

Re-examination of the use of seawater $\delta^7\text{Li}$ as a weathering proxy: a core-top study

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ABSTRACT

Lithium isotopic ratios ($\delta^7\text{Li}$) have historically been used as a proxy for silicate weathering intensity, one of the key surface processes that drive the carbon cycle. Because of lithium's long residence time in the ocean (~1.2 Ma), it was expected that foraminiferal $\delta^7\text{Li}$ recorded global seawater values. However, recent research on foraminiferal $\delta^7\text{Li}$ suggests that as lithium is incorporated into foraminifera, it may be fractionated according to vital effects and variations in environmental parameters like total dissolved inorganic carbon (DIC). This study explores variations in foraminiferal $\delta^7\text{Li}$ in the modern, finding that $\delta^7\text{Li}$ varies between species as well as with environmental parameters like temperature, DIC, and carbonate saturation state. These variations lead to a reinterpretation of the foraminiferal $\delta^7\text{Li}$ record as potentially long-term variation of species assemblage and environmental carbonate system variation rather than strictly following the global weathering signal. This allows for more detailed interpretation of periods of high $\delta^7\text{Li}$ variability (including the negative K-Pg $\delta^7\text{Li}$ excursion) in terms of rapid change in carbonate system parameters and species assemblage turnover.

INTRODUCTION

CARBON DIOXIDE, SILICATE WEATHERING, AND LITHIUM

Since the days of Arrhenius (1896), carbon dioxide has been recognized as being potentially crucial to the dynamics of the earth system on geological timescales. Fluctuations in carbon dioxide over time imply the past existence a wide range of potential climate states, from the hothouse climate like the relatively recent Paleocene-Eocene Thermal Maximum to the ancient Neoproterozoic world of Snowball Earth. As one of the main drivers for major shifts in Earth's climate over the Phanerozoic, understanding the processes that control CO₂ levels will be crucial to understanding what anthropogenic global warming will mean for environmental change of all kinds.

Atmospheric CO₂ levels are controlled by a variety of processes. One of these is the silicate weathering feedback, in which rising CO₂ levels increase global temperature, which then increases the rate of silicate weathering (i.e. CO₂ drawdown) and thus reduces CO₂ levels (e.g. Berner et al., 1983). The silicate weathering feedback is presumed to be historically the most important terrestrial sink for CO₂ (e.g. Berner et al., 1983; Zeebe, 2012). For this reason, studying the rates and extents of silicate weathering throughout the record is appealing as a way of understanding long-term stabilization of atmospheric CO₂ levels (Berner et al. 1983; Caldeira 1995).

Multiple isotope systems have been proposed to track different aspects of silicate weathering. The seawater Sr isotopic ratio has been interpreted to be dependent on the weathering of high-⁸⁷Sr/⁸⁶Sr silicate rocks (ratio>0.710) and the weathering of low-⁸⁷Sr/⁸⁶Sr carbonates (ratio<0.709) (Palmer and Edmond, 1992). By examining the ⁸⁷Sr/⁸⁶Sr ratio in the marine sedimentary record, it is possible to tease out the relative importances of silicate and carbonate weathering over time. However, the quantitative nature of strontium isotope interpretation is underdeveloped due to the confounding complexities in strontium isotope ratios of source rock, the decay of natural ⁸⁷Rb into ⁸⁷Sr, and the various sources that contain and also contribute to river and seawater strontium (Palmer and Edmond, 1992; Misra and Froelich et al., 2012). Similar issues exist for the osmium system, in which weathering-derived radiogenic ¹⁸⁷Os and mantle-derived unradiogenic ¹⁸⁸Os contribute to the seawater value (Peucker-Ehrenbrink and

Ravizza, 2000). Recent research suggests that the Cenozoic records of both of these isotopic systems have been largely influenced by exposure of radiogenic pockets in the Himalayas (Myrow et al., 2015), making the use of the strontium and osmium isotopic systems less robust for tracking silicate weathering.

