Measurement of lithium isotope ratios by quadrupole-ICP-MS: application to seawater and natural carbonates†

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We present an improved method for lithium isotope ratio (^{7}Li/^{6}Li) determinations with low total lithium consumption (<0.2 ng/quintuplicate analyses), high column yields (>99.98%), high isotope ratio precision (<±0.8‰, 2σ), and low blanks (1.0 ± 0.5 pg). We refine a single step ion chromatographic method to quantitatively recover and separate lithium from all matrix elements using small volume resin (2 ml/3.4 meq AG 50W-X8) and low volume elution (6 ml, 0.5 N HCl) with low procedural blanks (<500 fg/ml). We optimize the procedure for analyses of natural carbonates (foraminifera) containing 1 to 2 ppm lithium. This lithium separation method is applicable to other natural samples (*e.g.* seawater, pore-waters, mineral grains) by appropriate scaling. Isotope ratio measurements are made by a single collector Quadrupole ICP-MS (*Agilent* 7500*cs*) using cool plasma (600 W), soft extraction, peak jumping, and pulse detection mode with sample-standard bracketing. The precision is better than ±0.8‰ (2σ) for L-SVEC lithium standards and better than ±1.5‰ (2σ) for natural samples. We report a high matrix tolerance limit for sodium (~0.6 mol/mol, Li/Na) and calcium (<20 μmol/mol, Li/Ca) for our Quadrupole ICP-MS method. Our seawater δ^7Li value (30.75 ± 0.41‰, 2σ, $n = 10$) is the same as that reported by other workers (~31.0 ± 0.5‰). Species-specific and bulk sample δ^7Li analyses of two size fractions of core-top foraminifera yield values similar to modern seawater.

1. Introduction

Lithium isotopes have the potential to provide insights into Earth processes such as continental weathering,[1] hydrothermal circulation[2] and alteration of oceanic crust at active and passive margins.[3–7,9,10] The two stable isotopes of lithium (^{6}Li and ^{7}Li) have a large mass difference (~16%), resulting in a large mass-dependent fractionation factor. Consequently, the range in lithium isotope ratios observed in terrestrial samples is enormous, up to ±100‰.[8] This large fractionation provides enormous potential for application of lithium isotopes as a geochemical tracer. Unfortunately, fractionation of lithium is limited not only to natural processes but also occurs readily during sample preparation and analyses. Taylor and Urey[11] first reported large mass-dependent lithium isotope fractionation (~250‰) upon passing lithium through a zeolite cation exchange column. To avoid possible analytical artifacts in the measured isotope ratio it is thus important to prove quantitative recovery of lithium throughout all steps of separation and analysis.

Our interest in lithium isotope analyses stems from the creation of δ^7Li and Li/Ca record of long-term evolution of seawater chemistry using fossilized foraminifera. Such a record has the potential to elucidate changes in the factors driving variations of oceanic silica mass balances linked to continental and sea floor/hydrothermal weathering.[12–16]

High precision lithium isotope ratio measurements have been done traditionally by thermal ionization mass spectrometry (TIMS) (±0.7‰ to ±2.5‰, 2σ),[17–20] by quadrupole ICP-MS (±0.8‰ to ±2.1‰, 2σ)[21,22] and by MC-ICP-MS (±0.2‰ to ±1.4‰, 2σ).[23–25] All these measurements are susceptible to instrumental mass bias and to high concentrations of matrix elements like Na, Ca and K. Moreover, ICP-MS methods are also vulnerable to matrix-induced ionization interferences caused by low IP_1 (first ionization potential) elements. TIMS methods are characterized by large and non-constant instrumental fractionation of lithium, relatively large lithium mass requirement (>100 ng), large procedural lithium blanks (100 pg level) and variable matrix induced fractionation. Typically TIMS requires quantitative separation of lithium from matrix elements and filament loading of lithium as a heavy ion complex (Li-borate or Li-phosphate). Fractionation of lithium off the filament during TIMS analyses has plagued the precision and accuracy of TIMS.[26,18–20] Multi-Collector ICP-MS methods are more suitable for mass-limited natural samples but still require relatively large lithium masses (2 to 40 ng). However, instrumental lithium fractionation, relatively high sensitivity to matrix elements and variable matrix-induced mass bias still require pre-separation of lithium from matrix elements to achieve high precision. Quadrupole ICP-MS (Q-ICP-MS) methods have demonstrated significantly smaller lithium mass requirement (5 to 10 ng) and have achieved precision (±1.0‰, 2σ) comparable to TIMS and MC-ICP-MS.[21,22]

Lithium isotope measurements by ICP-MS are affected by the presence of trace quantity matrix elements, which result in

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changes of ionization equilibria in the plasma due to ionization of non-analytes.[22,23] Thus, for natural samples, especially marine, it is necessary to achieve quantitative separation of lithium from interfering elements (*e.g.* sodium, calcium and potassium) to avoid variable matrix-induced mass bias effects. Separation of lithium from sodium is difficult because of the small separation factor of the two ions and because of a large column-induced fractionation of lithium.[11,27–29] Application of single-step quantitative separation of lithium from sodium (and other alkali elements) is limited by large cumulative procedural blanks, tailing of lithium peaks, incomplete recovery of lithium off the columns, and subsequent column induced fractionation (James and Palmer, 2000[30]).[13,14,18] In the interest of combining the advantages of Q-ICP-MS with miniaturized chemical separation procedures applicable to foraminifera, we have thoroughly investigated the various limitations discussed above.

We report here an improved Q-ICP-MS method that achieves high precision using small masses of lithium with relatively high matrix tolerance limits. We apply this low blank (1.0 ± 0.5 pg), low mass (<0.2 ng/quintuplicate analyses) high precision (±0.64‰ to ±0.8‰, 2σ) Q-ICP-MS method to lithium isotope measurements in natural carbonate and fluid samples. We also demonstrate quantitative separation of lithium from sodium and other matrix-based elements in a single-step chromatographic separation with low blank and high recovery that eliminates both chromatographic fractionation in eluent lithium and matrix-induced mass bias fluctuations. Our chromatographic method is characterized by low procedural blank (<500 fg/ml), high yield (100 ± 0.02%) and absence of column induced fractionation effects. The development of this low blank, high sensitivity technique allows high quality lithium isotopic measurements from samples that are mass limited, such as foraminifera. Our analyses of seawater and core-top foraminifera samples yield lithium isotope ratios comparable to published values.

2. Experimental

Lithium isotopic composition is reported as per mil deviation from NIST SRM 8545 or L-SVEC ($^7Li/^6Li = 12.33 \pm 0.03$).[31] Where;

$$\delta^7\mathrm{Li}(‰) = \left\{ \left[\frac{\left(\frac{^7\mathrm{Li}}{^6\mathrm{Li}}\right)_{\mathrm{Sample}}}{\left(\frac{^7\mathrm{Li}}{^6\mathrm{Li}}\right)_{\text{L-SVEC}}} \right] - 1 \right\} \times 1000 \qquad (1)$$

All acids and standards were prepared under Class 100 clean lab conditions to minimize the lithium, boron, sodium, potassium and magnesium blanks. Pre-cleaned Nalgene® Teflon® bottles (leached in *aqua regia* and boiled in ~7 N HNO_3) were used for solution storage. Savillex® Teflon® beakers and ICP-MS vials (leached in *aqua regia* and boiled in ~7 N HNO_3) were used for sample preparation and analysis. Final steps of sample preparation including sample cleaning, column separation and dissolution as well as operation of *Agilent* 7500*cs* Quadrupole ICP-MS were done under Class 100 clean lab conditions.

