Assessing the Reliability of Planktic Foraminifera Ba/Ca as a Proxy for Salinity off the Sunda Strait

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Abstract

The Ba/Ca ratio of planktic foraminifera carbonate serves as a new geochemical proxy for seawater Ba/Ca and thus providing information on modern and past salinity and freshwater discharge. In this study the applicability of Ba/Ca ratio of core-top Globigerinoides sacculifer collected off the eastern tropical Indian Ocean (ETIO) for paleoceanographic reconstructions was investigated. In doing so, we conducted a series of cleaning experiments for Ba/Ca extraction by using different reductive solutions. Our new results suggest that the Ba/Ca ratio of G. sacculifer cannot be utilized as a tracer for modern and past salinity changes in the ETIO region off the Sunda Strait. We suggest that the existence of seasonal upwelling adds an additional signal to the seawater Ba/Ca in the ETIO, and thus complicates the interpretation of G. sacculifer Ba/Ca as a freshwater tracer. Moreover, our cleaning experiment results show that the cleaning protocol of Mg/Ca, DTPA, and hydroxylamine can be used to extract valuable Ba/Ca ratios from planktic foraminifera tests.

Keywords: *G. sacculifer Ba/Ca, foraminifera cleaning experiments, the Sunda Strait.*

Introduction

Ba/Ca ratios of planktic foraminifera have been used to trace modern and past salinity changes (Hall and Chan, 2004; Weldeab *et al.*, 2007; Schmidt and Lynch-Stieglitz, 2011; Bahr *et al.*, 2013; Saraswat *et al*, 2013). The main reason to use this ratio is that Ba/Ca ratio in foraminifera tests reflects the seawater barium (Ba) concentration as the Ba concentration in estuarine/coastal settings is elevated relative to the open ocean and inversely correlated with salinity (Lea and Spero, 1994). In addition, the incorporation of Ba into foraminifera shells is independent of temperature, salinity, pH, and symbiont photosynthesis (Lea and Spero, 1994; Hönisch *et al.*, 2011), thus, making it a seemingly well suited salinity indicator. Ba is supplied to the oceans through riverine input (Shaw *et al.*, 1998) and hydrothermal vents (Elderfield and Schultz, 1996). The mineral barite ($BaSO_4$) has been suggested as the primary carrier of particulate Ba in the water column (Dymond *et al.*, 1992) and it precipitates in the water column, on the sea floor and within marine sediments (Griffith and Paytan, 2012). Within the water column the euphotic zone is typically enriched in particulate Ba compared to the deep ocean (Collier and Edmond, 1984) and the enrichment is associated with the oxygen minimum zone (Paytan and Griffith, 2007). Therefore, upwelling regions usually contain high Ba concentrations what possibly also can influence the Ba/Ca ratio of planktic foraminifera (Saraswat *et al.*, 2013).

Ba/Ca ratios extracted from foraminifera tests can be biased by contaminant phases such as clay minerals, organic matter, or ferromanganese coatings. Hence, the removal of those contaminants requires a multiple step cleaning procedure of the samples. Commonly two different cleaning methods to extract reliable Ba/Ca ratio from foraminifera tests are used (Martin and Lea, 2002; Weldeab *et al.*, 2007; Schmidt and Lynch-Stieglitz, 2011; Bahr *et al.*, 2013). The major difference between these two methods is in the use of an additional step using diethylenetriamine penta-acetic acid (DTPA) (Lea and Boyle, 1991; 1993; Martin and Lea, 2002). DTPA has been suggested to effectively remove sedimentary barite that associated with shells, a potential source of contamination (Lea and Boyle,

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1991; 1993). However, Martin and Lea (2002) also suggest that the effect of employing reductive and DTPA cleanings might bias the measured Mg/Ca, Cd/Ca, Ba/Ca, and Mn/Ca ratios on two different benthic species show inconsistent results. On the other hand, other authors (Weldeab *et al*., 2007; Schmidt and Lynch-Stieglitz, 2011; Bahr *et al*., 2013;) have omitted the DTPA cleaning step due to its corrosiveness that can cause shell dissolution. In the perspective of foraminifera cleaning, another cleaning protocol proposed by Barker *et al*. (2003) to clean foraminifera for Mg/Ca measurements has been widely used is. According to their cleaning experiments, a reductive cleaning step systematically lowered the foraminifera Mg/Ca ratio by 10-15%. Thus their proposed cleaning method for foraminifera does not include a reductive step. Nonetheless, this finding contrasted the study of Martin and Lea (2002) that suggested that a reductive step does not reduce the values of the Mg/Ca ratio in foraminifera.

Here, for the first time, we examine the applicability of Ba/Ca ratio of planktic foraminifera *Globigerinoides sacculifer* as a tracer for freshwater discharge in the ETIO off the Sunda Strait. In this study we also conducted a set of cleaning experiments on ten surface sediment samples collected from off Sumatra to constrain the most suitable cleaning method for the analysis of Ba/Ca in planktic foraminifera. This region is particularly appropriate to address this issue as there is a persistent advection of low salinity Java Sea waters into the investigated area. However, our new data suggest that *G. sacculifer* Ba/Ca ratios cannot be used to trace freshwater discharge into the ETIO.

Materials and Methods

Surface sediments samples

A total of 69 surface sediment samples were collected from the ETIO off Western and Southern Indonesia during the expeditions of RV SONNE 184 and 189 in 2005 and 2006, respectively (Hebbeln, 2006). In the present study we only analyzed 10 surface sediment samples from off western and southern Sumatra. The locations and detailed information of the investigated surface samples are presented in Figure 1 and Table 1.

For the five different cleaning experiments *G. sacculifer* Ba/Ca ratios were measured using an Agilent 720 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) housed at the Department of Geosciences, University of Bremen. The Ba/Ca values are reported as $\mu mol.mol^{-1}$. The instrumental precision during measurement was monitored by analysis of an in-house standard solution, which was measured after every fifth sample, as well as the ECRM 752-1 standard (Greaves *et al*., 2008). The average 1σ error for the Ba/Ca analyses on external standard and ECRM 752-1 standard are 0.02 $\mu mol.mol^{-1}$ and $0.1 \mu mol.mol^{-1}$, respectively. It is important to notice that we did not measure reproducibility due to insufficient sample material.

