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RESEARCH ARTICLE
10.1029/2021GC009811

Key Points:

- Tetramethylammonium hydroxide and ammonium hydroxide can both be used to stabilize iodine in solution
- At least 20 foraminifera >300 μm give stable I/Ca results
- Clay removal steps and extended H_2O_2 cleaning steps yield the best results for I/Ca analysis

Supporting Information:

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

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Citation:

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*, e2021GC009811. https://doi.org/10.1029/2021GC009811

Received 2 APR 2021
Accepted 14 OCT 2021

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Foraminifera Iodine to Calcium Ratios: Approach and Cleaning

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Abstract Planktic and benthic foraminiferal iodine (I) to calcium (Ca) molar ratios have been proposed as an exciting new proxy to assess subsurface and bottom water oxygenation in the past. Compared to trace metals, the analysis of iodine in foraminiferal calcite is more challenging, as iodine is volatile in acid solution. Here, we compare previous analyses that use tertiary amine with alternative analyses using tetramethylammonium hydroxide (TMAH) and ammonium hydroxide (NH_4OH) to stabilize iodine in solution. In addition, we assess the effect of sample size and cleaning on planktic and benthic foraminiferal I/Ca. Our stabilization experiments with TMAH and NH_4OH show similar trends as those using tertiary amine, giving relatively low I/Ca ratios for planktic and benthic foraminifera samples from poorly oxygenated waters, and high ratios for well-oxygenated waters. This suggests that both alternative methods are suitable to stabilize iodine initially dissolved in acid. Samples that contain 5–10 specimens show a wide spread in I/Ca. Samples containing 20 specimens or more show more centered I/Ca values, indicating that a larger sample size is more representative of the average planktic foraminifera community. The impact of cleaning on planktic and benthic foraminifera I/Ca ratios is very similar to Mg/Ca, with the largest effect occurring during the clay removal step. The largest iodine contaminations were recorded at locations characterized by moderate to high organic carbon contents. In those circumstances, we recommend doubling the oxidative cleaning steps (4 instead of 2 repetitions) to ensure that all organic material is removed.

1. Introduction

Oxygen concentrations [O_2] in the oceans have been decreasing and oxygen minimum zones (OMZ) expanding since 1960 (Schmidtko et al., 2017). Climate models also show this decrease and predict that this trend will not only continue but accelerate in the future (Oschlies et al., 2008, 2018). To better understand the longer-term oxygen cycle in the past, on time scales typically exceeding centuries to millennia, we can use proxy reconstructions (Moffitt et al., 2015). Most proxy reconstructions assess in-situ bottom water [O_2] and rely on sedimentary samples (e.g., Choumiline et al., 2019; Crusius et al., 1996; Glock et al., 2014; Hoogakker et al., 2015; Nameroff et al., 2002). Reconstructions of low-oxygen environments are therefore commonly restricted to sediments directly immersed by low oxygen waters at the time of interest.

Today hypoxic waters ([O_2] < 60 μmol/kg, Breitburg et al., 2018) typically occur at water depths shallower than 1 km. In the open ocean, beyond the continental slopes and shelves immersed by these waters, it is more challenging to assess upper ocean oxygen conditions from sedimentary proxy methods. Recently, a new approach emerged to evaluate past seawater redox conditions using planktic foraminifera iodine/calcium (I/Ca) molar ratios (Lu et al., 2016a, 2016b, 2020). Planktic foraminifera reside in the upper ocean between the surface and ~1,000 m depending on species (Schiebel & Hemleben, 2017) and after reproduction the empty calcite tests may be buried in the underlying deep-sea sediments. Studying I/Ca of fossil planktic foraminifera tests facilitates the study of seawater redox conditions in the open ocean environment.

In seawater, there are two thermodynamically stable iodine species, iodide (I^-, reduced form) and iodate (IO_3^-, oxidized form), and their equilibration is highly redox sensitive. In the oxygenated ocean, the distribution of I^- and IO_3^- is thought to arise from the interplay of biologically mediated transformations, and the processes of physical mixing and advection (Bluhm et al., 2010; Campos et al., 1996; Chance et al., 2007, 2010, 2014; Jickells et al., 1988; Truesdale et al., 2000; Waite et al., 2006). In subsurface environments where oxygen is depleted (typical $[O_2]$ below 7 ± 2 μmol/kg), I^- is the prevalent iodine species (Cutter et al., 2018; Rue et al., 1997). This is because IO_3^- is one of the first molecules that serves as an electron acceptor when oxygen is depleted; it has a redox potential of 10–10.7, close to that of the O_2-H_2O couple (Wong & Brewer, 1977). Anoxic water bodies akin to the tropical OMZs of the eastern Pacific as well as the Black Sea, Cariaco Trench, and Orca basins, show an absence of IO_3^- in favor of I^- (Cutter et al., 2018; Wong & Brewer, 1977; Wong et al., 1985).

Lu et al. (2010) showed that IO_3^- is the primary ionic iodine species incorporated in laboratory grown carbonates, assumed to substitute for carbonate ion. The charge deficit is thought to be counterbalanced by Na^+ and H^+ in place of the Ca^{2+} (Feng & Redfern, 2018; Kerisit et al., 2018; Podder et al., 2017). Subsequent calibration work (Lu et al., 2016a, 2016b, 2020) suggests that subsurface $[O_2]$ may be the dominant control on planktic foraminiferal I/Ca ratios, showing that I/Ca ratios decrease when subsurface $[O_2]$ declines below 70–100 μmol/kg. The I/Ca redox proxy is used as a qualitative rather than quantitative oxygen proxy, and application of the planktic foraminifera I/Ca proxy has provided invaluable new insights into subsurface water oxygenation during the last glacial: Southern Ocean subsurface waters were depleted in oxygen during glacial times (Lu et al., 2016a, 2016b), and glacial subsurface waters of the tropical equatorial North Pacific were under the influence of low oxygen waters as they are today (Hoogakker et al., 2018).