2 a. Sample matrix and elution matrix preparation

All acids, ICP-MS standards and samples were prepared using 18.3 Megaohm MQ water and Seastar Optima® (Fisher) grade HNO_3. Double distilled hydrochloric acid for column chemistry was prepared in house from reagent grade HCl (Fischer) using a Teflon® sub-boiling still. Accurate normality determination of each batch of acid was done by titrating with reagent grade 1.0 N NaOH (Fischer). The 0.50 N HCl for column elution was prepared by gravimetric dilution and titrated using Optima grade 0.1 N NaOH to determine exact strength. Acid blanks for lithium, sodium, boron, magnesium, potassium, calcium and manganese were regularly monitored. On rare occasions acids had reagent blanks of more than 50 fg/ml of lithium or 0.1 ppb of sodium which were discarded.

2 b. L-SVEC standard preparation

Approximately 250 mg of L-SVEC lithium carbonate (Li_2CO_3) was weighed and dissolved in 3.0 ml of concentrated HNO_3, evaporated to dryness at sub-boiling temperature (80 °C) and dissolved in 500 ml 2% HNO_3 to prepare a 100 ppm L-SVEC lithium stock solution. The entire dissolution was performed gravimetrically. Subsequent lithium standards were prepared by gravimetric dilution of the stock solution.

2 c. ICP-MS standard preparation

ICP-MS standards were gravimetrically prepared from SPEX™ High-Purity ICP-MS standards. Lithium blanks of the elemental standards were closely monitored because of the large range in isotopic composition of commercially available lithium reagents.[32] Analytical reagent grade Alfa Aesar, 99.999% pure calcium carbonate was used for matrix matched standard preparation.

2 d. Column chromatography

Separation of lithium from sodium and calcium is controlled by their respective distribution coefficients (K_d) and the separation factor (α_{Li-Na}). The distribution coefficient is defined as the ratio of concentrations of an ion per unit mass of resin and per unit volume acid under equilibrium conditions (eqn (2)). Moreover, separation factor of an ion pair is the ratio of their distribution coefficient (eqn (3)).

$$K_d^{Li} = \left(\frac{[\mathrm{Li}]_{\mathrm{Resin}}}{[\mathrm{Li}]_{\mathrm{Acid}}}\right) \qquad (2)$$

$$\alpha_{\text{Li-Na}} = \left(\frac{K_d^{Li}}{K_d^{Na}}\right) \qquad (3)$$

For mineral acid media (HNO_3 or HCl) the K_d values of both lithium and sodium are similar so that the α_{Li-Na} is small (ranging from 1.18 to 1.63). This results in significant peak overlap, making quantitative separation of lithium from sodium analytically challenging.[27–29] The separation factor of lithium and divalent cations such as calcium (α_{Li-Ca}), magnesium and strontium is large, usually an order of magnitude larger than that of α_{Li-Na}. Thus, peak separation of lithium from calcium,

Table 1 Expected composition of 1 mg of cleaned foraminifera dissolved in 1 ml load solution[33,34]

Component	$[X^{n+}]_{Foram}$	Mass	Concentration
Foram	—	1.0 mg ($CaCO_3$)	0.02 meq/ml
Li	1 ppm	1.0 ng (Li^+)	$\sim 1 \times 10^{-7}$ meq/ml (as Li^+)
Na	0.1%	0.99 μg (Na^+)	$\sim 3 \times 10^{-5}$ meq/ml (as Na^+)
Ca	40%	0.40 mg (Ca^{2+})	0.02 meq/ml (as Ca^{2+})

magnesium, and strontium is easily effected. Cleaned planktonic forams contain μg/mg levels of magnesium, sodium, potassium and strontium distributed homogeneously in their shell, while calcium dominates the matrix of dissolved calcitic forams[33,34] (Table 1).

The success of lithium purification from other matrix elements, for foraminifera and seawater samples by column chromatography is thus limited by separation of lithium from sodium. Separation of lithium from sodium using poly-sulfonated cation exchange resins is usually done either by eluting with low normality mineral acid from large resin volume or by using small resin volume with mineral acid – organic solvent mixtures as the elution matrix.[29] However, elution by mineral acid – organic solvent mixture (methanol/ethanol/acetone) results in rapid resin degradation, lithium peak migration due to changes in eluant normality, plus high and variable lithium and sodium blanks.

We quantitatively separate lithium from sodium and other matrix elements using a small volume of cation exchange resin (2.0 ml) and dilute mineral acid (0.50 N HCl). Our chromatographic method is optimized for 1 to 2 mg of dissolved foraminifera ($CaCO_3$) having a total load of 0.04 mili-equivalent (meq). We use 5 ml Teflon® columns with Teflon® frits having 2.0 ml resin volume. The columns were packed with BioRad® AG 50W-X8 (100–200 mesh size) cation exchange resin to a height of 250 mm (Table 2). Total capacity of the wet resin is 3.4 meq (1.74 meq/ml). The load is ~1.5% of the resin capacity. This capacity to load ratio is an order of magnitude better than the range required for quantitative separation of lithium. The strength of the elution acid (0.50 N HCl) is carefully controlled to within ±2%.

Table 2 Column specifications for single step separation of lithium from sodium and matrix elements of foraminifera samples

Column characteristics	Specification
Column material	Teflon® (Savillex®) columns with Teflon® frits
Internal diameter of column	3.2 mm
Resin type	AG 50W-X8 (100–200 mesh size)
Resin volume	2.0 ml (wet)
Resin capacity	3.4 meq (1.74 meq/ml wet capacity)
Resin height	250 mm
Flow rate	0.03 ml/minute
Load volume	200 μl
Load	0.02 to 0.04 meq Ca^{2+} (1–2 mg of foraminifera)
Total elution time	9 h
Total turnaround time	36 h
Pre-wash	6 N HCl (three column volume)
Back-wash	0.5 N HCl (three column volume)
Conditioning	0.5 N HCl (three column volume)
Load matrix	0.5 N HCl
Elution matrix	0.5 N HCl
Li fraction	6 ml to 11 ml (gravimetric)
Operational temperature	20 °C

Prior to sample loading the columns are pre-washed with three column volumes of 6 N HCl, back-washed with three column volumes of 0.50 N HCl and then conditioned with three column volumes of 0.50 N HCl. Samples are loaded in 200 μl of 0.50 N HCl matrix and subsequently eluted with 15 ml of 0.50 N HCl. The 6 ml to 11 ml eluate fractions are collected in acid cleaned Savillex® Teflon® beakers for lithium analyses. Both pre-elution (0 ml to 6.0 ml) and post-elution (11 ml to 16 ml) fractions are collected to check for bleeding and tailing effects. The lithium fraction is evaporated to dryness at sub-boiling temperature (80 °C) and then dissolved in 2 ml of 2% HNO_3. For calibration purpose 0.50 ml of eluates are collected in 2 ml acid cleaned Savillex® Teflon® ICP vials. Each of the elution fractions are gravimetrically weighed to three significant figures, dried at sub-boiling temperature (80 °C) and then gravimetrically taken up in 0.50 ml of 2% HNO_3.