Cleaning of foraminifera tests

We used *G. sacculifer* (without sac) from 10 surface sediment samples in order to test the effect of reductive cleaning solution on the Ba/Ca ratio (Table 1.). For each surface sediment sample approximately 30-40 individuals of *G. sacculifer* were picked from the 250-355 µm size fraction and then were gently cracked using glass plates. Then, all shell fragments were split into five aliquots and these split aliquots were subjected to five different cleaning methods.

For the first aliquot the tests of *G. sacculifer* were cleaned using the cleaning procedure proposed by Barker *et al*. (2003) and was named as “Mg/Ca” cleaning. In brief, the samples were ultrasonically cleaned five times with de-ionized water and twice with distilled methanol to remove detrital and clay particles. Organic matter was oxidized by adding a NaOH-buffered 1%-H_2O_2 reagent to the samples and placed in a hot water bath for 10 minutes with a few seconds in an ultrasonic bath. After repeating this step, samples were rinsed and transferred into new acid-cleaned vials. Samples then underwent a weak acid leaching (0.001 M QD HNO_3) with 30 seconds ultrasonic treatment. Following this step, samples were dissolved using 0.075 M QD HNO_3, centrifuged for 10 minutes at 6000 rpm, transferred into new acid cleaned vials and diluted with water.

For another three aliquots the cleaning procedure of Barker *et al*. (2003) was modified by adding a reductive step after the oxidation step. In this reductive step a set of experiments was performed by employing two different reductive reagents, i.e. hydrazine and hydroxylamine, and DTPA. Each of the three aliquots received a different solution during this reductive treatment. The detailed composition of each reductive solution is given in Table 2. For experiments with hydrazine and hydroxylamine we added 100 µl of each solution into two aliquots, whereas for the DTPA only 50 µl was added to an aliquot. In the following step, these three samples were placed in a hot bath (~98 °C) for 30 minutes and were sonicated briefly every 2 minutes. After this step all reductive reagents and DTPA were removed and the samples were rinsed 3

Table 1. Measurement results of element ratios of *G. sacculifer* from a series of cleaning experiments.

GeoB	Longitude (°E)	Latitude (°N)	Depth (m)	Cleaning method	Ba/Ca (μmol^{-1}mol)	Al/Ca (μmol^{-1}mol)	Mn/Ca (μmol^{-1}mol)	Fe/Ca (μmol^{-1}mol)	$\delta^{18}O$* (‰ PDB)	Mg/Ca* (mmol^{-1} mol)	$\delta^{18}O_{sw}$ (‰ SMOW)	Opal $^{+}$ (%)	$C_{org.}$ $^{+}$ (%)	$\delta^{15}N$ $^{+}$ (‰)	*G. ruber* $\delta^{13}C$ $^{++}$ (‰ PDB)
10033-3	99.952	-1.563	1756	Hydrazine	73.39	3273.09	133.58	25.82	-2.47	4.14	0.43	3.3	2.2	4.0	0.89
				Water	1.45	-89.88	56.15	-64.19							
				Hydroxylamine	1.83	-43.35	55.50	-54.83							
				DTPA	-	-	-	-							
				Mg/Ca	1.59	-44.24	60.24	-53.79							
10034-3	101.499	-4.165	995	Hydrazine	1.29	-4.85	66.15	-15.20	-2.65	4.1	0.23	3.1	1.1	5.0	1.03
				Water	2.72	-59.32	157.67	-33.88							
				Hydroxylamine	3.16	-41.71	78.22	-6.69							
				DTPA	1.28	-62.90	38.37	-43.78							
				Mg/Ca	4.89	16.37	682.24	95.08							
10036-3	103.657	-5.339	1502	Hydrazine	1.48	-105.52	5.27	-94.64	-3.07	4.47	0.01	3.4	1.1	4.2	0.96
				Water	1.82	-57.48	64.02	-58.69							
				Hydroxylamine	2.35	-94.79	1.80	-77.44							
				DTPA	1.46	-107.27	10.73	-88.38							
				Mg/Ca	2.67	-41.11	38.66	-31.19							
10038-3	103.246	-5.937	1891	Hydrazine	1.41	-60.32	2.64	-50.41	-2.66	4.15	0.25	7.2	0.4	5.4	1.19
				Water	2.58	-78.82	14.63	-55.86							
				Hydroxylamine	1.96	-163.18	7.69	717.64							
				DTPA	1.83	-59.40	2.06	-92.11							
				Mg/Ca	7.60	509.46	23.82	336.20							
10039-3	103.294	-5.868	1799	Hydrazine	4.42	88.22	5.34	-22.50	-2.81	4.15	0.1	3.1	0.4	5.7	1.16
				Water	2.16	-53.53	1.95	-53.57							
				Hydroxylamine	2.23	75.67	5.37	-86.02							
				DTPA	2.85	-321.55	-0.69	-317.78							
				Mg/Ca	1.79	-74.07	1.88	-53.44							
10040-3	102.859	-6.476	2605	Hydrazine	3.46	-76.92	2.19	-154.49	-2.72	4.3	0.27	4.2	0.5	5.6	1.25
				Water	2.16	-51.51	6.05	-44.83							
				Hydroxylamine	-	-	-	-							
				DTPA	4.11	-93.43	0.40	-606.13							
				Mg/Ca	1.77	-50.29	3.62	-45.88							
10041-3	103.009	-6.274	1540	Hydrazine	1.74	13.98	13.78	-13.12	-2.67	4.04	0.18	3.3	0.5	6.0	1.00
				Water	2.47	-63.12	34.82	-17.67							
				Hydroxylamine	3.96	-100.73	13.80	-83.71							
				DTPA	1.85	-88.41	5.48	-59.43							
				Mg/Ca	5.18	-21.74	66.52	71.94							

