

Determination of the lithium isotopic composition of planktic foraminifera and its application as a paleo-seawater proxy

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Abstract

To investigate the potential use of Li isotopes in foraminifera as a paleo-lithium seawater proxy, the Li isotopic compositions of planktic foraminifera (*Orbulina universa*, *Globigerinoides sacculifer*, *Globorotalia menardii*, and *Globorotalia truncatulinoides*) were determined by thermal ionization mass spectrometry (TIMS), using phosphate as an ion source, and multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). Rigorous cleaning procedures were employed to purify foraminiferal tests of detrital, metal oxide, and organic phases in single species analyses. Data generated using both methods reveal that $\delta^7\text{Li}$ in planktic foraminifera resemble seawater such that the isotopic fractionation from the precipitation of foraminiferal calcite appears to be minimal. Down-core measurements indicate that the $\delta^7\text{Li}$ of *O. universa* has remained constant over the last 44 ka in the North Atlantic, suggesting little change of Li isotopic composition of ocean water during the last glaciation, consistent with the long mean residence time of Li. Results suggest that planktic foraminifera may provide a reliable record of the lithium isotopic composition of ocean water in the past.

The first measurements of seawater $\delta^7\text{Li}$ from the Indian Ocean average $33.0 \pm 1.2\text{‰}$ (2σ) throughout the water column. This value is within error of values previously reported for the Atlantic and Pacific Oceans as is expected based on the long mean residence time of Li in the ocean. There is no evidence for a significant decrease in Li/Cl ratios, as reported by some workers, with Indian Ocean waters averaging $9.10 \pm 0.11 \mu\text{g/g}$.

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1. Introduction

The Li isotopic composition of foraminifera has the potential to be a proxy of the isotopic variation of Li in past oceans. Calcareous foraminifera secrete a test from the surrounding seawater in which they live and

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incorporate Li as a trace element. Lithium exhibits conservative behavior in the ocean. It has an oceanic residence time of about 1.5 My (Huh et al., 1998) and has a constant concentration (26 μM) and isotopic composition (average $\delta^7\text{Li} \sim 32\text{‰}$) throughout the world oceans (see compilation of Chan, in press; Tomascak, 2004). The major sources of Li to the ocean are rivers (Huh et al., 1998) and hydrothermal interaction with oceanic crust (Von Damm et al., 1985; Chan et al., 1993). Hydrothermal and average river fluxes have distinctly different isotopic signatures. $\delta^7\text{Li}$ of mid-ocean ridge high temperature vent fluids are remarkably constant with a global average of 7‰ (Chan et al., 1993; Bray, 2001). Lithium isotope values of river waters are more variable (6‰ to 33‰) with a flow-weighted mean of 23.5‰ (Huh et al., 1998). The integrated input to the ocean from these two sources is lighter than contemporary seawater. Therefore, the removal of Li from the oceans involves phases that preferentially sequester the lighter Li isotope (Chan et al., 1992). As such, changes in the Li isotopic composition of seawater over time reflect changes in the relative contributions of the two Li sources, if the fractionation factor for the removal processes has remained constant.

Differences in foraminiferal $\delta^7\text{Li}$ likely reflect fluctuations in hydrothermal and continental weathering rates over million year time scales. The magnitude of hydrothermal flux through time is not well constrained and estimates vary by several orders of magnitude depending on how it is calculated. Preliminary data from MacConnell et al. (2003) from the mid-Cretaceous (122–98 Ma) shows a decrease in foraminiferal $\delta^7\text{Li}$. This is consistent with microfossil assemblages, a $^{87}\text{Sr}/^{86}\text{Sr}$ minima, and a significant decrease in foraminiferal Mg/Ca (Leckie et al., 2002; MacConnell et al., 2003), all indicative of increased hydrothermal activity across the Aptian–Albian boundary. Thus, long-term foraminiferal $\delta^7\text{Li}$ records could help refine our understanding of hydrothermal flux over the past 150 My.

There are, as yet, no comprehensive published results for the Li isotopic composition of foraminiferal tests. Previous studies reporting Li isotopic values for foraminifera failed to demonstrate precision or reproducibility and depicted unsystematic variation (You and Chan, 1996; Hoefs and Sywall, 1997; Košler et al., 2001). The difficulties associated with measuring

the Li isotopic composition of foraminiferal tests are threefold. (1) Li isotopes are easily fractionated due to the large relative mass difference between ^6Li and ^7Li . This mass dependent fractionation can occur during chemical separation with cation exchange columns and during instrumental analysis. (2) Current high precision techniques that were developed to measure Li isotopes in natural samples normally require a relatively large sample size, ranging from 40 to 120 ng of Li (You and Chan, 1996; Moriguti and Nakamura, 1998; Tomascak et al., 1999; James and Palmer, 2000). In comparison, several milligrams of foraminiferal tests from a sediment core horizon are required in order to yield several nanograms of Li. Moreover, analysis of a single species is necessary to prevent variations due to possible vital effects. Therefore, sample size is limited by the availability of single species foraminifera in a sediment core horizon. (3) Rigorous, labor intensive cleaning of foraminifera is necessary to remove impurities such as detrital sediments, which contain high levels of Li compared to calcareous foraminiferal tests. Various steps are involved in the cleaning procedure to ensure that the sample has been purified of detrital, metal oxide, and organic phases (Boyle and Keigwin, 1985). These phases can potentially change the Li isotopic composition of a sample. This kind of cleaning protocol was not used in previous investigations (You and Chan, 1996; Hoefs and Sywall, 1997; Košler et al., 2001), potentially compromising the quality of the results.