For seawater and pore-water samples with high matrix load we use high capacity (14 meq) 8 ml columns with 250 mm resin height. These columns are pre-washed, back-washed and conditioned using three column volumes each of 6 N HCl, 0.50 N HCl and 0.50 N HCl respectively. The load volume is set at 500 μl of 1 : 10 diluted seawater. The lithium fraction of the eluate is determined to be 24 ml to 44 ml.

2 e. Mass spectrometry

Lithium isotope ratios are measured by *Agilent*™ 7500*cs*, a single collector quadrupole-ICP-MS. The instrument is operated in cool plasma conditions (600 W) to eliminate $^{12}C^{2+}$ and $^{14}N^{2+}$ interferences on $^6Li^+$ and $^7Li^+$ respectively. We use an ESI™ self-aspirating 100 μl/min concentric PFA nebulizer, quartz spray chamber (Scott-type), quartz torch and quartz injector (2.5 mm internal diameter). The octopole collision/reaction cell is turned off. Platinum sampling and skimmer cones are used to minimize carry over effects and blanks (Table 3). To eliminate lithium memory effects a time-resolved analysis of lithium sensitivity was performed to determine optimal sample uptake (60 s) and washout time (240 s). For high signal stability and low background noise, soft extraction (both extraction lenses at negative potential) of ions is performed. To obtain equal numbers of ion counts for both lithium isotopes a dwell time ratio of 0.2 s : 2.6 s :: ^7Li : ^6Li is adopted, roughly in inverse proportion to their isotope abundance ratio. The mass calibration for ^6Li and ^7Li is performed to make the signal peak axes sit exactly on 6.00 amu and 7.00 amu respectively. The *Agilent* Q-ICP-MS 7500*cs* does not exhibit mass axis drift (±0.1 amu). To eliminate potential peak overlap between ^7Li and ^6Li peak, the peak width of the isotopes are tuned to be less than 0.75 amu at 10% peak height and less than 0.60 amu at 50% peak height. These tuning parameters are checked daily to maximize instrument sensitivity and stability (see ESI).†

To optimize precision, we forced lithium ion counting for both isotopes to occur in pulse detection mode, eliminating the possibility of ^7Li counts automatically crossing over into analog mode at high-count rates. Two key modifications, suggested by *Agilent* engineers, of the firmware are performed to achieve this:

Table 3 Quadrupole ICP-MS (*Agilent* 7500*cs*) settings for lithium isotope ratio determination

Instrumental parameter	Cool plasma setting (isotope ratio mode)
Plasma RF forward power	600 W (Cool plasma)
Nebulizer	Concentric (PFA) self aspirating
Sample uptake rate	~100 μl/min
Uptake time and washout time	60 s and 240 s
Spray chamber	Quartz
Spray chamber temperature	2 °C
Torch/Injector	Quartz/Quartz (2.5 mm i.d.)
Shield torch (bonnet)	Platinum
Sampling cone and skimmer cone	Platinum/Platinum
Sampling depth	6.5 to 7.5 mm (cool/outer)
Carrier gas	0.60 to 0.65 L/min
Make up gas	0.30 to 0.40 L/min
1st Extraction lens	−120.0 to −130.0 V (soft extraction)
2nd Extraction Lens	−10 to −5 V (soft extraction)
Analyzer pressure	2.25×10^{-4} Pa to 2.45×10^{-4} Pa
Interface pressure	365 to 375 Pa
^{6}Li/^{7}Li dwell time	0.26 s/0.02 s (actual)
Points per mass peak and no. of Reps	3 points per mass peak and 7 reps
Discriminator voltage	8.0 to 8.4 mV
Pulse detection limit[a]	3.0×10^6 cps
Detector dead time	34.6 to 39.6 ns

[a] For *Agilent* 7500*cs* the default pulse detection limit is 1.0×10^6 cps. This was increased to 3.0×10^6 cps by changing the detector parameter settings in the ICP-MS operating firmware.

(1) pulse mode threshold of the detector is increased from 1.0×10^6 cps to 3.0×10^6 cps; and (2) detector dead-time corrections are calibrated directly on ^{7}Li and ^{6}Li (dead time at $m/z = 6$ and 7 is 34.6 to 39.6 ns). The first step overrides the upper count limit, allowing the detector to remain in pulse mode at high (>10^6 cps) ion counts. There is a mass dependent dead-time correction built into the *Agilent* detector circuit that ensures the appropriate dead time correction for ^{7}Li at high-count rates. Note that in isotope ratio mode the effective threshold is about 2/3 of the firmware setting, 2.2×10^6 cps rather than 3.0×10^6 cps. The mass scan time of the quadrupole (fly time) in isotope ratio mode is ten times faster than the value set in the software. This faster scan rate produces proportionally larger volume of mass scan data. Instead of working with averaged isotope ratio data produced by the instrumental firmware we extracted this raw mass scan data and performed the data reduction offline in Excel spreadsheets.

In normal scanning or peak jumping acquisition mode a quadrupole mass filter operates by scanning the entire mass range (5 to 260 amu) at a speed in excess of 3000 amu/s. However, in isotope ratio peak jumping acquisition mode the Agilent quadrupole operates at a speed ten times faster. Due to this rapid peak jumping rate in isotope ratio mode the true dwell time on ^{6}Li and ^{7}Li are 0.26 s and 0.02 s respectively, one tenth of the *displayed* dwell time of 2.6 s and 0.2 s. Also the new generation quadrupoles have mass dependent Intelligent Settle Time™ feature instead of a fixed settle time. Consequently the one amu difference in mass between ^{6}Li and ^{7}Li requires minimal quadrupole settle time.

2 f. Sample preparation

Foraminifera shells are handpicked under an optical microscope to separate by species and size fractions. Shells with signs of diagenetic alteration or significant authigenic mineral deposits are discarded. A total of 1 to 2 mg sample (accurately weighed) is picked for every species. The tests are gently crushed between two glass plates to open the chambers. Diagenetic alteration of shells (dissolution and recrystallization to Mg-containing $CaCO_3$) and presence of authigenic mineral phases (Li and Mg rich clays) are thought to be the main reason for δ^7Li offset in unprocessed/uncleaned foraminifera samples.[35–37] We chemically clean foraminifera shells to eliminate artifacts of post depositional chemical alterations and retain the intrinsic (seawater) signature. A multi step sample cleaning technique[38,39] involving fine clay removal by sonication (DD-H_2O and methanol) – reductive cleaning (hydrazine) – oxidative cleaning (hydrogen peroxide) – reductive cleaning (hydrazine) is performed (R–O–R). Prior to final dissolution two weak acid etchings (0.001 N HNO_3) are done. Leached samples (~1 mg) are dissolved in 250 μl of 0.50 N HCl. A part of the dissolved sample (200 μl) is subjected to chromatographic separation. The remainder 50 μl is dried down and taken up in 1 ml of 2% HNO_3 for trace element analyses. The lithium eluent off the column is dried at sub-boiling temperature (80 °C) and dissolved in 2.0 ml of 2% HNO_3 for isotope ratio analyses.