Planktic foraminifera I/Ca ratios were previously measured using quadrupole inductively coupled plasma mass-spectrometry (ICP-MS) (Hoogakker et al., 2018; Lu et al., 2016a, 2016b), where cleaned samples are dissolved in 3% nitric acid (HNO_3) and diluted to 50 μg/ml calcium. As iodine is volatile in acid solution, a tertiary amine solution (Spectrasol, CFA-C) was added to stabilize the samples, and measurements were carried out immediately after dissolution to minimize potential iodine loss. In other studies, tetramethylammonium hydroxide (TMAH) was used as stabilizing base (Glock et al., 2014; Zhou et al., 2017). Since the tertiary amine solution can be difficult to procure, we will compare previously published data by Lu et al. (2016a, 2016b) with our measurements using TMAH and also ammonium hydroxide (NH_4OH), a less toxic alternative.

Prior to trace element analyses, foraminifera are cleaned to remove impurities. Barker et al. (2003) show that ultrasonification of the crushed tests, using ultrapure water followed by methanol to remove clays, causes a significant decrease in Mg/Ca ratios of planktic foraminifera. Removal of organic material using hot, NaOH-buffered solution of H_2O_2 causes a further reduction in planktic foraminifera Mg/Ca ratios (Barker et al., 2003). Lu et al. (2016a, 2016b) and Hoogakker et al. (2018) followed the Mg/Ca cleaning method of Barker et al. (2003) to prepare samples for I/Ca analysis. Recently, Glock et al. (2016, 2019) showed that consecutive oxidative cleaning steps may be essential to remove all organic material, which tends to be elevated with iodine, from benthic foraminifera from the poorly oxygenated Peruvian continental margin. Samples not sufficiently cleaned could provide qualitative estimates of paleo-bottom water oxygen concentrations that are unrealistically high. To our best knowledge, nobody has assessed this for planktic foraminifera, and we therefore expand on this here. We assess the effect of oxidative cleaning steps on planktic and benthic foraminifera from areas with well-oxygenated and poorly oxygenated subsurface waters from the Atlantic and Pacific oceans.

Iodine/calcium ratios in planktic foraminifera calcite are a hundred to a thousand times lower compared to other routinely analyzed element/Ca ratios, and iodine has a lower ionization potential (Houk, 1986). I/Ca ratios are reported as μmol/mol, whereas Mg/Ca, Sr/Ca, Mn/Ca, and Ba/Ca are often reported as mmol/mol (e.g., Barker et al., 2003). Variations between individual tests from the same sample have been shown for trace elements (e.g., Anand & Elderfield, 2005; Fehrenbacher et al., 2020) and stable isotopes (e.g., Ishimura et al., 2004). Variation in trace elements between individual tests could be caused by different living depths with different environmental forcing, different seasonal origin of the individual tests or bioturbation which brings older tests back to the surface. This leads to the question what minimum number of tests will represent the population.

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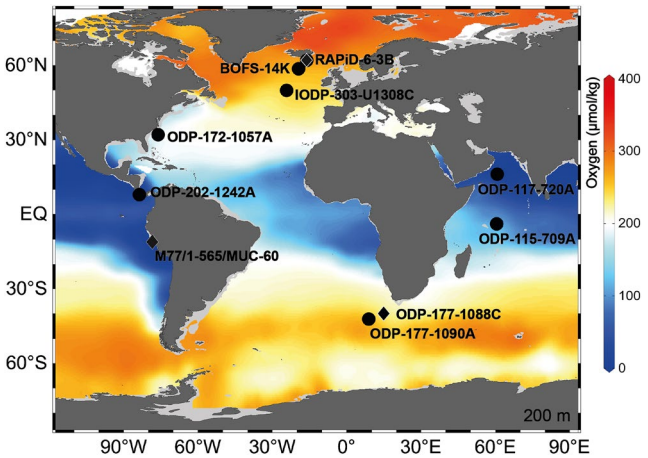

Figure 1. Map showing sample locations and oxygen concentration (µmol/kg) at 200 m water depth from GLODAPv2.2019 (Olsen et al., 2019). Areas in dark blue are characterized by hypoxic to suboxic conditions. The circles show sample sites for the iodine stabilization and the sample size experiments; the diamonds show the sites for the cleaning experiments. The map was created with the Ocean Data View software (Schlitzer, 2021).

Here, we report experiments for the reproducibility of results using different stabilization methods, we show the variability of I/Ca in samples with larger and smaller numbers of foraminiferal tests, and we show the effects of a range of different cleaning treatments using water, methanol, hydrogen peroxide, and dilute acid.

2. Materials and Methods

2.1. Iodine Stabilization

We measured I/Ca ratios in foraminifera from sediment samples in two different laboratories using NH_4OH as a stabilizer at Oxford University and TMAH at the British Geological Survey (BGS) in Keyworth. We compare these results to previously published data (Lu et al., 2016a, 2016b) from the same cores measured at Syracuse University, NY, USA. This section explains the detailed methods used in the two laboratories and the sample material used for each experiment.