GeoB	Longitude (°E)	Latitude (°N)	Depth (m)	Cleaning method	Ba/Ca (μmol^{-1}mol)	Al/Ca (μmol^{-1}mol)	Mn/Ca (μmol^{-1}mol)	Fe/Ca (μmol^{-1}mol)	δ^{18}O* (‰ PDB)	Mg/Ca* (mmol^{-1} mol)	$\delta^{18}O_{sw}$ (‰ SMOW)	Opal + (%)	$C_{org.}$ + (%)	δ^{15}N + (‰)	*G. ruber* δ^{13}C ++ (‰ PDB)
10042-2	104.643	-7.113	2457	Hydrazine	12.32	-142.76	17.67	-385.26	-2.76	4.63	0.4	5.2	-	-	1.09
				Water	3.53	-86.41	1.68	-65.81							
				Hydroxylamine	6.31	-19.32	1.97	-66.89							
				DTPA	-	-	-	-							
				Mg/Ca	5.75	-83.22	1.58	-68.57							
02MC	103.01	-5.48	1972	Hydrazine	1.89	-59.59	10.05	-53.88	-2.84	4.3	0.15	-	-	-	0.54
				Water	2.33	-69.41	18.77	-48.93							
				Hydroxylamine	2.88	-169.97	6.93	717.65							
				DTPA	2.28	-49.21	7.33	-57.37							
				Mg/Ca	2.59	-44.98	28.29	-27.01							
11MC	101.23	-3.83	911	Hydrazine	1.98	-5.96	16.65	-41.37	-2.68	4.42	0.38	-	-	-	1.21
				Water	2.24	-64.59	37.14	-28.96							
				Hydroxylamine	-	-	-	-							
				DTPA	1.74	-161.79	22.57	-134.39							
				Mg/Ca	2.67	-31.17	78.24	-7.01							

**G. sacculifer* δ^{18}O and Mg/Ca data are from Mohtadi *et al*. (2011).
$^{+}$data from Baumgart *et al.* (2010).
$^{++}$data from Mohtadi *et al.* (2007).

Table 2. Detailed reductive solutions used in this study.

Reductive reagent	Composition	Reference
100 µL of buffered hydrazine solution	750 µL anhydrous hydrazine (NH_2NH_2) + ~0.5 N (~0.25 M) ammonium citrate ($C_6H_{17}N_3O_7$) + 10 mL concentrated (~30%) ammonium hydroxide (NH_4OH)	Martin and Lea (2002)
100 µL of hydroxylamine solution	0.2 M NH_2OH + 1 M CH_3COONa	Shen *et al*. (2001), Steinke *et al*. (2010)
50µL of buffered DTPA (diethylenetriamine penta-acetic acid)	0.01N (0.002 M) DTPA + 0.1N sodiumhydroxide (NaOH)	Martin and Lea (2002)

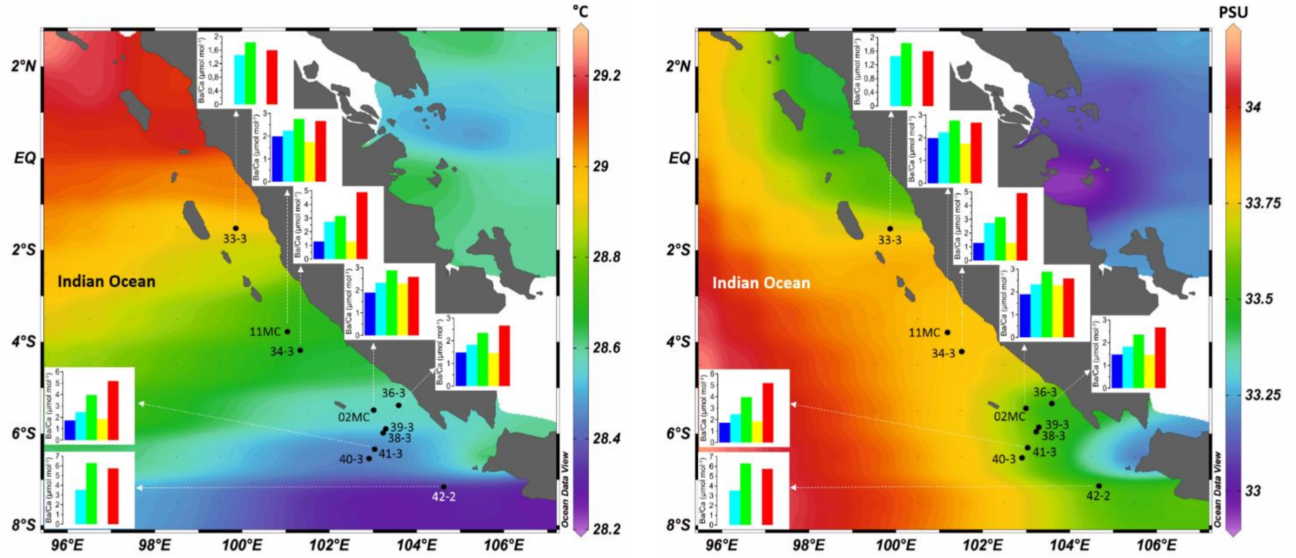

Figure 1. Annual mean maps of (a) sea surface temperature (°C) (Locarnini *et al*., 2013) and (b) sea surface salinity (psu) (Zweng *et al*., 2013) obtained from the World Ocean Atlas 2013. Black dots show the positions of surface sediment samples used in this study. Blue, cyan, green, yellow, and red bars are the values of Ba/Ca ratios resulted from cleaning experiments with hydrazine, water, hydroxylamine, DTPA, and of normal cleaning, respectively.

times with de-ionized water. For the next steps, i.e. weak acid leaching and dissolution, we followed Barker *et al*. (2003). Finally, for the last aliquot we purely cleaned the shells only using de-ionized water for all cleaning steps of Barker *et al.* (2003).