Seawater samples are first dried down with 6 N HCl (1 : 10 vol/vol) at sub boiling (80 °C) temperature. The dried samples are then dissolved in 0.50 N HCl for chromatographic separation. For 20 μl seawater aliquots 2 ml columns and for 50 μl seawater aliquots 8 ml columns are used. The lithium eluates off the column are processed identically as carbonate samples.

3. Results and discussion

3 a. Chromatographic separation of lithium

The limiting factors in single-step separation of lithium from sodium and other matrix elements using cation exchange resin and mineral acid are high cumulative blanks due to large elution volume, low lithium recovery, incomplete separation of lithium from sodium, and column induced fractionation (Table 4) (James

Table 4 Published single step lithium separation methods with AG 50W-X8 resin and mineral acid

Author	Resin Volume Resin Height	Elution Matrix	Elution Volume (Li Fraction)	Blanks/Load	% Blank	Yield
You and Chan[18]	11.78 ml 150 mm	0.5 N HCl	80 ml (42–62 ml)	190 pg/100 ng	0.19%	>98%
James and Palmer, 2000[30]	2.7 ml 85 mm	0.2 N HCl	18 ml (24–42 ml)	150 pg100 ng	0.15%	100%
Hall *et al.*[13]	11.78 ml 150 mm	0.5 N HCl	30 ml	57 ± 13 pg/100 ng	0.07%	100%
Hathorne and James[14]	4.3 ml 85 mm	0.2 N HCl	45 ml (24–42 ml)	12 pg/4 ng	0.3%	100%
This Study	2.0 ml 250 mm	0.5 N HCl	11 ml (6–11 ml)	1.0 ± 0.5 pg/0.5 ng	0.2%	100.02–99.98%

and Palmer, 2000[30]).[25,13,14,18] The low cumulative lithium blank (1.0 ± 0.5 pg), high lithium yield (99.98% to 100.02%) and absence of column-induced fractionation ($\delta^7Li = 0.27‰$, $n = 19$) are key features of our method.

Lithium is the first element to elute off the columns in the 6 to 11 ml elution fraction within 5 ml of total elution volume (Fig. 1). The pre-lithium fraction, 0 to 6 ml, has on average 100 fg/ml ($n = 19$) of lithium blank. The elemental composition of pre-lithium fraction is similar to the elution matrix. Sodium, the next element to elute after lithium, is absent in the first 13 ml of elution. Therefore, a quantitative separation between lithium and sodium is achieved with one column volume (2 ml) of peak separation. The average lithium blank of the post-lithium fraction, 11 to 15 ml, is 130 fg/ml. Low lithium blanks of both pre-lithium and post-lithium fractions demonstrate the absence of lithium breakthrough or tailing of the lithium elution peak.

Taylor and Urey[11] first demonstrated approximately 250‰ fractionation of lithium during cation exchange chromatography with zeolite columns. During elution of matrix-matched L-SVEC lithium (foraminifera composition) through AG 50W-X8 resin, the leading fraction of eluted lithium is ~100‰ ^{7}Li enriched whereas the tailing fraction is ~100‰ enriched in ^{6}Li. A total 200‰ fractionation range is observed across the lithium elution peak (Fig. 2). Preferential partitioning of ^{6}Li onto cation exchange resin (AG 50W-X8) results in large equilibrium fractionation effect on load lithium. Thus, complete recovery of lithium off the column is critical to avoid chromatographic fractionation effects. This simple requirement severely constrains the column repeatability characteristics. No drifts in elution times, volumes or separation constants can be tolerated.

Columns are periodically calibrated using matrix-matched L-SVEC lithium standards. During column calibrations, concentrations and isotopic composition of the load and eluant are determined to monitor quantitative recovery of lithium off the columns. On rare occasions samples with less than 100% lithium recovery are discarded. Average δ^7Li values of L-SVEC lithium standards ($n = 15$), column separated L-SVEC lithium ($n = 3$) and matrix matched L-SVEC standard ($n = 20$) are, within analytical uncertainty, identical (Fig. 3). Lithium concentration of pre-lithium and post-lithium fractions of foraminifera samples are monitored and the acceptability criteria is set at $<1 \times 10^{-3}$ of blank to load ratio (1 pg/1 ng).

Significant lithium peak migrations due to changes in matrix load and elution matrix strength have been reported.[5,30] To test the effect of changes in normality of elution matrix on lithium elution peak position we analyzed the lithium elution position of matrix matched L-SVEC lithium with 0.45 N HCl, 0.50 N HCl and 0.55 N HCl. This 10% increase or decrease in the normality of elution acid results in insignificant lithium peak migration within our lithium eluate volume (Fig. 4). To test the effect of matrix composition on lithium separation variable amounts of calcium (0.5 millimolar to 25 millimolar) and sodium (2 ppb to 100 ppb) doped L-SVEC lithium standards were eluted (data not shown). These changes in the composition and capacity of the load matrix did not result in lithium peak migration or overlapping of lithium and sodium peaks. During elution of natural samples, seawater and foraminifera with variable matrix strength, composition, and load, the lithium elution peaks remain fixed with quantitative separation from matrix sodium.

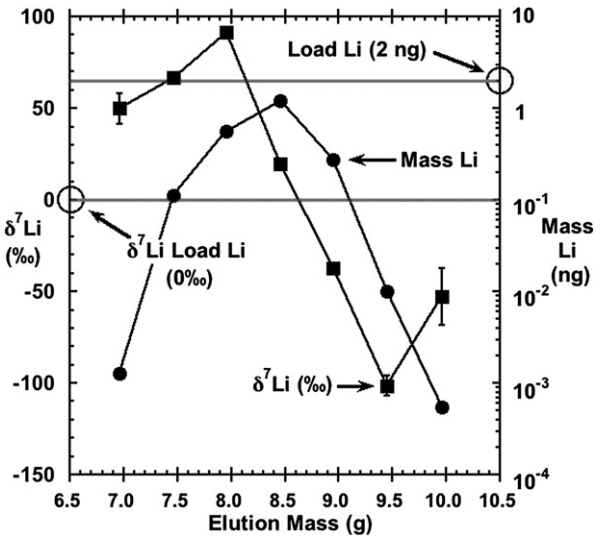

Fig. 2 Evolution of δ^7Li across elution peak. Isotopic evolution of δ^7Li across the elution peak of matrix matched L-SVEC lithium (2 ng). From the leading to the trailing edge of the elution peak, the δ^7Li of lithium (solid squares) undergoes a fractionation of approximately 200‰. The δ^7Li evolves from ~100‰ heavier than the load in the pre-elution fraction to ~100‰ lighter in the post-elution fraction. This 200‰ fractionation of lithium during elution requires 100% recovery of lithium off the column to eliminate any column-induced fractionation. Data to the left (<7 g elution mass) and to the right (>10 g elution mass) of the elution peak contain too little lithium to obtain δ^7Li values. This figure is very similar to zeolite elution of lithium by Taylor and Urey.[11]