Preliminary work by You and Chan (1996) on the planktic foraminifer *Pulleniatina obliquiloculata* from the Ontong-Java Plateau suggested large glacial–interglacial variation in the Li inventory and isotopic composition of oceanic Li during the past 1 Ma ($\delta^7\text{Li}=19\text{‰}$ to 42‰). Later work by Hoefs and Sywall (1997) showed large fluctuations (40‰) in the isotopic composition of mixed planktic species from the Quaternary and Tertiary. Such large variations cannot be accommodated in a steady state Li system. Hoefs and Sywall (1997) invoked a non-steady state ocean in the past to account for the observed shifts. These initial results were obtained using thermal ionization mass spectrometry (TIMS) with magnetic sector and quadrupole mass analyzers, respectively. Using quadrupole inductively coupled plasma mass spectrometry (ICP-MS), Košler et al.

(2001) investigated the planktic foraminifers *P. obliquiloculata* and *Globorotalia tumida* taken from surface sediments on the Ontong-Java Plateau and the Ceara Rise. Although the data set is limited, values reported for *P. obliquiloculata* are similar to the Li isotopic composition of modern seawater, whereas *G. tumida* shows substantial variability (39‰ to 51‰). Using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), Hathorne et al. (2003) determined $\delta^7\text{Li}$ values for planktic foraminifera that are slightly lighter than modern seawater with subtle variation among different species. Marriott et al. (in press), also using MC-ICP-MS, showed that $\delta^7\text{Li}$ values for the benthic genus *Uvigerina* are also slightly lighter than modern seawater values.

In this study we investigate the potential use of Li isotopes in foraminifera as a proxy of paleo-seawater Li isotope composition using single species analyses and rigorous cleaning procedures. We report Li isotopic compositions of seawater and foraminiferal tests from the surface sediments of the tropical Indian Ocean and central Pacific Ocean to determine the extent of isotopic fractionation accompanying the formation of biogenic calcite. In addition, we examine the extent of glacial–interglacial variation in foraminiferal $\delta^7\text{Li}$ using a sediment core taken from the Great Bahama Bank spanning the Holocene and last glacial maximum (Slowey and Curry, 1995). Two mass spectrometric methods were used for isotopic analyses: TIMS and MC-ICP-MS permitting a comparison of these two techniques.

2. Materials and methods

Lithium concentration measurements and isotopic analyses were conducted on seawater and planktic foraminifera (*Orbulina universa*, *Globigerinoides sacculifer*, *Globorotalia menardii*, and *Globorotalia truncatulinoides*) from the Atlantic, Indian, and Pacific oceans. Sediment cores OC205-2-103GGC and OC205-2-97JPC were taken from the Great Bahama Bank (Slowey and Curry, 1995) and RC17-177 from the Salomon Rise in the western equatorial Pacific (Shackleton, 1987). Bahaman core OC205-2-103GGC, spanning the Holocene and last glacial maximum was used to investigate glacial–interglacial

variation in foraminiferal $\delta^7\text{Li}$. Seawater from various depths and surface sediments from KNR162-13-D4 and KNR162-13-D7 from the tropical Indian Ocean were collected during cruise KN162-13 (Table 1). Reservoir corrected radiocarbon derived calendar ages for this core were obtained from Marchitto et al. (1998).

2.1. Lithium composition of seawater

Seawater samples were stored in HCl-cleaned, polypropylene bottles and acidified with HCl. Lithium concentrations were measured by flame emission with a Varian AA-475, atomic absorption spectrophotometer using standard additions. Based on replicate analyses of reference standard rock JB2, this method yields a precision of $\pm 1\%$ (RSD). Salinity measurements made during the CTD cast were used to calculate chlorinity. Calcium concentrations were measured on a PerkinElmer Optima 3300DV, inductively coupled plasma-optical emission spectrometer (ICP-OES) with a precision of $\pm 0.4\%$ (RSD).

