not been reported previously such as at $10\text{--}20 \mu\text{mol/kg}$ and also from a region with $\sim 130 \mu\text{mol/kg}$ (Figure 7). The combined data set of core top planktic I/Ca raises the possibility that the relationship between planktic I/Ca and $[O_2]_{min}$ in the upper ocean may not be constrained by a threshold value, but may show more gradual increase in areas with $[O_2]_{min} < 200 \mu\text{mol/kg}$, but further studies are needed to validate this hypothesis.

4. Summary and Conclusions

Here we assess the potential of measuring foraminiferal I/Ca in acidic solutions as is used for the analysis of other elemental ratios, owing to the slow kinetics of iodine volatilization. We conducted experiments to see whether I/Ca results obtained from acidic solutions, measured within hours of preparation, are comparable with results obtained from basic solutions containing TMAH buffer. We evaluated the effect of solution pH on I/Ca measurement by Element-XR sector-field ICP-MS. The effect of solution pH on I/Ca in a carbonate reference material, JCp-1, and a SGS solution is shown to be statistically insignificant. In core top foraminifera samples from widespread open-ocean sites, I/Ca values that are $>3 \mu\text{mol/mol}$ for samples analyzed in a basic solution are generally higher than for aliquots of the same samples analyzed in acidic solutions. Furthermore, foraminifera samples prepared with reductive and oxidative cleaning have values $\sim 23 \pm 5\%$ lower than in aliquots of the same samples that underwent only oxidative cleaning. The concentration of dilute HNO_3 used to dissolve foraminiferal shells (0.065N compared to 0.5N) seems to have a minimal effect on the measured I/Ca. Despite all these effects, we show that in samples in this study that underwent reductive cleaning, were acid leached before dissolution, and were measured in acidic solutions, the I/Ca values in planktic foraminifera can successfully separate oxygen-depleted from oxygen-enriched states. Furthermore, after correcting for cleaning effect, our I/Ca data are consistent with published data that were generated using TMAH-spiked solutions.

These results suggest that while the traditional analysis of I/Ca should be the preferred method for studies focusing only on I/Ca, when necessary it is also possible to generate reliable I/Ca data in samples that have been reductively cleaned and analyzed in an acidic solution. We show that if foraminifera samples are measured within hours of dissolutions, kept in closed vials that are opened minutes before the measurements, reliable I/Ca data can be obtained. The latter method allows for simultaneous measurement of other trace element data of paleoceanographic interest, such as Mg, on a sector field ICP-MS. With a suite of trace element data generated from the same foraminifera as I/Ca measurements, it may be possible to build a more comprehensive understanding of the controls on this proxy and how oxygenation varies with other paleoceanographic conditions.

Data Availability Statement

The iodine and calcium intensities and I/Ca data used for assessing viability of analyzing iodine in acidic solutions and ^{14}C age model for shallow down core sediments in the study are available at Zenodo via <https://doi.org/10.5281/zenodo.7218066> with license of Creative Commons Attribution 4.0 International.

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References

- Al-Ammar, A., Reitznerová, E., & Barnes, R. M. (2001). Thorium and iodine memory effects in inductively-coupled plasma mass spectrometry. *Fresenius' Journal of Analytical Chemistry*, 370(5), 479–482. <https://doi.org/10.1007/s002160100837>
- Babila, T. L., Rosenthal, Y., & Conte, M. H. (2014). Evaluation of the biogeochemical controls on B/Ca of globigerinoides ruber white from the oceanic flux program, Bermuda. *Earth and Planetary Science Letters*, 404, 67–76. <https://doi.org/10.1016/j.epsl.2014.05.053>
- Boyer, T. P., Baranova, O. K., Coleman, C., Garcia, H. E., Grodsky, A., Locarnini, R. A., et al. (2018). *NOAA Atlas NESDIS In A. V. Mishonov, & Technical (Eds.), (Vol. 87)*.
- Boyle, E. A., & Keigwin, L. D. (1985). Comparison of Atlantic and Pacific paleochemical records for the last 215,000 years: Changes in deep ocean circulation and chemical inventories. *Earth and Planetary Science Letters*, 76(1–2), 135–150. [https://doi.org/10.1016/0012-821x\(85\)90154-2](https://doi.org/10.1016/0012-821x(85)90154-2)
- Brix, K., Hein, C., Sander, J. M., & Kautenburger, R. (2017). Simultaneous quantification of iodine and high valent metals via ICP-MS under acidic conditions in complex matrices. *Talanta*, 167, 532–536. <https://doi.org/10.1016/j.talanta.2017.02.056>
- Chai, J. Y., & Muramatsu, Y. (2007). Determination of bromine and iodine in twenty-three geochemical reference materials by ICP-MS. *Geostandards and Geoanalytical Research*, 31(2), 143–150. <https://doi.org/10.1111/j.1751-908x.2007.00856.x>
- Cook, M. K., Dial, A. R., & Hendy, I. L. (2022). Iodine stability as a function of pH and its implications for simultaneous multi-element ICP-MS analysis of marine carbonates for paleoenvironmental reconstructions. *Marine Chemistry*, 245(20), 104148. <https://doi.org/10.1016/j.marchem.2022.104148>
- Glock, N., Liebetrau, V., & Eisenhauer, A. (2014). I/Ca ratios in benthic foraminifera from the Peruvian oxygen minimum zone: Analytical methodology and evaluation as a proxy for redox conditions. *Biogeosciences*, 11(23), 7077–7095. <https://doi.org/10.5194/bg-11-7077-2014>
- Glock, N., Liebetrau, V., Eisenhauer, A., & Rocholl, A. (2016). High resolution I/Ca ratios of benthic foraminifera from the Peruvian oxygen-minimum-zone: A SIMS derived assessment of a potential redox proxy. *Chemical Geology*, 447, 40–53. <https://doi.org/10.1016/j.chemgeo.2016.10.025>
- Hardisty, D. S., Lu, Z., Bekker, A., Diamond, C. W., Gill, B. C., Jiang, G., et al. (2017). Perspectives on Proterozoic surface ocean redox from iodine contents in ancient and recent carbonate. *Earth and Planetary Science Letters*, 463, 159–170. <https://doi.org/10.1016/j.epsl.2017.01.032>
- Hardisty, D. S., Lu, Z., Planavsky, N. J., Bekker, A., Philippot, P., Zhou, X., & Lyons, T. W. (2014). An iodine record of Paleoproterozoic surface ocean oxygenation. *Geology*, 42(7), 619–622. <https://doi.org/10.1130/g35439.1>
- Hasty, R. A. (1973). Reduction of iodate by hydrazine: Application of the iodide ion selective electrode to the uncatalyzed reaction. *Mikrochimica Acta*, 61(6), 925–933. <https://doi.org/10.1007/bf01218184>