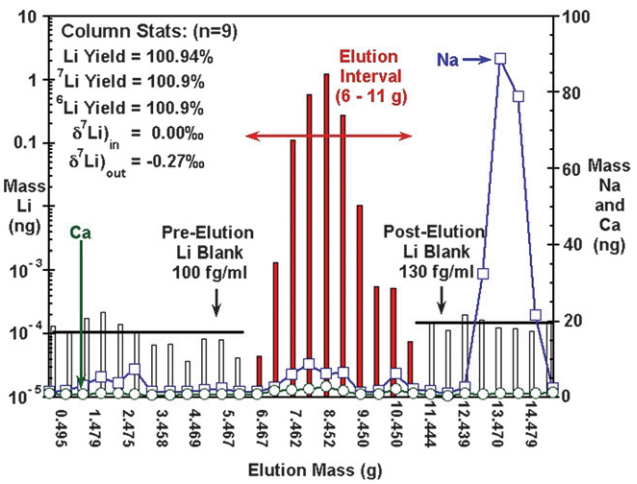

Fig. 1 Column separation of Li from Na and Ca. Average elution curve of lithium for matrix-matched (foraminifera composition) standards ($n = 9$) eluted through 2 ml of AG 50W-X8 ion exchange resin. All lithium was eluted within 6 ml to 11 ml elution fraction (solid bars). Pre-elution and post-elution lithium blanks (open bars) are approximately four orders of magnitude lower than the elution peak. Mass of sodium (open squares) and calcium (open circles) co-eluted with lithium fall far below ICP-MS matrix tolerance limit of this method. The low lithium blanks (<500 pg/ml) and high yield (99.98%–100.02%) off the columns confirms complete recovery of lithium.

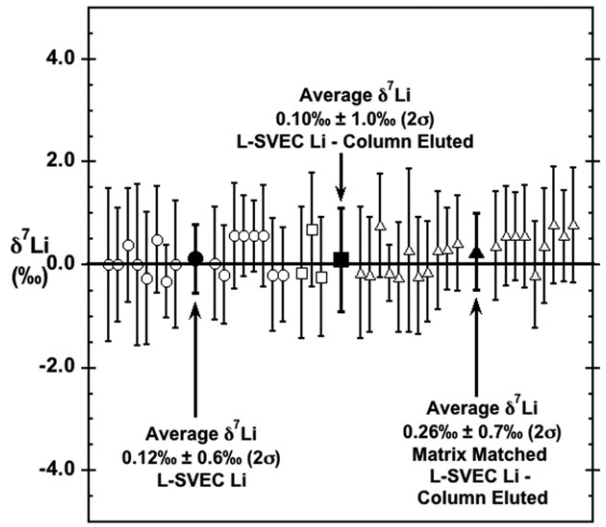

Fig. 3 δ^7Li of column eluted L-SVEC lithium standards and foram matrix-matched L-SVEC lithium standards. Replicate measurements of L-SVEC lithium standards (open circles), L-SVEC lithium standards subjected to column separation (open squares) and matrix-matched (foraminifera composition) L-SVEC lithium standards subjected to column separation (open triangles). The average values are given in solid symbols. Each open symbol represents an average of five separate analyses (quintuplicate) with 2σ external error. Note that isotopic composition of the lithium standards subjected to chromatographic separation is identical to those of the pure L-SVEC lithium standards. The absence of matrix effects during column separation signifies a constant lithium elution peak. The complete recovery of lithium off the column eliminates column-induced fractionation.

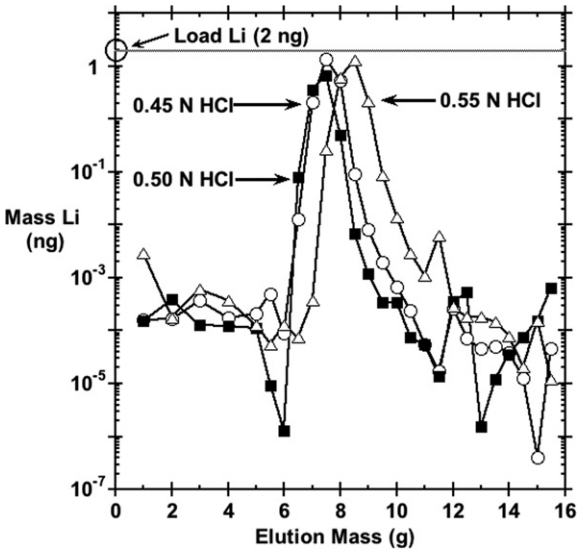

Fig. 4 Lithium elution of matrix-matched L-SVEC standard with 0.45 N, 0.50 N and 0.55 N HCl elution matrixes. Matrix-matched 2 ng of L-SVEC Lithium ($n = 3$) was eluted through 2 ml cation exchange column using 0.45 N (open circles), 0.50 N (solid squares) and 0.55 N (open triangle) HCl to qualitatively asses changes in lithium elution patterns due to ±10% change in elution acid strength. Two sigma external errors are smaller than symbols. Note the lithium elution peaks are identical for 0.45 N and 0.50 N HCl elution, falling within our lithium eluate-volume. The 0.55 N HCl elution peak is shifted by 0.5 ml towards the tailing edge and is well within our captured elution volume. Thus, no significant changes in lithium elution pattern is expected by increasing or decreasing the elution acid strength by 10% from 0.50 N HCl to 0.55 N HCl or 0.45 N HCl. The strength of the elution acid (0.50 N HCl) was carefully controlled to within <±2% to avoid lithium peak migration.

3 b. Isotope ratio determinations

Lithium isotope ratio determinations by Q-ICP-MS[21,22] have required large lithium mass (5–10 ng) and yield comparatively poor isotope ratio precision (±2.1‰). We have achieved an isotope ratio precision (2σ) of <±0.8‰ for L-SVEC standards to ±1.5‰ for foraminiferal samples with less than 0.2 ng of lithium. Existing TIMS and MC-ICP-MS methods are capable of achieving similar or better precision but require at least an order of magnitude more mass of lithium than the present study. For example, high precision TIMS methods[18] with comparable isotope precision (2σ, ±0.7‰) require 100 ng of lithium (500 times more than our method) and MC-ICP-MS methods with external precision (2σ) of ±0.2‰ to ±1.3‰ require 2 to 4 ng of lithium or more.[23,25] High precision TIMS and MC-ICP-MS methods both require ultra-clean matrix to eliminate matrix-induced mass bias. Our method has a higher tolerance limit for matrix elements Na^+ (~0.6 mol/mol of Li/Na) and Ca^{2+} (~20 μmol/mol of Li/Ca) and is comparatively more robust than either TIMS or MC-ICP-MS methods at low mass (0.1 to 0.2 ppb) of lithium concentrations.[18,24]

The quadrupole-ICP-MS is tuned to maximize lithium sensitivity and signal stability in cool plasma (600 W), soft extraction, with peak jumping mode. At very low plasma power, lithium is >99.97% ionized but plasma-based argon ionization in the central channel and other bulk plasma ions, such as oxides and doubly charged ($^{12}C^{2+}$ and $^{14}N^{2+}$) ion formation, are minimized. Moreover, in cool plasma conditions ionization of other matrix-based high first ionization potential interferences is also virtually eliminated.[23,24] Thus, in cool plasma, the lithium ions pass through the interface and ion lens system much more efficiently as they are not pushed to the outer region of the extracted ion beam by the presence of lots of plasma based or matrix based heavier ions. This phenomenon is called space charge repulsion and is the reason for the relatively low transmission of light elements in a normal (1500 W) hot plasma. The reduced space charge effect is the main reason for the very high ion transmission for lithium in cool plasma conditions. Moreover, by sampling in the cold outer region of the plasma, Na^+, K^+ and Ca^{2+} entry through the cones is minimized. Platinum cones and skimmers minimize drift and eliminate energy dispersive fringe fields minimizing the doubly charged ($^{12}C^{2+}$ and $^{14}N^{2+}$) and oxides. The Shield Torch (grounded plasma) and soft extraction (1st extraction lens −125 V and 2nd extraction lens −7 V) narrows the kinetic energy spread of light alkali elements which results in better focusing and less loss of lithium ion beam during transmission through ion optics. The chilled (2 °C) spray chamber limits H_2O based polyatomic oxide (LiO^+) and hydride (LiH^+) formation.