2.2. Foraminiferal cleaning and Li/Ca

Sediment samples were shaken in distilled water until disaggregated and then wet-sieved through a 150 μm polypropylene mesh. The coarse fraction remaining in the sieve was then dried in an oven for 30 min to an hour at 55 to 60 °C. Sediments were picked for planktic *O. universa*, *G. sacculifer*, *G. menardii*, and *G. truncatulinoides*. Lithium isotopic samples were prepared from 2.5 to 5 mg of planktic foraminifera,

Table 1
Seawater and sediment sample descriptions

Sample	Latitude	Longitude	Water depth (m)
<i>Bahama Banks</i>			
OC205-2-103GGC	26.07°N	78.06°N	965
OC205-2-97JPC	25.94°N	77.85°N	1183
<i>Indian Ocean</i>			
KNR162-13-D4	23.53°S	69.36°E	3398
KNR162-13-D7	24.50°S	69.92°E	2255
KNR162-13-CTD1	22.95°S	64.55°E	
<i>Pacific Ocean</i>			
RC17-177	1.75°N	159.43°E	2600

containing between 40 and 70 individual tests, whereas Li/Ca samples were prepared from 0.5 mg of planktic species, containing between 4 and 12 individual tests. The tests were gently crushed and then purified following procedures modified from [Lea and Boyle \(1993\)](#). Samples were ultrasonically cleaned four times with distilled water and twice with methanol to remove detrital grains and fine clay particles. Metal oxide coatings were reduced in a solution consisting of anhydrous hydrazine, citric acid, and ammonium hydroxide and organic matter was oxidized in a solution of hydrogen peroxide and sodium hydroxide. Sedimentary barite was dissolved in alkaline diethylenetriamine-pentaacetic acid and then removed by rinsing with ammonium hydroxide. Any remaining adsorbed metals were leached with 0.001 N nitric acid prepared from SEASTAR™ high purity acid.

The cleaning step removing sedimentary barite was initially performed for Li/Ca samples but was eliminated for samples for Li isotopic analyses as Li is not likely to be affected by the presence of small amounts of sedimentary barite. The foraminiferal test material that remained after the cleaning procedures was dissolved in 0.1 N SEASTAR™ nitric acid and simultaneously analyzed for Li and Ca with a ThermoQuest Finnigan Element 2 ICP-MS at the University of Southern Mississippi ([Hall and Chan,](#)

[2004](#)). Lithium to Ca ratios were determined from intensity ratios with an external matrix matched standard, according to the method developed by [Rosenthal et al. \(1999\)](#). Details of the measurement and standardization procedures are given in [Hall and Chan \(2004\)](#). Precision for foraminiferal Li/Ca is about 3.5% coefficient of variation based on replicate analyses of *O. universa*.

2.3. Lithium isotopic analyses using TIMS

Before cleaning, foraminiferal samples were conservatively estimated to contain between 2.5 and 5 ng Li. Typically, the cleaning procedure resulted in 20 to 50% sample loss. To test potential effects due to sample size, 100, 10, and 5 ng Li samples of seawater were processed and analyzed for Li isotopes ([Table 2](#)).

Lithium was extracted from seawater and foraminiferal samples by cation exchange chromatography based on procedures developed by [You and Chan \(1996\)](#). The pyrex glass columns (10 mm i.d.) were filled with Bio-Rad AG50WX8 (200–400 mesh) cation exchange resin to make up a total resin volume of 15 ml in 6 M HCl. The ion exchange columns were calibrated for Li separation with north Atlantic seawater (100 ng Li) and a multi-element standard with an elemental composition comparable to foraminiferal calcite but spiked with the NIST lithium

Table 2

Lithium in seawater from the tropical Indian (22°57'S, 64°33'E) and North Atlantic (36°15'N, 13°46'W) oceans at varying water depth and sample size analyzed using TIMS

Water depth (m)	Sample size Li (ng)	Temperature (°C)	Salinity (‰)	Li (μmol/kg)	Li/Cl (μg/g)	δ ⁷ Li (‰)
<i>Indian Ocean</i> ^a						
23	100	26.75	35.57	25.6	9.01	32.0
201	100	18.40	35.80	25.7	8.99	33.3
201	10	18.40	35.80	–	–	33.6
201	5	18.40	35.80	–	–	32.7
1001	100	5.51	34.46	25.5	9.27	33.5
2512	100	1.98	34.75	25.2	9.11	32.6
4010	100	1.44	34.70	25.2	9.10	33.2
Mean						33.0±1.2 (2σ)
<i>Atlantic Ocean</i> ^b						
1241	10					31.7
1241	5					32.5
Mean						32.1±1.2 (2σ)

^a Single column.

^b Two columns.

carbonate standard L-SVEC (Flesch et al., 1973). Both Li and Na contents in the eluant fractions were monitored by flame emission. To ensure quantitative recovery, the collected eluant volume extended 6 ml before and 4 ml after the Li elution peak. A total of 30 ml of eluant was collected.

Prior to sample loading, the resin was equilibrated with sub-boiling water. Purified foraminiferal fragments were dissolved in 0.5 M HCl (double-distilled) and diluted with sub-boiling water. After the sample solution was loaded on the column, the resin was washed with sub-boiling water to remove anions. The column was then eluted with 0.5 M HCl and the entire Li fraction was collected. The eluant was irradiated with an ultraviolet lamp to remove any organic matter present. The separated Li was converted to Li_3PO_4 using ultrapure H_3PO_4 . The entire procedural blank was determined by isotope dilution mass spectrometry to be 57 ± 13 pg.