The use of NH_4OH as an iodine stabilizer was tested using a magnetic-sector ICP-MS (Thermo Finnigan Element 2) at the Department of Earth Sciences, University of Oxford. Cleaned samples, containing a minimum of 30 specimens of the >300 µm fraction, were dissolved in 2% (v/v) ultrapure HNO_3 (stock solution was 70% w/w) and buffered with 3% (v/v) NH_4OH to create a solution at a pH of 9. Samples were centrifuged and split into two vials: (a) for preratio screening to determine calcium concentrations and (b) for I/Ca determinations, where each sample was diluted to 40 mg kg^{-1} Ca. For the calculation of I/Ca we used data from the measurements of ^{127}I and ^{43}Ca; ^{48}Ca and ^{27}Al were analyzed as controls and are not discussed here. An external standard material from ground coral called JCP-1 was used at regular intervals to ensure cross study comparability.

We used multiple interglacial samples from ODP Sites 1090 (South Atlantic), 720 (Arabian Sea) and 1242 (East Pacific). ODP Site 1090 has a well-oxygenated water column. ODP Sites 720 and 1242 have well-developed OMZs in subsurface waters. Samples from ODP Sites 1090 and 1242 are from the Holocene (current interglacial); samples from ODP 720 are from the previous interglacial, Marine Isotope Stage (MIS) 5, evidenced by the occurrence of the planktic foraminifera *Globigerinoides ruber* (pink) during the preceding deglaciation (see Supplementary Text and Figures S4 and S5 in Supporting Information S1). Low planktic foraminifera I/Ca during MIS 5, suggest that the OMZ was prevalent during the previous interglacial (Lu et al., 2016a, 2016b) (Figure 1).

Tetramethylammonium hydroxide (TMAH) was tested as an iodine stabilizer at the British Geological Survey in Keyworth using an Agilent Technologies 8900 ICP-QQQ instrument, connected to an Agilent SPS 4 autosampler. Cleaned samples, containing 20–50 specimens of the >300 µm fraction, were dissolved in ultrapure HNO_3 (0.5–3%). Samples were centrifuged and split into two vials, one for iodine counts and one for calcium counts. Iodine and calcium concentration were measured in different runs and the I/Ca in the original dilution was calculated from these separate values. The aliquot for iodine analyses was stabilized with TMAH so that basic pH (>7) was achieved. A mixed internal standard solution containing Sc, Ge, Rh, In, Te, and Ir (Te only for iodine determination) was added to the samples at a fixed ratio of approximately 1:10 via a dedicated port in the sample introduction valve. Any suppression of the instrument signal caused by the matrix was corrected by the software using the response of the internal standard. Blanks and quality control standards have been analyzed at the start and end or each run and after no more than every 30 samples.

I/Ca molar ratios were calculated using the molar amount of ^{127}I and ^{42}Ca. ^{43}Ca and ^{44}Ca were measured as controls. Furthermore, we analyzed ^{23}Na, ^{24}Mg, ^{27}Al, ^{55}Mn, ^{56}Fe, ^{88}Sr, and ^{137}Ba that are not discussed in this study. During these analyses, no external standard material was used. Sample material was derived from the Holocene Atlantic (BOFS 14K, RAPID-6-3B, ODP 1057A, IODP U1308C), the Indian Ocean (ODP 720A and 709A), and the Pacific (ODP 1242A) (see Table 1). ODP Sites 720A and 1242A both have a subsurface OMZ. All samples are of Holocene age, apart from ODP 720A, which is from the previous interglacial, as

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Table 1
Sample Details for Iodine Stabilization Chemicals (Tertiary Amine, TMAH, and NH_4OH)

Cruise	Sites	Longitude (degrees east)	Latitude (degrees north)	Depth (m)	Core depth (cm)	Foraminifera species	Type of treatment during stabilization
ODP-177	1090A	8.90	−42.91	3,699	0–1	*Globigerina bulloides*	Tertiary amine[a], NH_4OH
ODP-177	1088C-1H-1A	13.56	−41.14	2,082	0–1	*Globorotalia inflata*	TMAH
						Globorotalia truncatulinoides	
						Globorotalia hirsuta	
						G. bulloides	
ODP-115	709A	60.55	−3.92	3,047	1–3	*Trilobatus sacculifer*	Tertiary amine[a], TMAH
						Pulleniatina obliquiloculata	
						Globorotalia menardii	
ODP-202	1242A-1H-1A	−83.61	7.86	1,363	32–34[a] 57–58	*G. menardii*	Tertiary amine[a], TMAH, NH_4OH
						Neogloboquadrina dutertrei	
IODP-303	U1308C	−24.24	49.88	3,873	0–6	*G. bulloides*	Tertiary amine[a], TMAH
						G. inflata	
ODP-117	720	60.74	16.13	4,045	20–22[a] 12–18	*G. menardii*	Tertiary amine[a], TMAH, NH_4OH
						N. dutertrei	
						T. sacculifer	
ODP-172	1057A	−76.08	32.03	2,584	0–2[a] 14–15	*Orbulina universa*	Tertiary amine[a], TMAH
BOFS	BOFS14K	−19.43	58.63	1,756	0–1[a] 2–3	*G. bulloides*[a]	Tertiary amine[a], TMAH
						G. inflata	
RAPiD	6-3B	−16.06	62.06	2,228	0–1[a] 1–3	*G. bulloides*	Tertiary amine[a], TMAH

[a]From Lu et al. (2016a, 2016b).

discussed above (see Text S1 in Supporting Information S1 for approximate samples ages based mostly on stable isotope analysis).