The lithium isotope system has been proposed as a complement to the Sr and Os systems for tracking aspects of silicate weathering (Misra and Froelich, 2012). It has been observed that lithium isotopic ratios vary with weathering intensity; in weathering-limited regimes, riverine lithium isotopic values are lighter than in transport-limited regimes (Huh et al., 2001). When weathering of aluminosilicate source material is less extensive, i.e. incongruent, there may be secondary clay formation in which Li^+ may substitute for Mg^{2+} or with Mg^{2+} for Al^{3+} (Vigier et al., 2008; Huh et al., 1998). In a study of major rivers around the world, Huh et al. (1998) found that [Li] in the dissolved load was frequently heavier than [Li] in the suspended load. This could be interpretable in two ways: either there is fractionation of Li as it is incorporated into the suspended load, or the suspended and dissolved loads represent different source materials in the catchment. Kisakurek et al. (2005) found that $\delta^7\text{Li}$ did not differ between many Himalayan catchments, even between silicate- and carbonate-dominated areas, supporting the importance of the fractionation as Li is incorporated into clays. Huh et al. (2001) also showed that the weathering-limited Andean tributaries of the Orinoco River had heavier $\delta^7\text{Li}$ values than the transport-limited tributaries on the Guayara Shield. If the global riverine lithium input follows these studies, then the global seawater $\delta^7\text{Li}$ values should be representative of the weighted average of the individual inputs.

Thus, the global seawater $\delta^7\text{Li}$ value should represent the general intensity of weathering, and a record of $\delta^7\text{Li}$ would be expected to represent temporal variation in weathering intensity. Lithium in the oceans today is fairly homogenous at around $26\mu\text{M}$ and $\delta^7\text{Li}=31\text{‰}$ (Chan and Edmond, 1988; Broecker and Peng, 1982). This is because lithium has a long residence time of about 1.2-1.5 Ma (Misra and Froelich, 2012; Huh et al., 1998), which is much longer than the oceanic mixing time of about 1000 years, and as such the ocean is very well-mixed with respect to lithium. The large reservoir size relative to the input and output fluxes means it is unlikely that the changes in a single source could alter the $\delta^7\text{Li}$ record on a short timescale, so the seawater $\delta^7\text{Li}$ record likely represents a global value rather than one with local bias.

Several relatively recent publications have constructed $\delta^7\text{Li}$ records to explore global weathering rates and intensities during the Cenozoic (Hathorne and James, 2006; Misra and Froelich, 2012; von Strandmann et al., 2013). Hathorne and James (2006) use Li/Ca as a proxy for silicate weathering rate, since a higher marine Li/Ca ratios should correspond to more weathering of lithium-containing rocks (i.e. silicate minerals). Taking foraminifera from two different sites, they built an 18 million year record of Li/Ca and $\delta^7\text{Li}$. This was the second Cenozoic lithium isotope record to be published in the literature following Hoefs and Sywall (1997). However, Hathorne and James improved the methodology by cleaning the foraminifera and controlling for species. Using their record of $\delta^7\text{Li}$, they observed a correspondence in trends of Li (weathering rate), $\delta^7\text{Li}$ (weathering regime), and $p\text{CO}_2$, such that an increase in Li and a decrease in $\delta^7\text{Li}$ corresponded to an increase in $p\text{CO}_2$. The authors suggested that the rise in $p\text{CO}_2$ may have been due to the decrease of overall weathering and weathering intensity, justifying future use of lithium as a tracer for weathering intensity.

Most recently, Misra and Froelich (2012) produced a record of $\delta^7\text{Li}$ since 68 Ma (Figure 1). Using a box model of lithium fluxes and corresponding isotopic values, they inferred that large changes in the lithium isotopic value of the oceans (from the $\delta^7\text{Li}$ of foraminifera) must have been due to large changes in the extent of silicate weathering. They point to the $\delta^7\text{Li}$ minimum corresponding to the PETM, when high $p\text{CO}_2$ and hot temperatures would have driven more congruent silicate weathering. They also note that the cooling following the PETM is associated with a rise in $\delta^7\text{Li}$, meaning less extensive and more incongruent weathering.