Some of the foraminiferal samples exhibited large Na and K signals (>11 V) in the mass spectrometer which interfered with Li isotope analysis (see later discussion). To remove Na and K further, some Li samples recovered from the first ion exchange column were passed through a second ion exchange column with 1 ml AG50WX8 (200–400 mesh) resin. This column was equivalent to the third column of Moriguti and Nakamura (1998) and calibrated with seawater Li extracted from the first column. A solution of 30% ethanol in 0.2 M HCl (instead of 0.5 M HCl as in the original technique; Moriguti and Nakamura, 1998) was used for elution to improve the resolution of ion separation. A total of 25 ml of eluant was collected. The second column purification was successfully applied to planktic *G. menardii* and small seawater samples (Tables 2 and 3).

Isotopic analyses were conducted on a Finnigan MAT 262 TIMS at Louisiana State University following the procedures of You and Chan, (1996). In this technique, Li isotopic ratios were determined on Li^+ with ^7Li at ~ 1 V for foraminiferal samples using phosphate as an ion source and double rhenium filaments. The in run $2\sigma_m$ is typically 0.2‰, indicating minimal isotopic fractionation during a sample run. The isotopic ratio is expressed as $\delta^7\text{Li}$ relative to L-SVEC: $\delta^7\text{Li}$ (‰) = $\{[(^7\text{Li}/^6\text{Li})_{\text{sample}} / (^7\text{Li}/^6\text{Li})_{\text{L-SVEC}}] - 1\} * 1000$. This technique yields a precision of $\pm 1.2\%$ (2σ) for seawater samples.

Table 3

$\delta^7\text{Li}$ analyzed using TIMS and Li/Ca in planktic foraminifera from Hall and Chan (2004)

Species	Core depth (cm)	Calendar age (ky)	Li/Ca ($\mu\text{mol/mol}$)	$\delta^7\text{Li}$ (‰)
<i>OC205-2-103GGC</i>				
<i>Orbulina universa</i> ^a	8.5	0.4	9.3	30.6
<i>Orbulina universa</i> ^a	17.5	1.3	10.3	33.7
<i>Orbulina universa</i> ^a	57.5	5.2	10.9	30.4
<i>Orbulina universa</i> ^a	114	12.7	11.7	31.8
<i>Orbulina universa</i> ^a	122.5	14.4	14.7	30.5
<i>Orbulina universa</i> ^a	131	18.3	14.6	30.4
<i>Orbulina universa</i> ^a	131	18.3	n.d.	31.4
<i>Orbulina universa</i> ^a	200	35.8	13.1	32.3
<i>K162-13-D7</i>				
<i>Orbulina universa</i> ^a	s.s.	n.d.	10.3	32.5
<i>Globorotalia menardii</i> ^b	s.s.	n.d.	12.3	30.8
<i>Globorotalia menardii</i> ^b	s.s.	n.d.	12.7	31.7

Calendar ages of Bahaman samples based on Marchitto et al. (1998).

n.d. = not determined.

s.s. = surface sediment.

^a Single column.

^b Two columns.

2.4. Lithium isotopic analyses using MC-ICP-MS

Lithium was separated from foraminiferal samples by cation exchange chromatography based on multiple column separation procedures developed by Moriguti and Nakamura (1998). Three sets of cation exchange columns were used in this procedure, each column loaded with 1 ml of Bio-Rad AG50WX12 (200–400 mesh) resin. The first two columns are made from polypropylene and are prefabricated by Bio-Rad. The third column is made from quartz glass and has a smaller internal diameter than the first two columns. The columns were calibrated with L-SVEC isotopic standard.

Purified foraminiferal fragments were dissolved and loaded on the first column in 1 ml 4 M HCl. The column was eluted with 4 ml 2.5 M HCl and the entire sample plus eluant was collected. Samples were loaded on the second column in 1.5 ml 0.15 M HCl, eluted with 25 ml 0.15 M HCl, and the entire Li fraction was collected. Samples were loaded on the third column in 1 ml 0.15 M HCl. The column was then eluted with 12 ml of a fresh mixture of 30% ethanol in 0.5 M HCl and the entire Li fraction was collected. All samples were then dried and picked up

in 500 μl of 2% HNO_3 to make ~ 10 ppb solution for isotopic analyses.

Lithium isotopic measurements were made on a Nu Plasma MC-ICP-MS at the University of Maryland, Isotope Geochemistry Laboratory by simultaneous collection of ^6Li and ^7Li in opposing Faraday cups in accordance with the procedure of Teng et al. (2004). Samples were introduced to the plasma using a 50 $\mu\text{l}/\text{min}$ PFA nebulizer (Elemental Scientific). Sensitivity was on the order of 0.4 V of ^7Li in a 10 ng/g solution. Prior to isotopic analysis, the Na/Li ratio of each sample solution was measured semi-quantitatively, as ratios greater than ~ 5 may cause unstable instrumental fractionation (Tomascak et al., 1999). If the Na/Li ratio was found to be high, the sample was processed through the third column again for additional purification before isotopic analysis.