By keeping the sample introduction system and interface clean our lithium blanks (2% HNO_3) are <10 cps on $m/z = 6$ and <100 cps on $m/z = 7$. Typical ^{6}Li and ^{7}Li sensitivities are 0.9 million-cps/ppb-Li and 10 million-cps/ppb-Li, respectively (Table 5) and detection limits (3σ matrix blanks) are ~1 fg/ml and ~15 fg/ml for ^{6}Li and ^{7}Li respectively. The instrument is tuned at the

Table 5 Sensitivity, blank and detection limits[a]

Li isotope	Air blanks	Matrix blanks ($2\%HNO_3$)	Sensitivity (L-SVEC Li)	Detection limit (3σ blank)	Sensitivity – optimum working concentration range
^6Li	3 cps (0.3 fg/ml)	8 cps (0.9 fg/ml)	0.9×10^6 cps/ppb-$[Li]_{Total}$	~1 fg/ml (11 cps)	0.9×10^5 to 1.8×10^5 cps (0.1 ppb to 0.2 ppb)
^7Li	35 cps (3.5 fg/ml)	95 cps (9.5 fg/ml)	10×10^6 cps/ppb-$[Li]_{Total}$	~15 fg/ml (140 cps)	1.0×10^6 to 2.0×10^6 cps (0.1 ppb to 0.2 ppb)

[a] $[Li]_{Total}$ is total Li concentration of solution. Sensitivity in cps/ppb is for total Li concentration in solution not for concentration of individual isotopes.

beginning of each run. Lithium sensitivities for ^6Li and ^7Li, and δ^7Li calibrations are repeated at the beginning of each set of analyses. Typical values are given in Fig. 5.

By modifying the pulse mode detection limit and dead time correction, the isotope ratio response to increasing lithium concentration is invariant in the 0.05 ppb to 0.2 ppb concentration range (Fig. 5). However, during lithium analysis in pulse mode, at the upper-end of ^7Li detection range, for high ion count rates $\sim 2.2 \times 10^6$ cps approximately ~7% of the ^7Li ions reaching the detector are not counted. Large detector dead time, ~10% of acquisition time, is capable of causing concentration dependent instrumental mass bias in single collector Q-ICP-MS (data not shown). We avoid such concentration dependent mass bias by matching sample–standard concentrations, performing lithium-based dead time correction and by keeping the dead time less than <7% of the acquisition time.

All plasma source mass spectrometry suffers from instrumental mass bias caused by preferential extraction and transmission of heavier ions over lighter ions. Lithium-7 is ~16% heavier than ^6Li and consequently suffers less space charge effect and mutual repulsion of ions within the ion beam, caused by $^{40}Ar^+$, $^{14}N^+$ and $^{16}O^+$ in the plasma. This differential space charge effect on the two isotopes results in large instrumental mass bias (~100‰). Since lithium has only two isotopes and absence of any useable ions at $m/z < 6$ or >7, instrumental mass bias correction for lithium can only be done by external normalization also termed sample–standard bracketing.[23] Back to back analyses of L-SVEC lithium standards was done to measure instrumental drift (1‰–2‰ per h). The mass bias $\{^7Li/^6Li\}_{L\text{-}SVEC} \sim 13.40$ (~80‰) of our Q-ICP-MS is large but constant. To account for instrument drift and a large but constant mass bias, multiple short analytical runs bracketed by L-SVEC lithium standards are performed (Fig. 6). The external precision of the instrument ranges from ±0.64‰ to ±0.8‰ for L-SVEC standards, and 0.9‰ to 1.5‰ for natural samples.

A minimum of five replicates for each column-eluted sample is performed to produce statistically significant results. Samples are measured in blocks of five with concentration-matched standards used for bracketing. For each block an aliquot of the sample is analyzed, preceded and followed by bracketing lithium

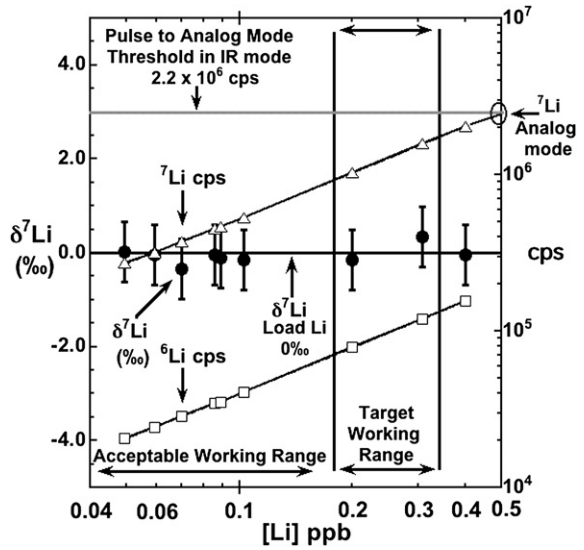

Fig. 5 ^6Li and ^7Li calibrations. Lithium isotope ratios (solid circles) of L-SVEC solutions with increasing lithium concentration (0.05 ppb to 0.2 ppb) with ^6Li (squares) and ^7Li (triangles) calibration. The lines through each set of squares (^6Li) and triangles (^7Li) are the calibration curves. Each data point represents an average of five replicates (quintuplicate) with 2σ external error (smaller than the symbols for ^6Li and ^7Li cps). Note the measured δ^7Li (‰) of L-SVEC standard is constant across 0.05 ppb to 0.4 ppb concentration range. The regression coefficients for both lithium isotope calibrations are ≥0.9999.

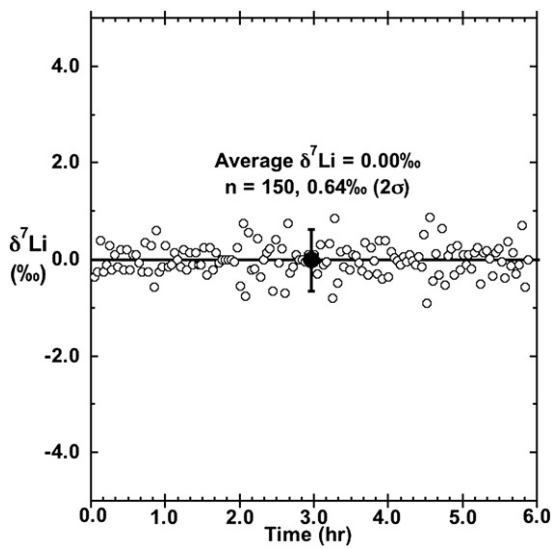

Fig. 6 Short-term instrument stability and precision of Li isotope ratio measurements (δ^7Li). Short-term instrumental stability determined by back-to-back runs of 0.1 ppb L-SVEC lithium standard in 2% HNO_3. The raw isotope ratios were normalized using averaged values from adjacent analyses mimicking standard–sample bracketing technique. Note the 2σ value of 150 individual analyses, performed over a 6 h period, is 0.6‰, identical to the instrumental limit of *Agilent* 7500*cs* Quadrupole ICP-MS.

standards. All lithium standards used for bracketing are eluted through the column. The duration of each of the sample analysis or bracketing standard run is 3 minutes/180 s (60 s uptake + 120 s acquisition). Thus for each block of sample run (standard–sample–standard) our total run time is 9 minutes. For a block of five (a complete sample run) the total run time is 45 minutes with 15 minutes (900 s) of sample analysis time. At 100 μl/min uptake rate and ~0.1 ppb total lithium concentration an entire block of sample run requires ~0.15 ng of total lithium.