Calculation of seawater $\delta^{18}O$

All of the *G. sacculifer* Mg/Ca ratios of surface sediment samples used in this study have been measured by Mohtadi *et al*. (2011). According to Mohtadi *et al*. (2011) *G. sacculifer* data represent mean annual mixed-layer conditions at ~50 m. In order to calculate the seawater $\delta^{18}O$ ($\delta^{18}O_{sw}$), we used the $\delta^{18}O$-temperature equation of Bemis *et al*. (1998):

$$T\ (°C) = 14.9 - 4.8\ (\delta^{18}O_{cc} - \delta^{18}O_{sw})$$

where $\delta^{18}O_{cc}$ and T are the measured $\delta^{18}O$ of calcite and Mg/Ca-based temperature, respectively. The values were then converted to Standard Mean Ocean Water (SMOW). The errors of the calculations of Mg/Ca-based temperature and$\delta^{18}O_{sw}$ are estimated by propagating the errors introduced by Mohtadi *et al*. (2014). The resulting errors for temperature and $\delta^{18}O_{sw}$ are on average 1°C and 0.23 ‰, respectively.

Results and Discussion

Planktic foraminifera G. sacculifer element to calcium ratios

Results of the Ba/Ca ratio measurements of five different cleaning protocols are given in Table 1 and shown in Figure 1. In general, most of the Ba/Ca ratio values of different cleaning methods show a consistent pattern. The *G. sacculifer* Ba/Ca ratio values cleaned with hydroxylamine and of Mg/Ca cleaning are always higher than Ba/Ca values cleaned with water. Whereas Ba/Ca values cleaned with hydrazine and DTPA are always lower than that cleaned with water.

For the Mg/Ca cleaning and the cleaning experiment with water the values of Ba/Ca ratio range between 1.59 and 7.60, and between 1.45 and 3.53 µmol.mol^{-1}, respectively. Whereas for the cleaning experiment using reductive solutions (Table 2.) the Ba/Ca ratio values vary between 1.28 and 73.39 µmol mol^{-1}. This extremely high value (73.39 µmol mol^{-1}) is found in the GeoB 10033-3 (cleaning experiment with hydrazine). Another high Ba/Ca ratio value (12.32 µmol mol^{-1}) is also appeared in GeoB 10042-2 (cleaning experiment with hydrazine).

Most of the values of *G. sacculifer* Al/Ca ratio are under detection limit (negative values). The Mn/Ca ratio values of *G. sacculifer* vary between 0.4 and 682.24 µmol.mol^{-1}. Our results revealed that there are only two surface sediment samples (GeoB 10033-3 and GeoB 10034-3) which have high Mn/Ca value >100 µmol.mol^{-1} (Table 1.). For the Fe/Ca ratios, our data also show that most of the values are negative and only two surface sediment samples (GeoB 10038-3 and SO189-02MC) which have Fe/Ca ratio value >100 µmol.mol^{-1}. Overall, there is no significant correlation between these three element ratios and Ba/Ca ratio ($r^2 \leq 0.01$; not shown).

Planktic foraminifera G. sacculifer $\delta^{18}O_{sw}$

The $\delta^{18}O_{sw}$ values of *G. sacculifer* from all surface sediment samples used in this study range between 0.01 and 0.43 (‰ SMOW). The lowest and highest values are observed in GeoB 10036-3 and GeoB 10033-3, respectively.

An issue in using elemental ratios as paleo-proxies is the possibility of contamination caused by silicate material during foraminifera cleaning (Barker *et al.*, 2003) and/or post-depositional Mn-rich carbonate (Pena *et al.*, 2005; 2008). Such contaminations can be assessed through Al/Ca ratio of foraminifera to detect silicate contamination and through Mn/Ca and Fe/Ca ratios to detect contamination by Mn-rich carbonate or early diagenetic ferromanganese oxides. We used the criteria of Ni *et al.* (2007) that suggests Al/Ca ratio of <100µmol mol^{-1} indicates not contamination by silicates. We also used a threshold of Boyle (1983) and Boyle and Rosenthal (1996) that suggests that a Mn/Ca ratio of 100-150 µmol.mol^{-1} is not contaminated by $MnCO_3$. Our data show that there are two surface sediment samples containing high Al/Ca ratio values, i.e. GeoB 10033-3 cleaned with hydrazine and GeoB 10038-3 of Mg/Ca cleaning. In addition, Mn/Ca ratios of GeoB 10034-3 (Mg/Ca cleaning and cleaned with water) also exhibit high values. Therefore we discarded the Ba/Ca ratio values of these samples when discussing our results. We also excluded all of the Ba/Ca ratio values of GeoB 10040-3 and GeoB 10039-3 as the values show an opposite trend compared to general pattern resulted from the experiments.

Higher Fe/Ca ratio values are observed in cleaning experiment with hydroxylamine in GeoB 10038-3 and SO189-02MC. However, we assume that Ba/Ca analyses for these surface samples were unaffected by silicate contamination as the Al/Ca ratio values are under the detection limit of the ICP-OES. Overall, the elemental ratios of the contamination indicators (Mn/Ca and Fe/Ca ratios) suggest that our *G. sacculifer* Ba/Ca ratio can be used for further analyses.

Examining G. sacculifer Ba/Ca as a proxy for salinity

Although seawater Ba concentration for the investigated area is unknown, we examined the applicability of *G. sacculifer* Ba/Ca ratio as a proxy for paleo-salinity by comparing it to the *G. sacculifer* $\delta^{18}O_{sw}$ from the same surface sediment samples. Compared to GeoB 10033-3, GeoB 10034-3, and SO189-11MC, the positions of surface sediments GeoB 10036-3, GeoB 10038-3, GeoB 10039-3, GeoB 10041-3, GeoB 10042-2, and SO189-02MC are suitable for this investigation as these sediments geographically should be influenced by the transport of low salinity Java Sea water into the ETIO via the Sunda Strait (Figure 1.). This inference is in accordance with the observation (Table 1.) that demonstrates the *G. sacculifer* $\delta^{18}O_{sw}$ values of GeoB 10033-3, GeoB 10034-3, and SO189-11MC are on average higher (0.23-0.43 ‰) compared to those located near the Sunda Strait (0.01-0.40 ‰). In addition, precipitation and runoff from Sumatra and Java are enhanced during the northwest monsoon season, hence, we expect that the transported freshwater to the Sunda Strait is enriched in Ba.