- Holak, W. (1987). Determination of iodine in foods by cathodic stripping voltammetry. *Analytical Chemistry*, 59(17), 2218–2221. <https://doi.org/10.1021/ac00144a047>
- Hoogakker, B. A. A., Lu, Z., Umling, N., Jones, L., Zhou, X., Rickaby, R. E. M., et al. (2018). Glacial expansion of oxygen-depleted seawater in the eastern tropical Pacific. *Nature*, 562(7727), 410–413. <https://doi.org/10.1038/s41586-018-0589-x>
- Lear, C. H., Billups, K., Rickaby, R. E. M., Diester-Haass, L., Mawbey, E. M., & Sostian, S. M. (2016). Breathing more deeply: Deep ocean carbon storage during the mid-Pleistocene climate transition. *Geology*, 44(12), 1035–1038. <https://doi.org/10.1130/g38636.1>
- Lear, C. H., & Rosenthal, Y. (2006). Benthic foraminiferal Li/Ca: Insights into Cenozoic seawater carbonate saturation state. *Geology*, 34(11), 985–988. <https://doi.org/10.1130/g22792a.1>
- Liu, Y., Lo, L., Shi, Z., Wei, K. Y., Chou, C. J., Chen, Y. C., et al. (2015). Obliquity pacing of the western Pacific intertropical convergence zone over the past 282,000 years. *Nature Communications*, 6(1), 10018. <https://doi.org/10.1038/ncomms10018>
- Lu, W., Dickson, A. J., Thomas, E., Rickaby, R. E. M., Chapman, P., & Lu, Z. (2020). Refining the planktic foraminiferal I/Ca proxy: Results from the Southeast Atlantic Ocean. *Geochimica et Cosmochimica Acta*, 287, 318–327. <https://doi.org/10.1016/j.gca.2019.10.025>
- Lu, W., Ridgwell, A., Thomas, E., Hardisty, D. S., Luo, G., Algeo, T. J., et al. (2018). Late inception of a resiliently oxygenated upper ocean. *Science*, 361, 174–177. <https://doi.org/10.1126/science.aar5372>
- Lu, Z., Hoogakker, B. A. A., Hillenbrand, C., Zhou, X., Thomas, E., Gutchess, K. M., et al. (2016). Oxygen depletion recorded in upper waters of the glacial Southern Ocean. *Nature Communications*, 7(1), 11146. <https://doi.org/10.1038/ncomms11146>
- Lu, Z., Jenkyns, H. C., & Rickaby, R. E. M. (2010). Iodine to calcium ratios in marine carbonate as a paleo-redox proxy during oceanic anoxic events. *Geology*, 38(12), 1107–1110. <https://doi.org/10.1130/g31145.1>
- Lu, Z., Lu, W., Rickaby, R. E. M., & Thomas, E. (2020). *Earth history of oxygen and the iprOxy*. In T. Lyons, A. Turchyn, & C. Reinhard (Eds.), Cambridge University Press.
- Mezger, E. M., de Nooijer, L. J., Siccha, M., Brummer, G.-J. A., Kucera, M., & Reichert, G.-J. (2018). Taphonomic and ontogenetic effects on Na/Ca and Mg/Ca in spinose planktonic foraminifera from the Red Sea. *Geochemistry, Geophysics, Geosystems*, 19(11), 4174–4194. <https://doi.org/10.1029/2018gc007852>
- Muramatsu, Y., & Wedepohl, K. H. (1998). The distribution of iodine in the Earth's crust. *Chemical Geology*, 147(3–4), 201–216. [https://doi.org/10.1016/s0009-2541\(98\)00013-8](https://doi.org/10.1016/s0009-2541(98)00013-8)
- Oppo, D. W., & Rosenthal, Y. (1994). Cd/Ca changes in a deep cape basin core over the past 730,000 years: Response of circumpolar deepwater variability to northern hemisphere ice sheet melting? *Paleoceanography*, 9(5), 661–675. <https://doi.org/10.1029/93pa02199>
- Rosenthal, Y., Boyle, E. A., & Labeyrie, L. (1997). Last glacial maximum paleochemistry and deepwater circulation in the Southern ocean: Evidence from foraminiferal cadmium. *Paleoceanography*, 12(6), 787–796. <https://doi.org/10.1029/97pa02508>