Before analysis, samples for the stabilization experiments (described above) and specimen number (see Section 2.2), were cleaned using the same method as Lu et al. (2016a, 2016b). This includes ultrasonification with ultrapure water, methanol, and an oxidative cleaning step, all based on the Mg/Ca cleaning protocol of Barker et al. (2003). The process is explained in more detail in Section 2.3 where it corresponds to treatment T3.

2.2. Planktic Foraminifera Specimen Numbers

We assess intrasample variability of I/Ca ratios through analyses of different sample sizes from locations with high and low $[O_2]$ in subsurface waters. Samples are from the Atlantic (BOFS 14K, RAPID-6-3B), Indian Ocean (ODP 709A, 720), and South Atlantic (ODP 1088) and are mostly Holocene in age, except ODP 720 which is from the previous interglacial (Text S1 in Supporting Information S1). We used foraminifera samples with 5, 10, 20, 30, 40, or 50 individuals where possible and made multiple measurements of smaller and larger samples. We could not use all the sample size classes for all samples. The samples were picked from the >300-μm size fraction. The analysis method is the same as in Section 2.2 for the iodine stabilization at the BGS in Keyworth using TMAH, except for three samples with 50 individuals from ODP 1088 and BOFSS14K which were measured later and stabilized with NH_4OH.

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Table 2
Cleaning Treatments: W = 18.2 MΩ cm Ultrapure Water, M = Methanol (Chromatography Grade), P = Buffered Hydrogen Peroxide, A = 0.001 mol/L Nitric Acid

Treatment	Procedure
T0	No cleaning
T1	5W
T2	5W + 2M + 2W
T3	5W + 2M + 2W + 2P + 2W
T4	5W + 2M + 2W + 2P + 2W + A + 2W
T5	5W + 2M + 2W + 4P + 2W
T6	5W + 2M + 2W + 6P + 2W
T7	5W + 2M + 2W + 10P + 2W

Note. See text for exact reagent preparations. Note that we rinsed out the reagents with two extra water rises before using the next reagent and in the end.

2.3. Cleaning Methods

The Mg/Ca cleaning procedure of Barker et al. (2003) was used as a blueprint for our different treatments. First, the foraminifera were gently crushed between two glass plates and transferred into 0.5 ml polypropylene centrifuge tubes. Further steps include ultrasonication for 1–2 min with (a) ultrapure water (18.2 MΩ cm) (5 times) and (b) methanol (2 times), (c) oxidative cleaning using buffered hydrogen peroxide (H_2O_2) (0–10 times) and (d) a dilute 0.001 mol/L nitric acid leach (Table 2). After the cleaning steps 2–4 using methanol, H_2O_2, and dilute nitric acid, the samples were rinsed with ultrapure water twice to rinse out remnant reagents.

During cleaning steps T3 to T7 organic material was removed using 1% v/v H_2O_2 (stock solution 30% w/w) buffered in 0.1 mol/L NaOH while bathing the sample tubes in slightly boiling water. Treatment T3 represents the recommended "normal" Mg/Ca organic carbon removal step of Barker et al. (2003). For this, samples are immersed with the fresh, buffered H_2O_2, 2 times in a row (each time lasting 10 min), with brief ultrasonification of a few seconds at 5 min and agitation every 2.5 min. For T5, T6, and T7, the samples were immersed 4, 6, and 10 times with fresh buffered H_2O_2. For T4, we also carried out a weak acid leach. The water and methanol rinses follow the suggestion of Barker et al. (2003) and the rest of the treatments focuses mainly on the amount of oxidative cleaning because iodine contamination might strongly be related to organic heterogeneities (Glock et al., 2016, 2019). We did not test reductive cleaning as it has been shown by Zhou et al. (2014) that Mn coatings, which are removed by reductive cleaning, have no influence on I/Ca rations.

We examined the effects of the different cleaning treatments on both benthic and planktic foraminifera from Holocene samples from high-oxygen and low-oxygen environments (Table 3).

Typically, samples contained between 20 and 50 specimens of the >300-μm size fraction, except *Neogloboquadrina dutertrei*, which was from >250 μm. Average precleaning sample weights for *Melonis* spp., *N. dutertrei*, and *Globorotalia inflata* were 950 μg. For the benthic foraminifera, we used samples from well-oxygenated bottom water (O_2 > 160 μmol/kg) from the Iceland Basin (shallow infaunal species *Melonis* spp. from RAPID 6-3B) and poorly oxygenated bottom water (O_2 ~ 8 μmol/kg) from the Peruvian margin (epifaunal species *Planulina limbata*, and infaunal species *Uvigerina striata* from M77/1). *P. limbata* specimens were generally larger in size, and between 10 and 25 specimens were used for the various experiments.

For planktic species, we focused on the well-oxygenated Agulhas Ridge in the south Atlantic (*G. inflata* at ODP Site 1088) and Cocos Ridge in the eastern tropical Pacific off Panama with a well-developed OMZ in its subsurface waters (*N. dutertrei* from ODP Site 1242). Table 2 provides details of cleaning steps involved with the different treatment numbers. The analysis for the cleaning experiments has been conducted at the BGS in Keyworth with the same method as for the iodine stabilization experiment (see Section 2.2).