In line with our expectation the average Ba/Ca ratio value of each different cleaning method for surface sediments located in the proximity of the Sunda Strait indicates slightly higher Ba/Ca ratio values compared to surface sediments located far from the Sunda Strait (Table 3.), with an exception in Ba/Ca value cleaned with hydrazine that shows identical value. It is important to note here that we excluded Ba/Ca values of GeoB 10042-2 in this calculation. Even if we added this surface sample to the calculation, the yielded difference in the average Ba/Ca for two different locations becomes larger. Indeed, this finding strengthens our assumption that the fresher Java Sea waters transported to the Sunda Strait are slightly enriched in Ba concentration. However, this observation may also lead to a suggestion that *G. sacculifer* Ba/Ca in the GeoB 10042-2 as well as *G. sacculifer* Ba/Ca of the surface samples close to the Sunda Strait are substantially affected by the upwelling and from the advection of fresher Java Sea waters.

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The correlation plot between *G. sacculifer* $\delta^{18}O_{sw}$ and *G. sacculifer* Ba/Ca of different cleaning procedures for surface sediments nearby the Sunda Strait is shown in Figure 2. Positive correlations are observed in Ba/Ca of Mg/Ca cleaning (r^2=0.65, n=4), in Ba/Ca cleaned with water (r^2=0.97, n=5) and hydroxylamine (r^2=0.57, n=6). However, we expect that higher Ba/Ca ratios should correspond to lower $\delta^{18}O_{sw}$ values. Hence, we suggest that the Ba/Ca ratios do not represent salinity. A weak correlation is also observed between *G. sacculifer* $\delta^{18}O_{sw}$ values and the values of Ba/Ca ratios cleaned with hydrazine (r^2<0.01, n=4) and DTPA (r^2=0.27, n=4). In summary, according to our new results, we suggest that *G. sacculifer* Ba/Ca cannot be applied as a tracer for freshwater discharge in the ETIO off the Sunda Strait due to the fact that Ba/Ca ratio of *G. sacculifer* appears to be influenced not only by freshwater discharge and but also by upwelling. Moreover, cleaning experiments, as indicated by Table 3, suggest that a Mg/Ca cleaning method introduced by Barker *et al.* (2003), DTPA and hydroxylamine can be used to extract Ba/Ca

Table 3. Average Ba/Ca ratio values of different cleaning experiments for surface sediments located proximal to and distal from the Sunda Strait.

Average Ba/Ca ratio value cleaned with Surface sediments location:	Hydrazine (µmol.mol^{-1})	Water (µmol.mol^{-1})	Hydroxylamine (µmol.mol^{-1})	DTPA (µmol.mol^{-1})	Mg/Ca cleaning (µmol.mol^{-1})
Near the Sunda Strait (GeoB 10036-3, GeoB 10038-3, GeoB 10041-3, and SO189-02MC)	1.63	2.30	2.79	2.05	3.48
Far from the Sunda Strait (GeoB 10033-3, GeoB 10034-3, SO189-11MC)	1.64	2.14	2.49	1.51	3.05

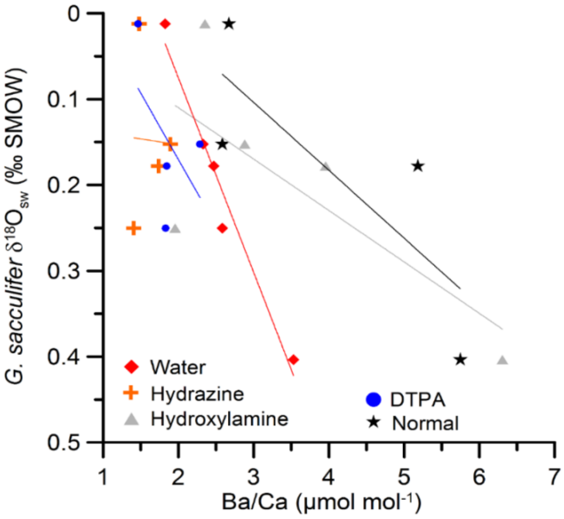

Figure 2. Correlation plots between *G. sacculifer* seawater $\delta^{18}O$ (‰ SMOW) and *G. sacculifer* Ba/Ca ratios of different cleaning experiments.