- Rosenthal, Y., Field, M. P., & Sherrell, R. M. (1999). Precise determination of element/calcium ratios in calcareous samples using sector field inductively coupled plasma mass spectrometry. *Analytical Chemistry*, 71(15), 3248–3253. <https://doi.org/10.1021/ac981410x>
- Rosenthal, Y., Perron-Cashman, S., Lear, C. H., Bard, E., Barker, S., Billups, K., et al. (2004). Interlaboratory comparison study of Mg/Ca and Sr/Ca measurements in planktonic foraminifera for paleoceanographic research. *Geochemistry, Geophysics, Geosystems*, 5(4), 1–29. <https://doi.org/10.1029/2003gc000650>
- Sostian, S. M., Greenop, R., Hain, M. P., Foster, G. L., Pearson, P. N., & Lear, C. H. (2018). Constraining the evolution of Neogene ocean carbonate chemistry using the boron isotope pH proxy. *Earth and Planetary Science Letters*, 498, 362–376. <https://doi.org/10.1016/j.epsl.2018.06.017>
- Takaku, Y., Shimamura, T., Masuda, K., & Igarashi, Y. (1995). Iodine determination in natural and tap water using inductively coupled plasma mass spectrometry. *Analytical Sciences*, 11(5), 823–827. <https://doi.org/10.2116/analsci.11.823>
- Taylor, M. A., Hendy, I. L., & Chappaz, A. (2017). Assessing oxygen depletion in the Northeastern Pacific Ocean during the last deglaciation using I/Ca ratios from multiple benthic foraminiferal species. *Paleoceanography*, 32(8), 746–762. <https://doi.org/10.1002/2016pa003062>
- Vanhoe, H., Van Allemeersch, F., Versieck, J., & Dams, R. (1993). Effect of solvent type on the determination of total iodine in milk powder and human serum by inductively coupled plasma mass spectrometry. *Analyst*, 118(8), 1015–1019. <https://doi.org/10.1039/an9931801015>
- Weldeab, S., Lea, D. W., Schneider, R. R., & Andersen, N. (2007). Centennial scale climate instabilities in a wet early Holocene West African monsoon. *Geophysical Research Letters*, 34(24), L24702. <https://doi.org/10.1029/2007gl031898>
- Winkelbauer, H., Cordova-Rodriguez, K., Reyes-Macaya, D., Scott, J., Glock, N., Lu, Z., et al. (2021). Foraminifera iodine to calcium ratios: Approach and cleaning. *Geochemistry, Geophysics, Geosystems*, 22, 1–11. <https://doi.org/10.1029/2021gc009811>
- Zhou, X., Jenkyns, H. C., Owens, J. D., Junium, C. K., Zheng, X., Sageman, B. B., et al. (2015). Upper ocean oxygenation dynamics from I/Ca ratios during the Cenomanian-Turonian OAE 2. *Paleoceanography*, 30(5), 510–526. <https://doi.org/10.1002/2014pa002741>
- Zhou, X., Rosenthal, Y., Haynes, L., Si, W., Evans, D., Huang, K.-F., et al. (2021). Planktic foraminiferal Na/Ca: A potential proxy for seawater calcium concentration. *Geochimica et Cosmochimica Acta*, 305, 306–322. <https://doi.org/10.1016/j.gca.2021.04.012>
- Zhou, X., Thomas, E., Rickaby, R. E. M., Winguth, A. M. E., & Lu, Z. (2014). I/Ca evidence for upper ocean deoxygenation during the PETM. *Paleoceanography*, 29(10), 964–975. <https://doi.org/10.1002/2014pa002702>
- Zhou, X., Thomas, E., Winguth, A. M. E., Ridgwell, A., Scher, H., Hoogakker, B. A. A., et al. (2016). Expanded oxygen minimum zones during the late Paleocene-early Eocene: Hints from multiproxy comparison and ocean modeling. *Paleoceanography*, 31(12), 1532–1546. <https://doi.org/10.1002/2016pa003020>

References From the Supporting Information

- Schlitzer, R. (2021). Ocean data view.