Accurate lithium isotope ratio determination by ICP-MS is sensitive to the presence of matrix elements, especially in the cold plasma mode.[24] Variability in concentration of elements between sample matrix and standard can lead to unquantifiable instrumental mass bias (fractionation) resulting in erroneous isotope ratio values.[22–25] Samples from marine foraminifera have high concentrations of calcium, sodium, magnesium, potassium and strontium. Our instrumental sodium tolerance limit is ~0.6 mol/mol of Li/Na and that for total matrix sodium is 10 ppb Na. Similarly the calcium tolerance limit is ~20 μmol/mol of Li/Ca and that for total matrix calcium is 250 ppb Ca (see ESI).† Column purified samples with sodium or calcium concentrations above the instrumental threshold are discarded.

3 c. Seawater δ^7Li

In the open ocean, lithium is a conservative element, well mixed with uniform concentration and isotopic composition.[3,18,40] The average δ^7Li value of seawater is generally taken as 31.0‰ ± 0.5‰,[8] with reported values ranging from 29.3 ± 0.6‰[41] to 33.3 ± 1.2‰[3] (Table 6). This large range in published seawaer δ^7Li values may result from difference in column chemistry, mass spectrometric methods, and sample handling.[13] The accuracy and precision of our method was assessed by comparing measured seawater δ^7Li values to other published results.

The comparatively high lithium concentration of seawater ($[Li]_{Seawater}$ ~ 26 μmolar or ~175 ppb) and low mass requirement of present method (<0.2 ng) enables high precision isotope ratio determination with 1 to 2 μl of seawater. Five aliquots of 20 μl and 50 μl each of Sargasso Sea surface water were processed with 2 ml and 8 ml columns. The average ($n = 5$) δ^7Li values of 20 μl and 50 μl samples are 30.70 ± 0.39‰ and 30.80 ± 0.41‰, respectively (Fig. 7). The overall average ($n = 10$) of seawater δ^7Li by the present method, 30.75 ± 0.41‰, is identical to the average published value of 31.0 ± 0.5‰.[8] The absence of δ^7Li offset in seawater samples processed by different column methods (present study) as well as between this study and published values establishes the consistency and reproducibility of the methods.

Table 6 Reported δ^7Li values of seawater relative to L-SVEC

Author	δ^7Li Seawater	Instrument
You and Chan[18]	32.4 ± 2.6‰	TIMS
Chan and Edmond[3]	33.3 ± 1.2‰	TIMS
Moriguti and Nakamura[5]	30.0 ± 0.7‰	TIMS
James and Palmer[30]	32.5 ± 1.6‰	TIMS
Hall *et al.*[13]	33.0 ± 1.2‰	TIMS
Tomascak *et al.*[23]	31.8 ± 1.9‰	MC-ICP-MS
Nishio and Nakai[41]	29.3 ± 0.6‰	MC-ICP-MS
Bryant *et al.*[24]	31.0 ± 1.8‰	MC-ICP-MS
Jeffcoate *et al.*[25]	31.14 ± 0.2‰	MC-ICP-MS
Hall *et al.*[13]	29.6 ± 0.6‰	MC-ICP-MS
Hathorne and James[14]	31.03 ± 0.5‰	MC-ICP-MS
This study	30.75 ± 0.4‰	Q-ICP-MS

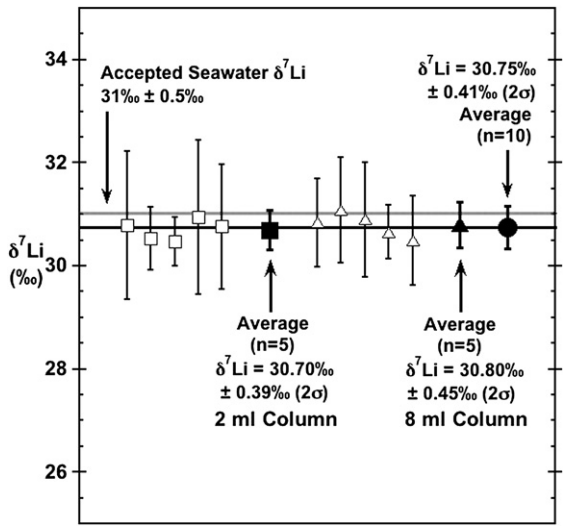

Fig. 7 Lithium isotopic composition (δ^7Li ‰) of Sargasso seawater. Analyses of Sargasso Sea surface water aliquots after chromatographic separation. Open squares represent 20 μl of seawater sample eluted through 2 ml cation exchange column (this method). Open triangles represent 50 μl of seawater sample eluted through 8 ml cation exchange column (scaled up method). The average δ^7Li value of samples processed through 2 ml column was 30.70 ± 0.39‰ (solid square) and average δ^7Li value of samples processed through 8 ml column was 30.80 ± 0.45‰ (solid triangle). The total average ($n = 10$) of seawater analyses yields a δ^7Li value of 30.75 ± 0.41‰. The average seawater δ^7Li value determined by two different column methods and load volumes are identical. Also the δ^7Li value of seawater determined in this study (30.75 ± 0.41‰) is comparable to accepted δ^7Li value of seawater (31.0 ± 0.5‰).[8]

3 d. δ^7Li of planktonic foraminifera

The lithium isotope ratio of seawater (δ^7Li) incorporated into planktonic foraminiferal shells has the potential to record changes in seawater chemistry, help unravel the changing factors that drive variations of oceanic silica mass balances linked to continental and sea floor/hydrothermal weathering. To establish the validity of foraminifera as a recorder of seawater δ^7Li, we measured lithium isotope ratios and Li/Ca, Mg/Ca, Mn/Ca, V/Ca, Sr/Ca and Ba/Ca in cleaned core top foraminiferal shells from Caribbean Sea and Gulf of Mexico sediment cores from (a) nine individual species; (b) size fractions of the same species; and (c) bulk samples of different size fractions. Samples were chemically cleaned with a reductive–oxidative–reductive (R–O–R) cleaning sequence.[38,39] The high precision (±0.9‰ to ±1.5, 2σ), low blank (1.0 ± 0.5 pg) and low lithium mass requirement (<0.2 ng/quintuplicate analyses) of this method allows δ^7Li determination using <1.0 mg of foraminifera. Species-specific δ^7Li analyses of coretop (modern day) *Orbulina universa* (>300μm) from both the Caribbean Sea (30.72 ± 1.43‰, $n = 5$) and the Gulf of Mexico (30.16 ± 1.37‰, $n = 4$) yield δ^7Li values identical to modern seawater (30.75 ± 0.41‰, $n = 10$) (Fig. 8).