Table 3
Details of Samples Used for the Cleaning Experiments

Cruise	Site	Core depth (cm)	Species	Latitude (degrees north)	Longitude (degrees east)	Bottom depth (m)	$[O_2]$ (μmol/kg)
RAPiD	6-3B	1–3	*Melonis* spp.	62.06	−16.06	2,228	>160[a]
ODP-177	1088C-1H-1A	0–1	*G. inflata*	−41.136	13.563	2,082	178–270[b]
M77/1	565/MUC-60	0–1	*Uvigerina striata*	−11.133	−78.357	640	8.2[a]
M77/1	565/MUC-60	0–1	*Planulina limbata*	−11.133	−78.357	640	8.2[a]
ODP-202	1242A-1H-1A	52–62	*N. dutertrei*	7.86	−83.61	1,360	5.3–208[b]

Note. The $[O_2]$ is from bottom waters for benthic species and the water column for planktic species.
[a]From CTD measurements. [b]From WOA13 yearly averages (Garcia et al., 2013).

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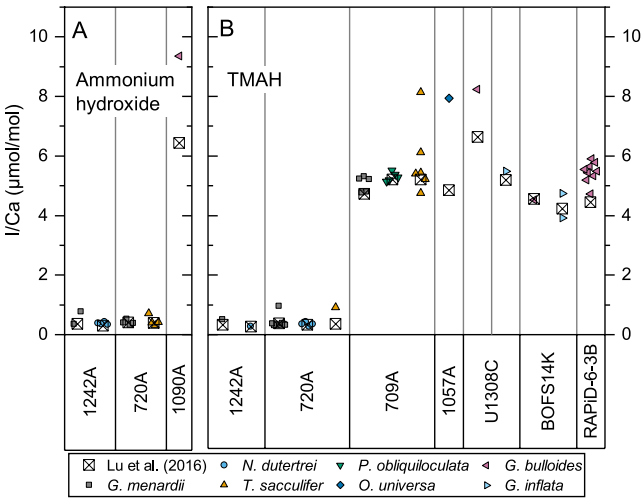

Figure 2. Iodine stabilization experiments. Crossed boxes in (a) and (b) show planktic foraminifera I/Ca ratios (µmol/mol) stabilized with tertiary amine (Lu et al., 2016a, 2016b). (a) shows details of planktic foraminifera I/Ca ratios with iodine stabilized by NH_4OH, whereas (b) shows them stabilized using TMAH.

3. Results and Discussion

3.1. Iodine Stabilization

Iodine is volatile in acidic solution, and to minimize any potential iodine loss a base is added. Lu et al. (2010, 2016a, 2016b) added the tertiary amine solution Spectrasol CFA-C immediately after dissolution. Figure 2 shows the results of our assessment of using NH_4OH and TMAH as alternative stabilization solutions.

Results obtained using NH_4OH as a stabilizer show similar features as those using the tertiary amine solution (Figure 2a): at ODP Site 720 from the Arabian Sea, with a subsurface OMZ, Lu et al. (2016a, 2016b) report a value of 0.39 µmol/mol for mixed layer dweller *Trilobatus sacculifer* and 0.40 µmol/mol for thermocline dweller *Globorotalia menardii*. Those values are within one standard deviation of our results that use NH_4OH as a stabilizer: 0.39 ± 0.17 µmol/mol (*T. sacculifer*, $n = 4$) and 0.41 ± 0.09 µmol/mol (*G. menardii*, $n = 4$). However, at the well-oxygenated Site ODP 1090, we find a much higher I/Ca ratio of 9.46 µmol/mol in *Globigerina bulloides* while Lu et al. (2016a, 2016b) found 6.43 µmol/mol. Both values fit to well-oxygenated conditions with I/Ca ratios >2.5 µmol/mol as suggested by Lu et al. (2016a, 2016b, 2020). Part of the difference between our value and the previously published one may be explained by a general slight tendency of our method for higher values as shown by the result of the JCP-1 standard, that we measured with NH_4OH in Oxford. While our result is 4.53 ± 0.11 µmol/mol, Lu et al. (2010) reports 4.27 ± 0.06 µmol/mol and Glock et al. (2014) 3.82 ± 0.08 µmol/mol. The higher I/Ca ratios in our NH_4OH stabilized samples could mean that it retains iodine better, but the limited samples do not allow us to draw a final conclusion. The interstudy differences also point toward the iodine heterogeneity in the JCP-1 material as shown by Glock et al. (2014) and JCP-1 has never been certified for iodine homogeneity. As the I/Ca redox proxy is a qualitative proxy, with the general trend agreeing with that of samples stabilized by tertiary amine solution, we conclude that NH_4OH is a suitable substitute for tertiary amine to stabilize iodine dissolved in acid.

Using TMAH to stabilize iodine dissolved in acid solution also shows very similar results to those using tertiary amine solution (Figure 2b). At our ODP Site 1242 from the Pacific, with subsurface OMZ, I/Ca for *G. menardii* is 0.36 µmol/mol (Lu et al., 2016a, 2016b, tertiary amine), versus 0.52 µmol/mol (this work with TMAH), and for *N. dutertrei* it is 0.29 µmol/mol (tertiary amine) versus 0.28 (TMAH; µmol/mol). Similarly, in the Arabian Sea ODP Site 720A stabilization with TMAH provided I/Ca ratios of 0.41 ± 0.21 µmol/mol for *G. menardii* and 0.36 ± 0.06 µmol/mol for *N. dutertrei*, which are very similar to those measured using tertiary amine (0.40 and 0.30 µmol/mol, respectively).