However, in several parts of the Misra and Froelich (2012) the large variability on short time scales despite the very long residence time of lithium of approximately 1.2 Ma. Vigier et al. (2015) point out that in four separate short time periods in the most recent 18 Ma of the Misra and Froelich (2012) record, $\delta^7\text{Li}$ variation is too large on short timescales be explained by changes in source/sink fluxes (like weathering), the importance of which would be dictated by the residence time of lithium. The most visible of these periods of short-term variability is the negative excursion of $\delta^7\text{Li}$ values across the K-Pg. Because the sheer magnitude of the K-Pg negative $\delta^7\text{Li}$ excursion, Misra and Froelich (2012) tentatively suggest “massive continental denudation and acid rain weathering” following the impact of the Chicxulub bolide, but the exact cause of the excursion is left unexplained.

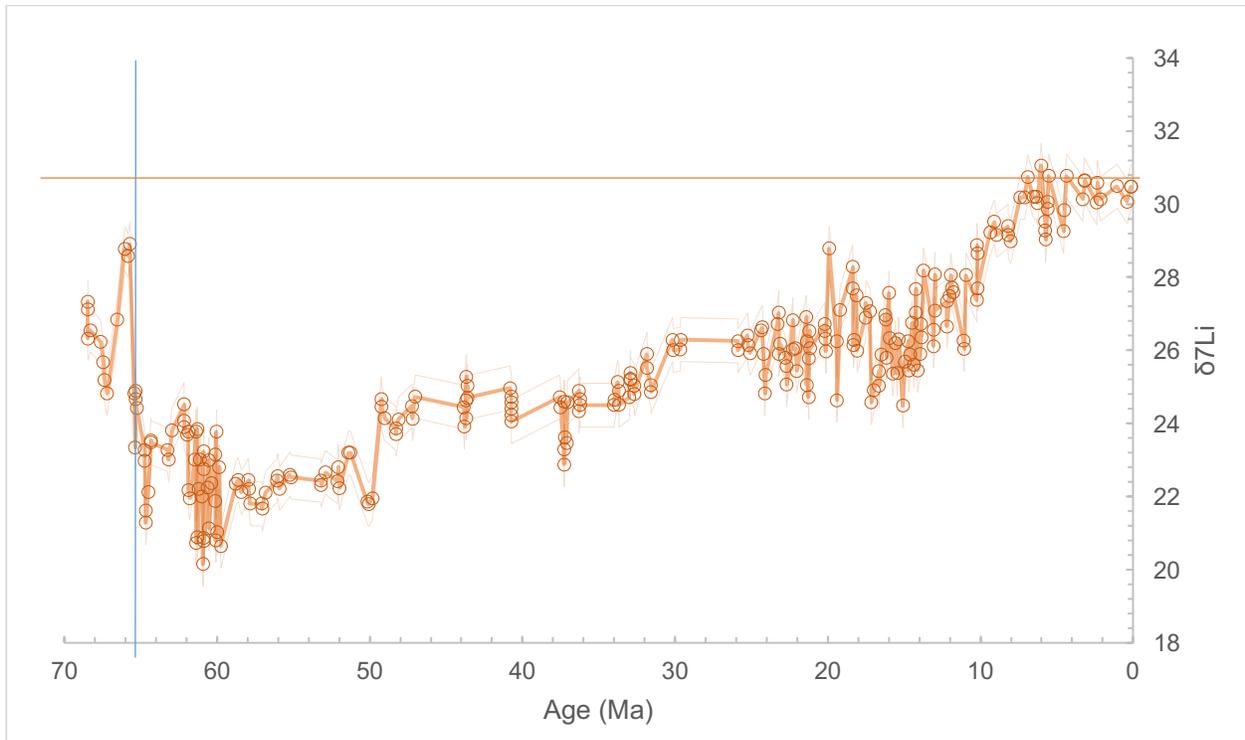


Figure 1: lithium isotope record across the Cenozoic. Blue line indicates the K-Pg boundary; orange straight line indicates approximate modern seawater values. Adapted from Misra and Froelich (2012). Error represents the 2σ variation of the average S.D. of all foraminiferal measurements as used by the original study ($2\sigma = \pm 0.55\text{‰}$).