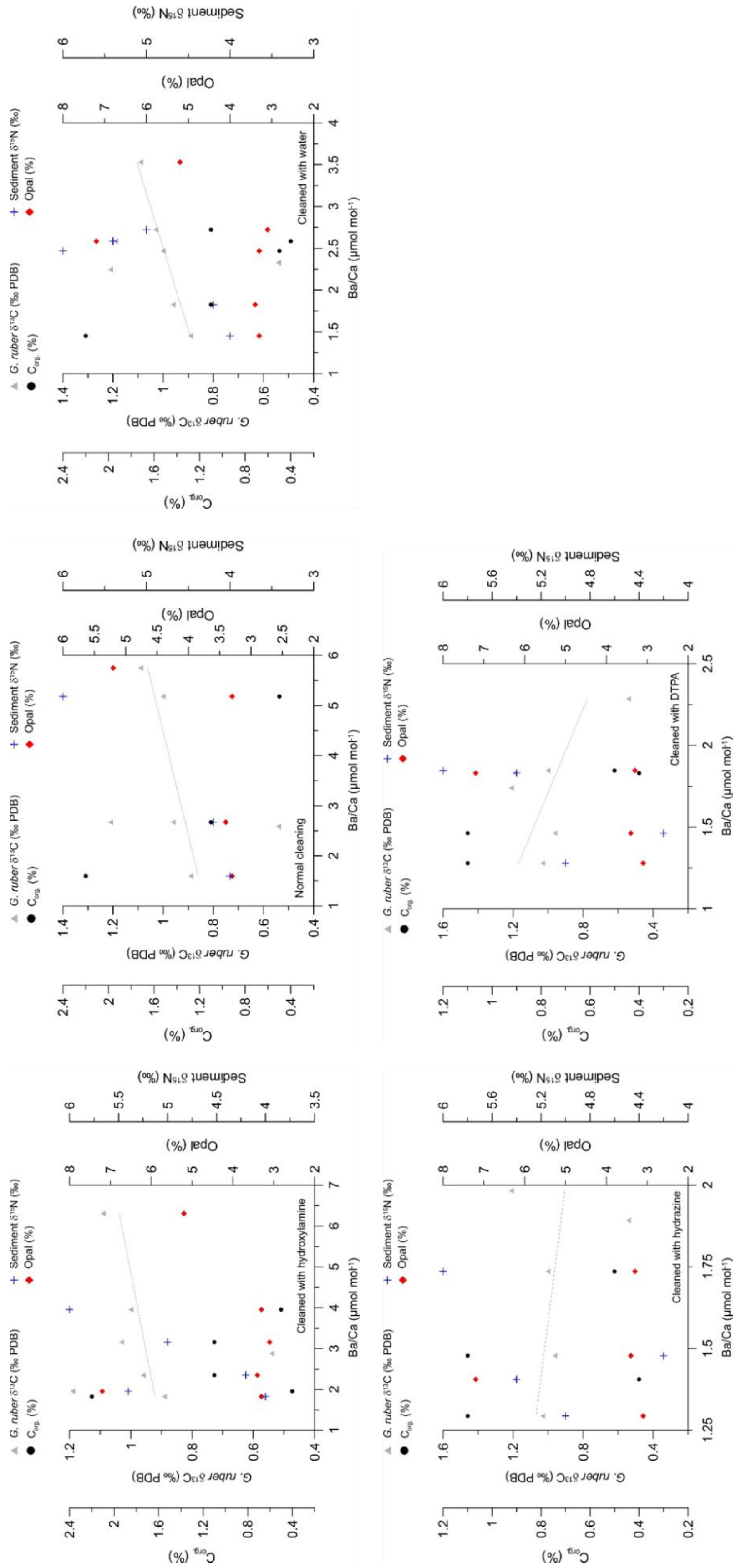

Figure 3. Correlation plots between *G. sacculifer* seawater δ18O (‰ SMOW) and *G. sacculifer* Ba/Ca ratios of different cleaning experiments.

ratio from the planktic foraminifera tests for the region of ETIO due to their reliability to preserve seawater Ba/Ca. The similar Ba/Ca values between “freshwater discharge” region (proximity to the Sunda Strait) and “non-freshwaterdischarge” region (distal from the Sunda Strait) in the hydrazine experiment imply that this reductive reagent cannot be used for cleaning the Ba/Ca foraminifera.

Examining G. sacculifer Ba/Ca as an indicator for marine productivity

In order to investigate the potential use of *G. sacculifer* Ba/Ca as a proxy for marine productivity we compare our Ba/Ca data to the published data of marine productivity indicators in the ETIO like bulk content of organic carbon ($C_{org.}$), the isotopic composition of nitrogen ($\delta^{15}N$) (Baumgart *et al*., 2007), opal content and planktic foraminifera *G. ruber* $\delta^{13}C$ (Mohtadi *et al*., 2011). Our comparison suggests that there is a lack of correlation between *G. sacculifer* Ba/Ca and those marine productivity indicators (Figure 3.). For Ba/Ca cleaned with reductive reagents of hydrazine and hydroxylamine, and DTPA the resulted r^2 are 0.07, 0.04, and 0.31, respectively. Furthermore, the r^2 for Ba/Ca cleaned with water and of Mg/Ca cleaning are 0.09 and 0.12, respectively. Although we do not have values for Ba/Ca ratio cleaned with hydrazine and DTPA, interestingly, the Ba/Ca ratios of GeoB 10042-2, which is located closed to the South Java upwelling core, differs from the other samples. The Ba/Ca ratios of GeoB 10042-2 indicate higher values than the other regions (Figure 1. and Table 1.).

Congruent with this observation opal concentration in surface sediment GeoB 10042-2 also exhibits a relatively high concentration (5.2 %) compared to other surface sediment samples used in this study (Table 1). The highest opal concentration (7.2 %) in the studied area is found in GeoB 10038-3. In addition to opal, a systematic trend in concentration is pronounced in the region off Sumatra, with higher (lower) concentration is observed in the southern (northern) Sumatra. Mohtadi *et al*. (2007) suggest that opal is a reliable proxy for marine productivity in the ETIO as its spatial distribution is tightly coupled to the south Java-Lesser Sunda Island upwelling that occurs during the southeast monsoon season. In corroboration with this suggestion a sediment trap study by Romero *et al*. (2009) also revealed that the highest flux of opal occurred during the southeast monsoon season (>150 mg m^{-2} d^{-1}). Furthermore, according to the findings of Mohtadi *et al*. (2007) there is a strong northwest-southeast gradient in the spatial distribution of opal concentration in the ETIO. High opal concentrations of 6.37, 7.26, and 9.02 % are found in the surface sediments off south Java, Lombok Basin, and in the Savu Sea, respectively, whereas low opal concentrations (≤ 4.2 %) are observed in the surface sediments off western Sumatra, where the upwelling influence is diminished.