At locations where subsurface waters are characterized by well-oxygenated conditions, we find I/Ca ratios in the region of 4–8 µmol/mol, similar to results obtained by Lu et al. (2016a, 2016b) using tertiary amine to stabilize iodine (Figure 2b). For North Atlantic Site BOFS 14K I/Ca, ratios are very similar using either stabilization method (*G. bulloides*: 4.18 µmol/mol (tertiary amine) versus 4.52 µmol/mol (TMAH); *G. inflata*: 4.25 µmol/mol (tertiary amine) versus 3.91 µmol/mol (TMAH)). Furthermore, for Indian Ocean ODP Site 709A, I/Ca ratios obtained using TMAH as a stabilizing solution are within one standard deviation from those obtained using tertiary amine for *T. sacculifer* (6.04 ± 1.83 µmol/mol versus 5.24 µmol/mol) and *Pulleniatina obliquiloculata* (5.32 ± 0.18 µmol/mol versus 5.24 µmol/mol), but TMAH results for *G. menardii* are somewhat elevated (5.21 ± 0.25 µmol/mol versus 4.76 µmol/mol). The ODP Site 709A *T. sacculifer* sample shows larger variation within replicates pointing to large intertest variability or contamination retained after the cleaning procedure in one sample with particular high I/Ca of 8.14 µmol/mol. For the well-oxygenated North Atlantic ODP Sites 1057, IODP U1308C, and RAPiD-6-3B results obtained using TMAH as a stabilizer generally seem somewhat elevated compared to those obtained with tertiary amine as a stabilizing solution by Lu et al. (2016a, 2016b). This may be due to impurities in TMAH. However, a lack of elevated values for TMAH stabilized solutions at sites with I/Ca ratios <1 µmol/mol recorded for both

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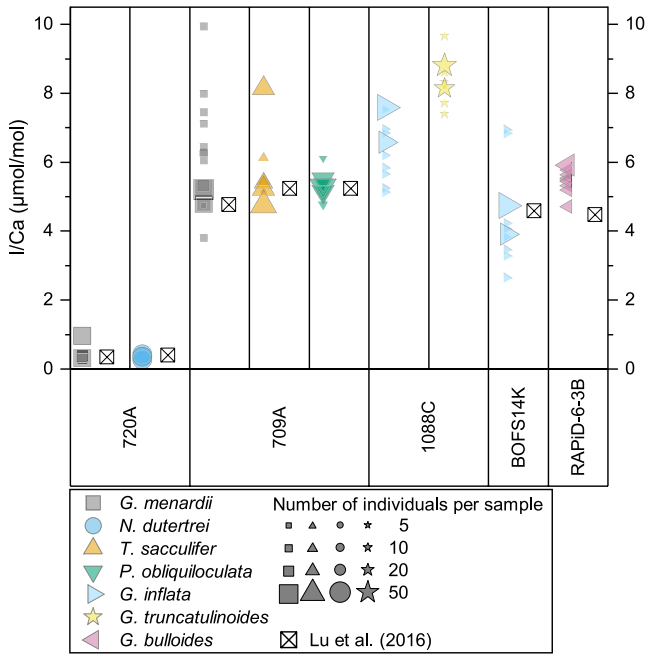

Figure 3. Planktic foraminifera I/Ca measurements of various samples sizes: including samples with 5, 10, 20, 30, or 40–50 specimens for various species, which is indicated by symbol size for all species. Symbols are transparent for better readability of overlapping points. Note that Site 720A has two *G. menardii* samples with 40 individuals and seven with 20 individuals the latter of which are on top of each other. There are also four samples with 40 *N. dutertrei* in 720A.

stabilization methods strongly suggest this is not the case. The sample from ODP Site 1057 is not from the same depth interval but 14 cm deeper than the surface 0–2 cm used by Lu et al. (2016a, 2016b) (see Table 1). Even though the isotopes clearly show Holocene values for our samples (Table S2 in Supporting Information S1) the difference in sampling depth may explain our higher I/Ca values, due to, e.g., Holocene variations in [O_2]. Our RAPiD 6-3B sample depth is just below the sample from Lu et al. (2016a, 2016b) potentially causing the I/Ca offset. For the samples from ODP 1242, ODP 720, and BOFS14K differences in the sampling depth did not cause any I/Ca offset.

3.2. Planktic Foraminifera Specimen Numbers

The minimum number of planktic foraminifera specimens needed to obtain a signal above the detection limit varies. Figure 3 shows that for a heavier calcified species like *G. inflata* (BOFS 14K, ODP1088C), *Globorotalia truncatulinoides* (ODP 1088C), and *P. obliquiloculata* (ODP 709A) 10 specimens are sufficient to provide enough calcite for a detectable iodine signal. However, for some sizeable (>300 µm size fraction) lighter calcifiers, such as *T. sacculifer* (ODP 709A), it was possible to get a detectable signal with samples containing five specimens. Our analyses show, however, that for the smaller samples containing only 5–10 specimens there is a wide spread in the data (Figure 3). On the other hand, samples containing 20 specimens or more generally center within this spread, indicating that the larger samples are more representative of the average sample community, even though there is still a spread in I/Ca ratios of up to 1.2 µmol/mol (except the previously mentioned outlier at ODP Site 709, *T. sacculifer*) in samples with 20–50 individuals. This suggests that there is a degree of analytical uncertainty in high I/Ca samples. Results shown in Figure 3 are from relatively low sediment accumulation environments, with individual 1 cm samples likely covering ~1,000 years. The variability and spread shown in the smaller samples likely represent temporal and/or seasonal variations in subsurface water conditions.