Mass analysis of each sample was bracketed by analyses of the lithium carbonate standard L-SVEC. Sample $\delta^7\text{Li}$ values were calculated by normalizing the sample $^7\text{Li}/^6\text{Li}$ values to the average of the bracketing L-SVEC values. The total Li procedural blank was ~ 200 pg, and has a $\delta^7\text{Li}$ of $-31 \pm 11\%$. Based on repeated analyses of seawater, this technique yields a precision of about $\pm 1.1\%$ (2σ).

3. Results and discussion

3.1. Lithium in seawater

Lithium concentrations, Li/Cl ratios, and $\delta^7\text{Li}$ values in Indian Ocean seawater are given in Table 2. The Li concentration of Indian Ocean seawater is largely uniform throughout the water column with an average value of 25.4 ± 0.2 $\mu\text{mol}/\text{kg}$. Previous work by Stoffyn-Egli and Mackenzie (1984) in the North Atlantic Ocean suggests that reactions with marine sediments may cause Li/Cl ratios in deep ocean water to decrease by 2% compared to the surface water. Our study shows no significant variation in Li/Cl versus depth for the tropical Indian Ocean. The Li/Cl ratio averages 9.10 ± 0.11 $\mu\text{g}/\text{g}$ throughout the water column (Table 2).

Previous $\delta^7\text{Li}$ seawater studies have focused on the Atlantic and Pacific Oceans (Tomascak, 2004). This work represents the first $\delta^7\text{Li}$ seawater analyses from the Indian Ocean. Seawater samples yield an average

value $\delta^7\text{Li}$ of $33.0 \pm 1.2\%$ (2σ) throughout the water column using the TIMS method (Table 2). Previous seawater analyses using TIMS yielded similar $\delta^7\text{Li}$ values ($\pm 2\sigma$) at $33.4 \pm 1.0\%$ (Chan, 1987; Chan and Edmond, 1988), $32.4 \pm 2.6\%$ (You and Chan, 1996), $30.0 \pm 0.8\%$ (Moriguti and Nakamura, 1998), and $32.5 \pm 1.4\%$ (James and Palmer, 2000). Therefore, Indian Ocean seawater is the same as Atlantic and Pacific Ocean water values within error and is consistent with the standard seawater value of $32.5 \pm 1\%$ recommended by James and Palmer (2000).

Small Indian Ocean seawater samples containing 10 and 5 ng Li, processed with a single pass through the large column, yield $\delta^7\text{Li}$ values of 33.6‰ and 32.7‰, respectively, which agrees with the results from 100 ng Li samples (Table 2). Atlantic seawater samples containing 10 and 5 ng Li with two column passes gave $\delta^7\text{Li}$ values of 31.7‰ and 32.5‰. Hence, 5 to 10 ng seawater Li samples are proven to yield isotopic ratios with similar precision and accuracy as 100 ng Li samples. This result validates the use of this TIMS method on foraminiferal samples containing approximately 5 ng Li.

Compared to TIMS, seawater analyses by MC-ICP-MS generally result in lower $\delta^7\text{Li}$ values. Previously reported values by this technique include $31.8 \pm 1.9\%$ (Tomascak et al., 1999), $29.3 \pm 0.6\%$ (Nishio and Nakai, 2002), $31.0 \pm 1.8\%$ (Bryant et al., 2003) and 29.6‰ (Pistiner and Henderson, 2003). Six aliquots of Atlantic seawater measured at the University of Maryland processed according to the present technique give a value of $29.6 \pm 0.6\%$ (McDonough, unpublished data). These MC-ICP-MS determinations yield an average of $30.3 \pm 2.2\%$ (2σ) for seawater.

3.2. Lithium isotopes in planktic foraminifera

O. universa from the Great Bahama Bank have $\delta^7\text{Li}$ values between 30.4‰ and 33.7‰ using the TIMS method (Table 3). Exceptions were samples which showed very high ^{23}Na and ^{39}K ion currents (>11 V) during the mass spectrometric run. These samples yielded higher $\delta^7\text{Li}$ values between 35‰ and 39‰. Contamination with significant amounts of extraneous ions can result in elevated measured $\delta^7\text{Li}$ of the sample (Kořler et al., 2001). The values from the samples with high Na and K signals were therefore

excluded from the data set. The average $\delta^7\text{Li}$ in *O. universa* from Bahama core OC205-2-103GGC using the TIMS method is $31.4 \pm 2.4\text{‰}$ (2σ , $n=8$). The mean value for the Holocene samples ($31.4 \pm 2.8\text{‰}$) is identical within analytical uncertainty to samples from the last glacial maximum and older, thus showing no glacial–interglacial variation in Li isotopic composition in ocean water over the last 36 ka.