It is likely that high Ba/Ca ratio values in GeoB 10042-2 are strongly coupled to the south Java upwelling. During the upwelling season the primary productivity in the regions off south Java and Lesser Sunda Island chain are increased. The upwelling-induced chlorophyll a bloom leads to enhanced barite precipitation and flux in the water column (Paytan and Griffith, 2007). Therefore it is plausible that the higher Ba/Ca ratios of *G. sacculifer* in GeoB 10042-2 may reflect higher seawater Ba concentration in the region. However, as the position of GeoB 10042-2 is also closed to the Sunda Strait, we believe that the higher value of Ba/Ca ratios in *G. sacculifer* may also be influenced by freshwater advection of the Java Sea waters into the Sunda Strait (detailed explanation in the next section). In order to validate this observation a similar study on other multiple planktic foraminifera species collected from the upwelling region of southern Java-Lesser Sunda Island chain (e.g. southern Bali, Lombok and Sumba) is ultimately needed.

Spatial distribution of the surface sediment $\delta^{15}N$ off Sumatra also shows similar northwest-southeast gradient as opal (GeoB 10033-3, GeoB 10034-3, GeoB 10040-3 and GeoB 10041-3; Table 1). In addition, the $\delta^{15}N$ values also exhibits a nearshore-offshore trend (GeoB 10036-3, GeoB 10039-3, GeoB 10038-3, GeoB 10041-3, and GeoB 10040-3). For both patterns the highest $\delta^{15}N$ value is observed in the GeoB 10041-3 (6.0 ‰). Unfortunately, the $\delta^{15}N$ data of GeoB 10042-2 was not available, hence, we cannot suggest whether this increase relates to upwelling or not. Meanwhile, spatial distributions of the C_{org}. and *G. sacculifer* $\delta^{13}C$ show an opposite trend compared to opal concentration. Higher values for both parameters are found in the GeoB 10033-3, GeoB 10034-3, and SO189-11MC, which are located distal from the upwelling region. This finding suggests that upwelling is not a major contributor for the high values of C_{org}. and *G. sacculifer* $\delta^{13}C$.

Conclusion

It can be concluded that Ba/Ca ratio of *G. sacculifer* cannot be used to reconstruct freshwater discharge, but it has a potential to trace modern and past marine productivities in the ETIO off south Java and Lesser Sunda Islands. Based on cleaning experiment on planktic foraminifera *G. sacculifer* for

Ba/Ca ratio extraction, according to our experiment results, it concluded that a cleaning protocol of Mg/Ca, DTPA, and hydroxylamine can be used to extract Ba/Ca ratio from planktic foraminifera tests in the ETIO.

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References

Bahr, A., Schönfeld, J., Hoffmann, J., Voigt, S., Aurahs, R., Kucera, M., Flögel, S., Jentzen, A. & Gerdes, A. 2013. Comparison of Ba/Ca and $\delta^{18}O_{WATER}$ as freshwater proxies: A multi-species core-top study on planktonic foraminifera from the vicinity of the Orinoco River mouth, *Earth and Planetary Sci. Lett.* 383: 45–57. doi: 10.1016/j.epsl.2013.09.036.

Barker, S., Greaves, M. & Elderfield, H. 2003. A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry, *Geochemistry, Geophysics, Geosystems.* 4(9). doi: 10.1029 /2003GC000559.

Bemis, B.E., Spero, H.J., Bijma, J. and Lea, D.W., 1998. Reevaluation of the oxygen isotopic composition of planktonic foraminifera: Experimental results and revised paleotemperature equations. *Paleoceanography.* 13(2):150-160. doi: 10.1029/98PA00070

Boyle, E.A. 1983. Manganese carbonate overgrowths on foraminifera tests. *Geochimica et Cosmochimica Acta*, 47:1815–1819, doi: 10.1016/0016-7037(83)90029-7.

Boyle, E.A. & Rosenthal, Y. 1996. Chemical hydrography of the South Atlantic during the last glacial maximum: Cd vs. δ13C. In The South Atlantic. pp. 423-443. Springer, Berlin, Heidelberg.

Baumgart, A., Jennerjahn, T., Mohtadi, M. & Hebbeln, D. 2010. Distribution and burial of organic carbon in sediments from the Indian Ocean upwelling region off Java and Sumatra, Indonesia. *Deep Sea Res. Part I: Oceanographic Res. Papers*. 57(3):458-467. doi: 10.1016/j. dsr.2009.12.002.

Collier, R.W. & Edmond, J.M. 1984. The trace elements geochemistry of marine biogenic particulate matter. *Prog. Oceanograp. 13*, 113–199. doi: 10.1016/0079-6611(84)90 008-9.

Dymond, J., Suess, E. & Lyle, M. 1992. Barium in Deep-Sea Sediment: A Geochemical Proxy for Paleoproductivity, *Paleoceanography*, 7(2):163-181. doi: 10.1029/92PA00181.

Elderfield, H. & Schultz, A. 1996. Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean. *Ann. Rev. Earth Planetary Sci.* 24:191–224. doi: 10.1146 /annurev.earth.24.1.191.

Greaves, M., Caillon, N., Rebaubier, H., Bartoli, G., Bohaty, S., Cacho, I., Clarke, L., Cooper, M., Daunt, C., Delaney, M. & DeMenocal, P. 2008. Interlaboratory comparison study of calibration standards for foraminiferal Mg/Ca thermometry. *Geochemistry, Geophysics, Geosystems.* 9(8). doi: 10.1029/2008GC001974.

Griffith, E.M. & Paytan, A. 2012. Barite in the ocean – occurrence, geochemistry and palaeoceanographic applications, *Sedimentology*, 59(6): 1817-1835. doi: 10.1111/j.1365-3091.2012. 01327.x.

Hall, J.M, & Chan, L.H. 2004. Ba/Ca in Neogloboquadrina pachyderma as an indicator of deglacial meltwater discharge into the western Arctic Ocean. *Paleoceanography.* 19 (1). doi: 10.1029/2003PA000910.

Hebbeln, D. 2006. Report and Preliminary Results of RV Sonne Cruise SO-184: Pabesia, Durban (South Africa)-Cilacap (Indonesia)-Darwin (Australia), July 8th-September 13th, 2005. Forschungszentrum Ozeanränder, RCOM, Universität Bremen.