Table 7 Comparison of published mass spectrometric methods for lithium isotope ratio determination in foraminifera

Instrument	Author	Mass Li	Foram Wt.	Precision (2σ)	Elution matrix	Blanks
TIMS	You and Chan[18]	100 ng	100 mg	±0.7–2.5‰	0.2 M HCl	100–190 pg
TIMS	Hall *et al.*[13]	2–5 ng	2–5 mg	±1.2‰	0.5M HCl	57 ±13 pg
MC-ICP-MS	Hall *et al.*[13]	5 ng	5 mg	±1.1‰	1 M HNO_3 in 80% Methanol	200 pg
MC-ICP-MS	Hathorne and James[14]	4 ng	4 mg	±1.0‰	0.2 M HCl	12 pg
Q-ICP-MS	Kosler *et al.*[22]	5–10 ng	5–10 mg	±2.1‰	1 M HNO_3 in 80% Methanol	120 pg
Q-ICP-MS	This Study	<0.2 ng	0.2 mg	±0.8–1.5‰	0.5 M HCl	<1.5 pg

Moreover, the δ^7Li values of two size fractions of different species (*e.g. G. triloba*, *G. menardii*, *G. ruber*) and bulk samples are identical, within analytical uncertainties, to seawater δ^7Li.

Samples with high Mn/Ca ratio (>20 μmol/mol) produce δ^7Li values significantly lower (4‰–6‰) than seawater, emphasizing the importance of multiple oxidative–reductive cleaning of forams to remove metal oxide deposits. For this study, samples with Mn/Ca values >20 μmol/mol were rejected. No significant correlation was observed between δ^7Li and Li/Ca ratio of foram samples, suggesting that the lithium isotope ratio of a foram is independent of its lithium concentration.

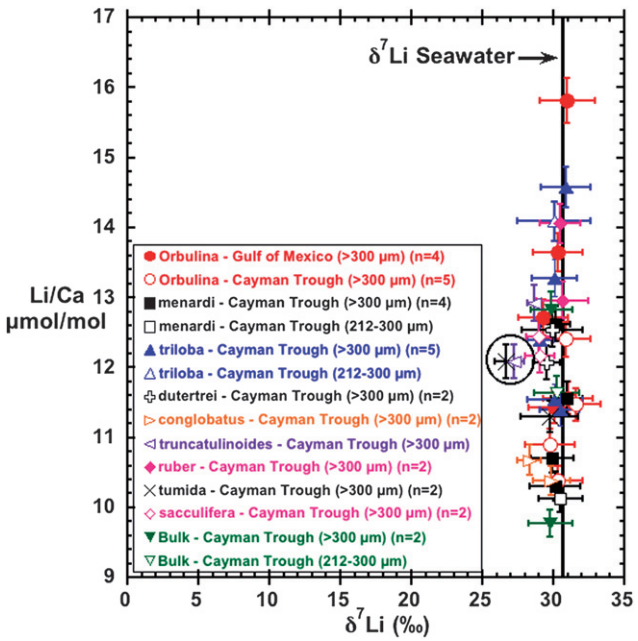

Fig. 8 Li/Ca (μmol/mol) and δ^7Li (‰) of coretop foraminiferal shells from Gulf of Mexico and Caymen Trough sediments. Lithium isotope ratio (δ^7Li ‰) and Li/Ca (μmol/mol) measurements of planktonic foraminiferal shells collected from box-core sediments in the Gulf of Mexico and the Caribbean Sea (Cayman Trough). Each data point represents five replicate analyses with 2σ errors. All foraminiferal shells were subjected to chemical cleaning to remove metal oxide coatings and organic matters (see text for discussion). *Orbulina universa* (open and solid circles) samples from both sites produced identical δ^7Li values. Also two size fractions, >300 μm and 212 to 300 μm, of *G. menardi* (solid and open squares), *G. triloba* (solid and open up-triangles) and bulk (solid and open down-triangles) samples from Cayman Trough produced δ^7Li values identical, within error, to seawater. *G. conglobatus* (right-triangle), *G. truncatulinoides* (left-triangle) and *G. tumida* (cross) samples consistently produced δ^7Li values lower than seawater. Note that the δ^7Li of the two size fractions of multiple species and bulk samples are within the range of seawater value and the absence of any correlation between Li/Ca ratio and δ^7Li. Results indicate that reconstruction of the long-term δ^7Li history of seawater can be done by using both species-specific analyses and by bulk sample analyses irrespective of size fraction.

The results from our δ^7Li and Li/Ca analyses of extensively chemically cleaned coretop foraminifera samples are in good agreement with other studies where forams were exhaustively cleaned.[13,14] The range of δ^7Li values of cleaned coretop *Orbulina univera* reported by Hall *et al.*[13] are 31.39‰ ± 2.36‰ (2σ, $n = 8$) for TIMS analyses and 28.33‰ ± 1.80‰ (2σ, $n = 7$) for MC-ICP-MS analyses. The approximately 2‰ differences in δ^7Li values for samples from the same site is attributed to the difference in column chemistry preceding the two measurements. However, Hathorne and James[14] reported more consistent δ^7Li values for coretop *Orbulina univera*, 31.07‰ ± 0.7‰ ($n = 3$, MC-ICP-MS). The δ^7Li values of cleaned coretop foraminifera from the same study (*sacculifera*, 29.3‰; *dutertrei*, 28.4‰; *conglobatus*, 29.0‰; *cultrata*, 29.75‰ and *truncatulinoides*, 27.3‰) are consistent, within analytical uncertainties, with the present study (Fig. 8). Moreover the range of Li/Ca values reported in the present study (9.77–15.81 μmol/mol) is consistent with the values reported by Hall *et al.* (9.3–15.0 μmol/mol) and Hathorne and James. (10.4–14.5 μmol/mol).

4. Conclusions

We present here a high precision (<±0.8‰, 2σ), low blank (1.0 ± 0.5 pg) and low mass consumption (<0.2 ng/quintuplicate analyses) lithium isotope ratio method by quadrupole ICP-MS. A new lithium separation method with quantitative recovery, complete separation from matrix elements and no column-induced fractionation was also developed. This technique is optimized for natural carbonate samples with 1 to 2 ppm of lithium and can also be applied to seawater samples. This allows for high precision lithium isotope ratio determination of lithium-limited samples.

Seawater lithium, average δ^7Li 30.75 ± 0.4‰ (2σ, n = 10), is comparable to published data (~31.0 ± 0.5‰). Measurements of coretop foraminifera (*O. universa*, *G. triloba*, *etc.*) δ^7Li establishes foraminifera as a faithful recorder of modern day seawater δ^7Li and are in good agreement with published data. Future applications include creating a long-term (0 Ma to 65 Ma) δ^7Li evolution history of seawater as recorded by planktonic foraminifera to elucidate changes in seawater chemistry and the factors driving variations of oceanic silica mass balances linked to continental and sea floor/hydrothermal weathering. However, the method we have developed can be applied to numerous other problems requiring the precise determination of lithium isotopic composition in geochemistry, cosmochemistry or forensic sciences.

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