Samples from the Great Bahama Bank have $\delta^7\text{Li}$ values between 27.4‰ and 29.9‰ using the MC-ICP-MS method (Table 4). The average $\delta^7\text{Li}$ in *O. universa* using the three column chemistry and MC-ICP-MS method is $28.4 \pm 1.6\text{‰}$ (2σ , $n=9$). The mean

Table 4
 $\delta^7\text{Li}$ analyzed using MC-ICP-MS and Li/Ca in planktic foraminifera from Hall and Chan (2004)

Species	Core depth (cm)	Calendar age (ky)	Li/Ca ($\mu\text{mol/mol}$)	$\delta^7\text{Li}$ (‰)
<i>OC205-2-103GGC</i>				
<i>Orbulina universa</i>	27.5	2.2	10.1	27.4
<i>Orbulina universa</i>	37.5	3.2	9.4	27.4
<i>Orbulina universa</i>	101.5	11.0	10.4	29.9
<i>Orbulina universa</i>	170	29.5	15.0	28.2
<i>Orbulina universa</i>	200	35.8	13.1	28.1
<i>Orbulina universa</i>	229.5	42.0	12.3	28.2
<i>Orbulina universa</i>	270	43.6	n.d.	29.1
<i>OC205-2-97JPC</i>				
<i>Orbulina universa</i>	104.5	n.d.	12.1	29.0
<i>Orbulina universa</i>	104.5	n.d.	n.d.	28.1
<i>RC17-177</i>				
<i>Globigerinoides sacculifer</i>	s.s.	n.d.	11.5	28.7
<i>Globigerinoides sacculifer</i>	17.5	11.7	10.7	28.7
<i>K162-13-D4</i>				
<i>Orbulina universa</i>	s.s.	n.d.	n.d.	30.2
<i>Orbulina universa</i>	s.s.	n.d.	n.d.	29.8
<i>Orbulina universa</i>	s.s.	n.d.	n.d.	29.2
<i>Orbulina universa</i>	s.s.	n.d.	n.d.	29.0
<i>Orbulina universa</i>	s.s.	n.d.	n.d.	31.4
<i>K162-13-D7</i>				
<i>Globorotalia menardii</i>	s.s.	n.d.	12.6	29.1
<i>Globorotalia truncatulinoides</i>	s.s.	n.d.	14.8	30.0

Calendar ages based on Marchitto et al. (1998).

n.d. = not determined.

s.s. = surface sediment.

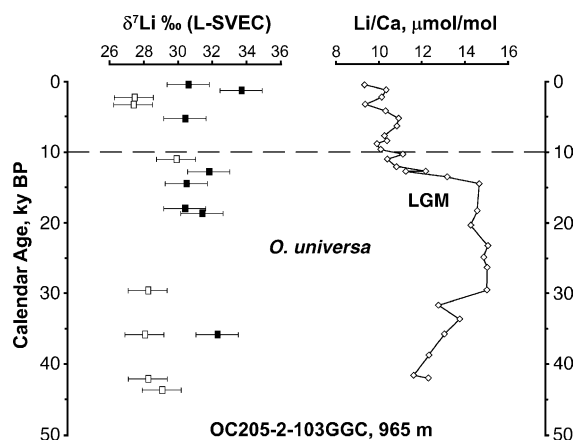


Fig. 1. $\delta^7\text{Li}$ analyzed using TIMS (closed squares) and MC-ICP-MS (open squares) and Li/Ca in planktic *Orbulina universa* from the Great Bahama Bank (Hall and Chan, 2004). Error bars of $\pm 1.2\text{‰}$ (2σ) (closed squares) and $\pm 1.1\text{‰}$ (2σ) (open squares) are based on the external reproducibility of seawater. Age model is based on calendar ages reported by Marchitto et al. (1998). The dashed line represents the Holocene boundary. See Tables 3 and 4 for data summary.

value for the Holocene samples ($28.7 \pm 3.5\text{‰}$) is identical within analytical uncertainty to samples from the last glacial maximum and older ($28.4 \pm 0.9\text{‰}$), showing no glacial–interglacial variation in Li isotopic composition in ocean water over the last 44 ka. The foraminiferal values obtained with MC-ICP-MS are on average 3‰ lower than those from TIMS. Possible causes of the discrepancy are discussed in Section 3.4.

Li/Ca in planktic and benthic foraminifera are elevated during glacial time relative to the Holocene (Burton and Vance, 2000; Hall and Chan, 2004; Fig. 1). Given the long residence time of Li in the ocean (approximately 1.5 My), the concentrations and isotopic compositions in seawater are not expected to change over the glacial–interglacial time scale. As such, glacial–interglacial variation in foraminiferal Li/Ca appears to be influenced by factors other than seawater composition alone (Hall and Chan, 2004). The glacial–interglacial variation in foraminiferal Li/Ca has been attributed to environmental factors and the effect of calcification rate (Hall and Chan, 2004) and not to changes in the Li input to the ocean. The constancy in $\delta^7\text{Li}$ over the last 44 ka (Fig. 1) is supportive that the sources and sinks of Li in the ocean did not change significantly during the last glaciation.

The $\delta^7\text{Li}$ value for an *O. universa* sample from Indian Ocean surface sediment (K162-13-D7) determined by TIMS is 32.5‰, while five other samples (K162-13-D4) using the MC-ICP-MS method yielded an average of $29.9 \pm 1.0\text{‰}$ (Tables 3 and 4). These values are within analytical uncertainty of the mean values measured in the Holocene samples from the Great Bahama Bank for each respective method (Fig. 1). This is consistent with the homogeneous Li isotopic composition of the oceans.