FORAMINIFERAL VARIATION IN $\delta^7\text{Li}$

One explanation of the short-term variation in $\delta^7\text{Li}$ has been proposed in recent literature. Vigier et al. (2015) controlled for all three of temperature, pH, and DIC in a lab culture experiment using *Amphistegina*, a symbiont-bearing benthic genus of foraminifera. In growing these foraminifera, Vigier et al. found a very strong correlation ($r^2 = 0.92$) between the DIC of the seawater solution and the incorporated $\delta^7\text{Li}$ (Figure 2). According to the trends established by Vigier et al., an increase in

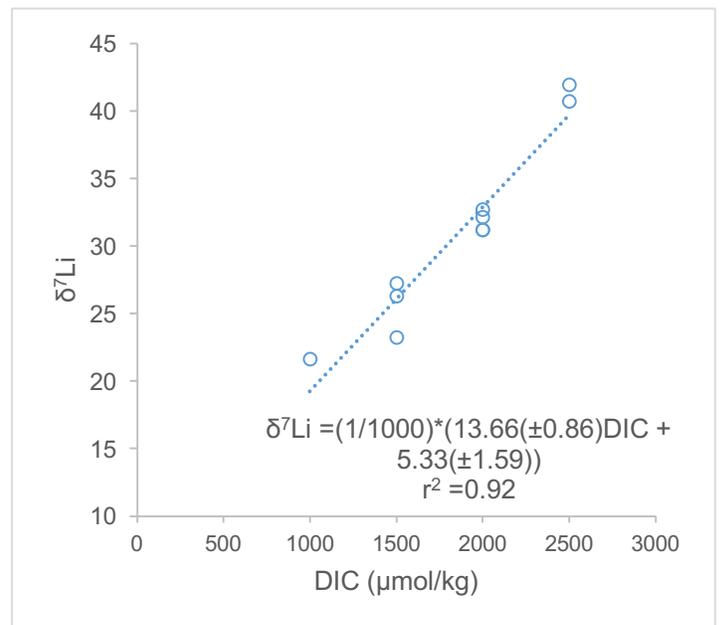


Figure 2: correlation and data for variable-DIC culture experiment. Adapted from Vigier et al. (2015).

DIC correlated to smaller Li/Ca and larger $\delta^7\text{Li}$. They speculated on a tentative mechanism in which proton pumps send protons out in exchange for Na^+ in, and because of similar chemical behavior of Na^+ and Li^+ , Li^+ would be pumped in as well. This would imply that at higher DIC values there would be less of a need to alter pH, meaning less import of Na^+ and therefore less Li^+ . At lower DIC, with more transport of lithium, there would be a larger pool of lithium, allowing fractionation of Li in favor of the lighter isotope. This mechanism is supported but not proven by the data, requiring further research (Vigier et al., 2015).

Regardless of the mechanism, that study suggests that lithium isotopes may not in fact faithfully record the global weathering signal; rather, $\delta^7\text{Li}$ values may be subject to short-term variation. Using the linear regression equation provided by Vigier et al. (2015), we plotted the data of Misra and Froelich (2012) as DIC (Figure 3) with other DIC historical estimates as compiled by the study of Mesozoic-Cenozoic carbonate ion concentration in Tyrrell and Zeebe (2004). The different DIC curves are taken from the analysis by Tyrrell and Zeebe (2004) of their own compilation of other published carbonate system parameter records. The Misra and Froelich (2012) record reinterpreted as DIC values is well within DIC record estimates. This is partly due to the fact that the DIC estimates are so varied, especially past 20 Ma. However, the reinterpreted record within the last 20 Ma is comparable to the DIC estimates. If the variation in the $\delta^7\text{Li}$ record can be attributed to environmental factors, then perhaps lithium cannot be relied on as a proxy for weathering only.

This may also shed light onto the negative excursion of $\delta^7\text{Li}$ across the K-Pg, perhaps due to the various environmental changes associated with the K-Pg mass extinction. Using the regression line created by Vigier et al. (2015), the excursion of about 5‰ could be interpreted as being a decrease in global or local DIC of about 400 $\mu\text{mol/kg}$, more plausible on a hundred-thousand-year timescale than significantly input/output fluxes and their isotopic deflections. It is likely that foraminiferal $\delta^7\text{Li}$ does record oceanic values, but it may also be confounded by short-term variation in local environmental variables. The potential for variation in foraminiferal incorporation of $\delta^7\text{Li}$ is the focus of this study.