Hönisch, B., Allen, K.A., Russell, A.D., Eggins, S.M., Bijma, J., Spero, H.J., Lea, D.W. & Yu, J. 2011. Planktic foraminifers as recorders of seawater Ba/Ca, *Mar. Micropaleontology.* 79(1–2): 52–57. doi: 10.1016/j.marmicro.2011.01.003

Lea, D.W., & Boyle, E.A. 1993. Determination of carbonate-bound barium in foraminifera and corals by isotope dilution plasma-mass spectrometry, *Chemical Geology*. 103: 73–84. doi: 10.1016/0009-2541(93)90292-Q.

Lea, D.W. & Boyle, E.A. 1991. Barium in planktonic foraminifera, *Geochimica et Cosmochimica Acta.* 55:3321–3331. doi: 10.1016/0016-7037(91)90491-M.

Lea, D.W. & Spero, H.J. 1994. Assessing the reliability of paleochemical tracers: Barium uptake in the shells of planktonic foraminifera, *Paleoceano-graphy*, 9:445-452. doi: 10.1029/94PA00151.

Locarnini, R.A., Mishonov, A.V., Antonov, J.I., Boyer, T.P., Garcia, H. E., Baranova, O.K., Zweng, M.M., Paver, C.R., Reagan, J.R., Johnson, D.R., Hamilton, M. & Seidov, D. 2013. World Ocean Atlas 2013, Volume 1: Temperature. S. Levitus, Ed., A. Mishonov Technical Ed.; NOAA Atlas NESDIS 73, 40 pp.

Martin, P.A. & Lea, D.W. 2002. A simple evaluation of cleaning procedures on fossil benthic foraminiferal Mg/Ca, *Geochemistry, Geophysics, Geosystems*, 3(10):1-8. doi: 10.1029/200 1GC000280.

Mohtadi, M., Oppo, D.W., Lückge, A., DePol-Holz, R., Steinke, S., Groeneveld, J., Hemme, N. & Hebbeln, D. 2011. Reconstructing the thermal structure of the upper ocean: Insights from planktic foraminifera shell chemistry and alkenones in modern sediments of the tropical eastern Indian Ocean. *Paleoceanography.* 26: PA3219, doi: 3210.1029/2011pa002132.

Mohtadi, M., Max, L., Hebbeln, D., Baumgart, A., Krück, N. & Jennerjahn, T. 2007. Modern environmental conditions recorded in surface sediment samples off W and SW Indonesia: Planktonic foraminifera and biogenic compounds analyses. *Marine Micropaleontology.* 65:96–112, doi: 10.1016/j.marmicro.2007.06.004.

Mohtadi, M., Prange, M., Oppo, D.W., De Pol-Holz, R., Merkel, U., Zhang, X., Steinke, S. & Luckge, A. 2014. North Atlantic forcing of tropical Indian Ocean climate, *Nature*. 509(7498): 76-80. doi: 10.1038/nature13196.

Ni, Y., Foster, G.L., Bailey, T., Elliott, T., Schmidt, D.N., Pearson, P., Haley, B. & Coath, C. 2007. A core top assessment of proxies for the ocean carbonate system in surface-dwelling foraminifers, *Paleoceanography.* 22(3). doi: 10.1029/2006PA001337.

Paytan, A. & Griffith, E.M. 2007, Marine barite: recorder of variations in ocean export productivity, *Deep-Sea Research II.* 54:687–705. doi: 10.1016/j.dsr2.2007.01.007.

Pena, L.D., Cacho, I., Calvo, E., Pelejero, C., Eggins, S. & Sadekov, A. 2008. Characterization of contaminant phases in foraminifera carbonates by electron microprobe mapping, *Geochemistry, Geophysics, Geosystems,* 9(7). doi: 10.1029/2008GC002018.

Pena, L.D., Calvo, E., Cacho, I., Eggins, S. & Pelejero, C. 2005. Identification and removal of Mn-Mg-rich contaminant phases on foraminiferal tests: Implications for Mg/Ca past temperature reconstructions, *Geochemistry, Geophysics, Geosystems,* 6(9). doi: 10.1029/2005GC000930.

Romero, O.E., Rixen, T. & Herunadi, B. 2009. Effects of hydrographic and climatic forcing on diatom production and export in the tropical southeastern Indian Ocean. *Mar. Ecol. Progr. Ser.* 384:69-82. doi: 10.3354/meps08013.

Saraswat, R., Lea, D.W., Nigam, R., Mackensen, A. & Naik, D.K. 2013. Deglaciation in the tropical Indian Ocean driven by interplay between the regional monsoon and global teleconnections, *Earth and Planetary Science Letters, 375*:166–175. doi: 10.1016/j.epsl.2013.05.022.

Schmidt, M.W. & Lynch-Stieglitz, J. 2011. Florida Straits deglacial temperature and salinity change: Implications for tropical hydrologic cycle variability during the Younger Dryas, *Paleoceanography*, 26(4). doi: 10.1029/2011PA002157.

Shaw, T.J., Moore, W.S., Kloepfer, J. & Sochaski, M.A. 1998. The flux of barium to the coastal waters of the southeastern USA: the importance of submarine groundwater discharge, *Geochimica et Cosmochimica Acta 62:*3047–3054. doi: 10.1016/S0016-7037(98)00218-X.

Weldeab, S., Lea, D.W., Schneider, R.R. & Andersen, N. 2007. 155,000 Years of West African Monsoon and Ocean Thermal Evolution, *Sci. 316*(5829):1303-1307. doi: 10.1126/science.1140461.

Zweng, M.M., Reagan, J.R., Antonov, J.I., Locarnini, R.A., Mishonov, A.V., Boyer, T.P., Garcia, H.E., Baranova, O.K., Johnson, D.R., Seidov, D. & Biddle, M.M. 2013, World Ocean Atlas 2013, Volume 2: Salinity. S. Levitus, Ed., A. Mishonov Technical Ed.; NOAA Atlas NESDIS 74, 39 pp.