In addition to *O. universa*, we measured two *G. menardii* samples from the surface sediment of the Indian Ocean (K162-13-D7) using TIMS, yielding 30.8‰ and 31.7‰ and one sample (K162-13-D4) using the MC-ICP-MS method, yielding 29.1‰. The two TIMS *G. menardii* samples were processed through two columns and had relatively low $\delta^7\text{Li}$ compared to the Indian Ocean TIMS *O. universa* sample processed with a single column (32.5‰). However, the mean value for TIMS *G. menardii* (31.3‰) is identical to that of the average Bahama Bank TIMS *O. universa* samples (31.4‰). Similarly, the MC-ICP-MS *G. menardii* sample from the Indian Ocean (29.1‰) is equivalent to MC-ICP-MS Indian Ocean *O. universa* samples (29.9‰). This suggests that *O. universa* and *G. menardii* have similar Li isotopic compositions.

Using the MC-ICP-MS method, additional samples of planktic *G. sacculifer* from the Pacific Ocean (RC17-177) and *G. truncatulinoides* from the Indian Ocean (K162-13-D7) yielded $\delta^7\text{Li}$ values of 28.7‰ and 30.0‰ respectively. The average Bahama Bank *O. universa* sample using the MC-ICP-MS method is $28.4 \pm 1.6\text{‰}$ (2σ). As such, both *G. sacculifer* and *G. truncatulinoides* also appear to have similar Li isotopic compositions to *O. universa* and *G. menardii*. Therefore, the Li isotopic compositions of various planktic species measured by both TIMS and MC-ICP-MS are indistinguishable from one another within the range of analytical uncertainty.

Using MC-ICP-MS, Hathorne et al. (2003) reported that Holocene/Pleistocene samples of *O. universa* have $\delta^7\text{Li}$ values similar to seawater (31‰), while *G. truncatulinoides* were lighter ($27 \pm 0.3\text{‰}$). Quadrupole ICP-MS data reported by Košler et al. (2001) for *P. obliquiloculata* from surface sediments from the Ontong-Java Plateau, range between 28‰ and 32‰ ($30.2 \pm 3.3\text{‰}$). Two

G. tumida samples from the same location showed disparate isotopic values of 38.8‰ and 50.6‰. Given the wide range of values, the isotopic composition of *G. tumida* should be confirmed. The observed range of isotopic composition for other species (27‰ to 31‰) in these recent studies suggests that there may be subtle isotopic variation among different species of planktic foraminifera. However, such species variation appears indistinguishable given the limited data set and analytical uncertainty.

3.3. Isotopic fractionation in foraminiferal tests

We calculate the isotopic fractionation that occurs during the incorporation of seawater Li into foraminiferal calcite using data from TIMS and MC-ICP-MS relative to seawater values obtained with the respective methods, with errors based on two standard deviations of the mean. Considering only the modern TIMS technique using phosphate as the ion emitter, the average $\delta^7\text{Li}$ for seawater is $32.0 \pm 1.4\text{‰}$ ($2\sigma_m$) (You and Chan, 1996; Moriguti and Nakamura, 1998; James and Palmer, 2000; this study). The mean $\delta^7\text{Li}$ for *O. universa* from uncontaminated Holocene/Pleistocene samples using the TIMS method is $31.5 \pm 0.8\text{‰}$ ($2\sigma_m$, $n=9$) (Table 3). Thus, the fractionation factor between *O. universa* and seawater is 0.9995 ± 0.0016 . Using the respective foraminiferal and seawater averages of $28.8 \pm 0.5\text{‰}$ ($2\sigma_m$, $n=11$) (Table 4) and $30.4 \pm 1.2\text{‰}$ ($2\sigma_m$) by the MC-ICP-MS method (cf. Section 3.1), the isotopic fractionation factor is 0.9984 ± 0.0013 , identical within error to the estimation based on TIMS data. Thus, *O. universa* shows virtually no isotopic fractionation. Based on the present data, there also appears to be little or no isotopic fractionation associated with other planktic species. These results are also in agreement with the findings of Hathorne et al. (2003) and Marriott et al. (in press) and support the hypothesis that $\delta^7\text{Li}$ in planktic foraminifera is a proxy of the Li isotopic composition of seawater in the past.

The lack of isotopic fractionation in *O. universa* (and other planktic species) is in contrast to inorganically precipitated calcite and coralline aragonite which are isotopically lighter than the solutions from which they precipitated (Marriott et al., 2004). This suggests a distinct difference in the

biological effect of planktic foraminifera compared to corals. Additionally there may also be a mineralogical effect in the biological precipitation of calcite versus aragonite.

3.4. Comparison of results from the two methods

As noted earlier, measurement of foraminiferal samples by MC-ICP-MS generally result in lower $\delta^7\text{Li}$ values (by $\sim 3\%$) compared to those using TIMS. Measurements of $\delta^7\text{Li}$ of modern seawater by various methods also show a spread of 3% to 4% (Section 3.1; Tomascak, 2004). Tomascak (2004) suggests that the variation in seawater analyses is caused by analytical artifacts. In this section we examine possible causes of discrepancies in the results of foraminiferal analyses by the two methods.