Several recent and older studies have used individual specimen analyses to look at natural sample variability, potentially induced by seasonality or other effects. This has been successful for elements that are present in mmol/mol concentrations, including Mg and Sr (Anand & Elderfield, 2005; Fehrenbacher et al., 2020). Iodine is present in concentrations a thousand times less, and the lower ionization potential and background levels of iodine in the lab preclude the measurement of individual specimen I/Ca ratios using ICP-MS. Other methods like secondary ion mass-spectrometry (SIMS) or nano-SIMS may be used for the qualitative analysis of iodine distribution in individual foraminiferal tests (Glock et al., 2016, 2019).

3.3. Cleaning Methods

In most cases, with the exception of RAPiD 6-3B, the first clay removal step (T1 ultrasonification in ultrapure water) has the biggest impact on benthic and planktic foraminifera I/Ca ratios, reducing I/Ca by two-thirds for epifaunal *P. limbata* and infaunal *U. striata* benthic foraminiferal species from M77/1–565/MUC-60, and causing a 10-fold decrease in planktic foraminifera *N. dutertrei* at ODP Site 1242 (Figure 4). Uncleaned benthic foraminifera at M77/1–565/MUC-60 show very high I/Ca ratios (42–53 µmol/mol for *P. limbata* and 20–30 µmol/mol for *U. striata*). A methanol step (T2) only has a limited effect on benthic foraminifera I/Ca at M77/1–565/MUC-60 (Figure 4). Results from Barker et al. (2003) on planktic foraminifera Mg/Ca show a similar result.

For benthic foraminifera from M77/1–565/MUC-60 the effect of organic material removal has large impacts on the I/Ca ratios with an almost 10-fold decrease in I/Ca ratios (Figure 4). For planktic foraminifera species *G. inflata* at ODP Site 1088 the combined clay and first organic carbon removal step (T1–T3) only causes a

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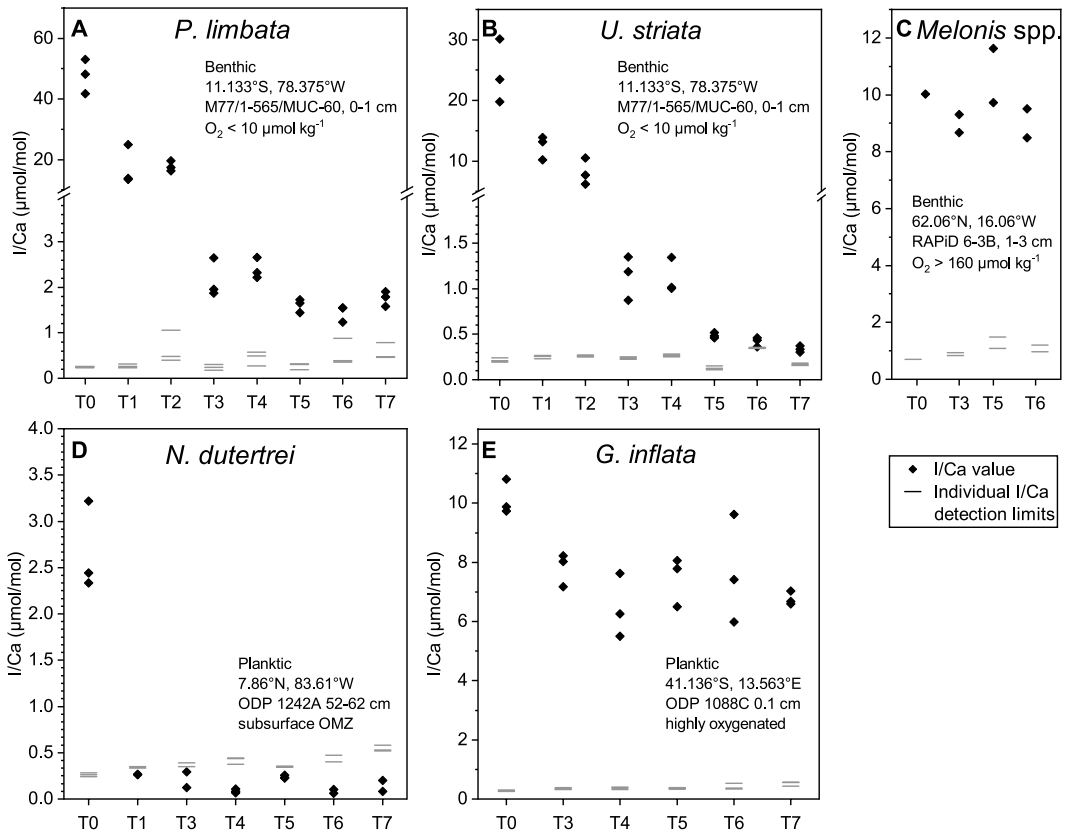

Figure 4. Details of effects of different cleaning treatments on benthic (a–c) and planktic (d, e) foraminifera. T0: uncleaned samples; T1 samples ultrasonically cleaned with ultrapure water to remove clays; T2 samples ultrasonically cleaned with ultrapure water and methanol to remove clays, T3 samples ultrasonically cleaned with ultrapure water and methanol to remove clays, and two hydrogen peroxide steps to remove organic material. T4 is similar to T3, but with an added acid leach step. T5 is similar to T3, but with four hydrogen peroxide steps to remove organic material. T6 is similar to T3, but with six hydrogen peroxide steps to remove organic material. Finally, for T7, samples were cleaned like T3, but with 10 hydrogen peroxide steps to remove organic material.