3.4.1. Differences in column chemistry

The chemical processes prior to isotope analysis are different for the two techniques. The TIMS method mostly employed one larger cation exchange column with 15 ml resin volume. Later sample processing included a second pass through a smaller column (1 ml) to further purify Li from Na and K contamination. The MC-ICP-MS method employed a multi-stage purification procedure (Moriguti and Nakamura, 1998). Lithium fractionates greatly in the ion exchange process. Hence, the leading eluant from a column is enriched in ^7Li and the trailing fraction is enriched in ^6Li (Taylor and Urey, 1938; Moriguti and Nakamura, 1998). Incomplete recovery would affect the measured isotopic ratio. All ion exchange columns in this work were carefully calibrated to ensure quantitative recovery. For the MC-ICP-MS samples, the early fractions would have to be lost to result in a $\delta^7\text{Li}$ value that is too light. In this procedure, eluant collection began with sample loading, so the first fractions were always retained. For the TIMS samples, the last trailing fraction would have to be lost to lead to a high $\delta^7\text{Li}$. In practice, the collected range extended several milliliters before and after the calibrated elution curve as defined by the highly sensitive flame emission method. Furthermore the same column calibration procedure was employed for analyses of

standard reference rocks which yielded results that agree with other laboratories (Chan and Frey, 2003). We therefore conclude that column chemistry is probably not the prime cause of inter-method differences.

3.4.2. Impurities in the ion source

It is known that extraneous ions in the Li sample interfere with isotopic analyses. Ions present in the sample matrix may cause mass discrimination in ICP-MS due to space charge effects. Hence samples were monitored for Na prior to MC-ICP-MS measurement and were purified by repeated column separation when high Na was detected. Impure ion source in TIMS would require higher filament current during ionization, causing isotopic fractionation. It is evident in the TIMS analyses of foraminiferal samples that measured $\delta^7\text{Li}$ values increased when ^{23}Na and ^{39}K signals exceeded 11 V. The sources of Na and K contamination are unknown. The blanks for these elements in the sub-boiling water and high purity acid reagents used in this study were below detection. Potential sources include the breakdown of ion exchange resin and impurities introduced during sample preparation. The effect of a slight Na or K contamination would be magnified during the ionization process in the mass spectrometer because the amount of Li in foraminiferal samples was so small. An additional purification step through a small ion exchange column was found to alleviate the contamination problem and results in successful ratio determinations.

3.4.3. Analytical sensitivity

Because of the high ionization efficiency of lithium phosphate, even a small sample of several ng Li produces a strong Li^+ beam in TIMS. The 2.5 to 5 ng Li in the foraminiferal samples were measured with at least 1 V signal of Li^+ with very low background (0.2 mV). By comparison, the same sample size typically yielded an intensity of 0.25 to 0.4 V for ^7Li in MC-ICP-MS. A smaller signal is more readily affected by counting statistics and memory effects.

3.4.4. Procedural blank

The procedural blank for the TIMS sample preparation was 1% to 2% of sample size and

therefore would not significantly affect foraminiferal analyses. The chemical processing for the MC-ICP-MS samples resulted in a procedural blank that amounted to 4% to 8% of the Li in samples. Moreover, the isotopic composition of the blank is very light. It is conceivable that such contribution from the blank could lower the measured value of $\delta^7\text{Li}$ in the foraminiferal samples.

4. Conclusions

Based on both TIMS and MC-ICP-MS measurements, the $\delta^7\text{Li}$ of the planktic foraminifer *O. universa* is within error of seawater. Thus, isotopic fractionation accompanying the precipitation of foraminiferal calcite appears to be negligible. The Li isotopic composition in down-core measurements of *O. universa* from the North Atlantic remains constant for the last 44 ka, indicating little change of Li isotopic composition of ocean water during the last glacial–interglacial transition. Based on limited data, several planktic species including *G. sacculifer*, *G. menardii*, and *G. truncatulinoides* also have seawater-like $\delta^7\text{Li}$, similar to *O. universa*.

The results reported here indicate that $\delta^7\text{Li}$ in planktic foraminifera is a useful proxy for seawater composition in the past. Possible species effects have to be explored to allow the use of a range of foraminiferal species to be used as seawater Li isotope proxies. The effects of post-depositional dissolution and diagenesis also need to be assessed in order to meaningfully evaluate ancient samples.

A consistent difference of about 3‰ exists between the Li isotope analyses of *O. universa* using different column procedure and mass spectrometric methods. Possible causes of the discrepancy are sample purity, signal intensity, and blank effects. Further developmental work must aim at low-blank and high-purity isotope sample preparation.

This investigation presents the first Li analyses of Indian Ocean seawater. The results indicate that Li concentrations and $\delta^7\text{Li}$ values are uniform throughout the water column. Indian Ocean waters are analytically indistinguishable from Atlantic and Pacific waters in Li isotopic composition. In contrast to previous work, we did not find a depletion of Li/Cl ratios in deep water by reactions with marine sediments.

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