slight decrease in I/Ca ratios by ~2 µmol/mol. The effect of a weak acid leach (T4) has either no effect (*P. limbata* and *U. striata* at M77/1–565/MUC-60, *N. dutertrei* at 1242) or only a minor effect (*G. inflata* at ODP Site 1088) on foraminifera I/Ca ratios. Four buffered H_2O_2 steps only seem to have a significant impact on I/Ca ratios of benthic foraminifera at M77/1–565/MUC-60, with I/Ca ratios further reduced by 0.6 µmol/mol. For planktic foraminifera at ODP 1242 and 1088 further organic cleaning steps seem to have negligible effects (Figure 4). Six or even 10 buffered H_2O_2 steps do not seem to cause further reductions in benthic/planktic foraminifera I/Ca ratios (Figure 4). Therefore, it is recommended to use four buffered H_2O_2 steps to remove organic material for foraminiferal I/Ca analyses.

In *N. dutertrei* from ODP core 1242A, T1 lead to a decrease in I/Ca below the detection limits for these samples. This shows the removal of iodine contamination from the fine fraction attached to the tests during the water rinses but prevents us from assessing the cleaning success of T3–T7. The detection limits (bars in Figure 4d) for I/Ca in *N. dutertrei* rise with more cleaning steps reflecting an increased loss of sample mass during cleaning.

Our benthic foraminifera I/Ca ratios from M77/1–565 are similar (within 0.12 µmol/mol) to those found by Glock et al. (2014), with values of 1.22 µmol/mol for epifaunal *P. limbata* (Glock et al. [2016] reported 1.14 µmol/mol) and 0.49 for infaunal *U. striata* (Glock et al. [2016] measured 0.54 µmol/mol). Lower I/Ca ratios in infaunal benthic foraminifera have been attributed to depleted pore-waters O_2 levels, driving down IO_3^- (Taylor et al., 2017).

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The cleaning effects seem to have the biggest impact on benthic and planktic foraminifera from M77/1–565/MUC-60 and ODP Site 1242. Both locations are characterized by considerable organic carbon contents (ODP Site 1242 ~2–3%, M77/1–565/MUC-60 ~11%) (Henson et al., 2013; Mix et al., 2003). Ultrasonification removes the fine fractions, including clays held within the foraminifera chambers, that are crushed before cleaning. This fine fraction must contain considerable amounts of iodine, as its removal, using ultrasonification with ultrapure water, causes a substantial reduction in I/Ca at those sites. Conversely, for I/Ca ratios of *Melonis sphaeroides* (shallow infaunal species) at the well-oxygenated North Atlantic Site RAPiD 6-3B the various cleaning steps did not have significant effects on I/Ca ratios (Figure 4). Fe/Ca, Al/Ca, and Mg/Ca ratios of all the uncleaned sample are much higher than in the cleaned samples indicating high amounts of clay contamination (Figures S6–S8 in Supporting Information S1). In RAPiD 6-3B, this clay is likely low in iodine, because the I/Ca values are not significantly elevated.

4. Conclusions

Our results indicate that both TMAH and NH_4OH are suitable stabilizers of iodine dissolved in acid in addition to tertiary amine.

While small planktic foraminifera samples (5–10 specimens) provide detectable I/Ca ratios for both light and heavy calcified specimens, there is a wide spread in these ratios. The wide spread diminishes when using samples with 20 specimens or more, suggesting the latter are representative of the average sample community. It is possible that the variability and spread observed mainly in the smaller samples relates to temporal and/or seasonal variations in subsurface water conditions.

The first cleaning step (ultrasonification in ultrapure water) has the biggest impact on planktic and benthic foraminifera I/Ca ratios, especially those from high productivity settings, where the sediments contain high organic material. Furthermore, a substantial decrease in I/Ca ratios was observed following oxidative cleaning of benthic foraminifera from those settings. We recommended, where possible, to use four buffered H_2O_2 cleaning steps to remove organic material for foraminiferal I/Ca analyses.

Acknowledgments
This research used samples provided by the Ocean Drilling Program (ODP). ODP was sponsored by the US National Science Foundation and participating countries (Natural Environment Research Council in the UK) under the management of Joint Oceanographic Institutions (JOI). The authors thank the crews and scientific team of the R/V *Meteor* cruise M77/1 and RRS *Discovery* cruise 184 for help with the sample acquisition. This work was supported by a James Watt Scholarship awarded to H. A. Winkelbauer. D. Reyes-Macaya was supported by a PhD joint grant of Becas Chile (17342817-0) and DAAD (57144001). Additional thanks to the National Fund for Scientific, Technological Development and Technological Innovation (FONDECYT) in Peru for funding the 3 months internship at the Lyell Centre granted to K. Cordova-Rodriguez. GLOMAR and IMPULSE programs from the University of Bremen in Germany support 3 months internship of D. Reyes-Macaya at the Lyell Centre. B. A. A. Hoogakker acknowledges support from UKRI Future Leaders Grant MR/S034293/1 and UK Natural Environment Research Council (NERC) grant NE/I020563/1. Z. Lu acknowledges support from National Science Foundation (NSF) grants OCE-1232620 and OCE-1736542. N. Glock acknowledges support from the German Research Foundation (DFG) grants GL 999/3-1 und SFB754.

Data Availability Statement

Data generated during this study are available on https://doi.org/10.1594/PANGAEA.932767.

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