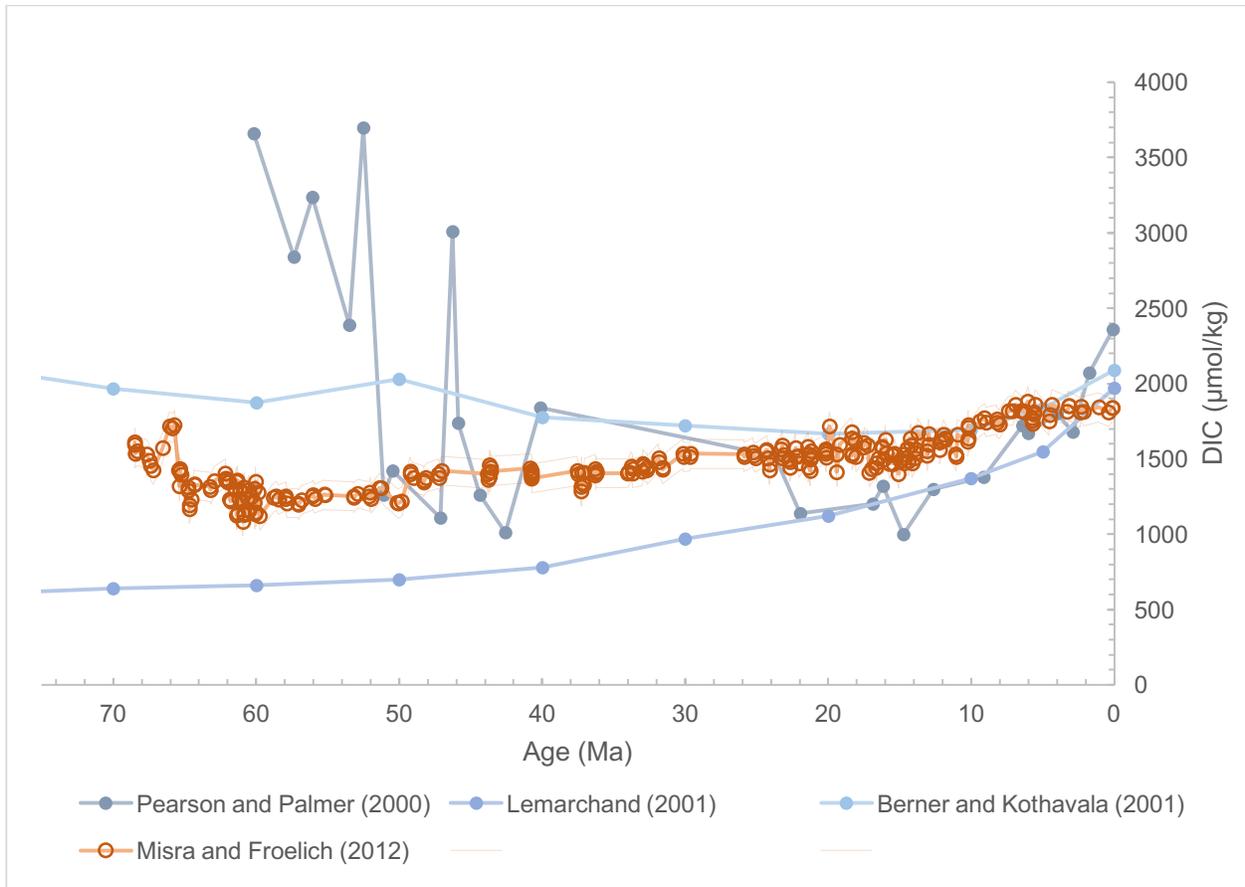


Figure 3: Misra and Froelich (2012) data curve reinterpreted as DIC following the equation in Vigier et al. (2015). DIC record estimates are taken from Tyrrell and Zeebe (2004).

$\delta^7\text{Li}$ AND THE CARBONATE SYSTEM

DIC is one of many parameters in the carbonate system, the set of equilibrium equations that determine speciation of carbon dioxide and other forms of inorganic carbon. On timescales of about one thousand years, i.e. the mixing time of the ocean, marine absorption and release of carbon dioxide is very significant (e.g. Zeebe 2012), and the general chemistry of carbon dioxide and inorganic carbon on the Earth's surface is largely governed by exchange between the atmosphere and the ocean. As atmospheric carbon dioxide concentrations shifted over Earth's history, the state of the marine geochemical carbonate system has changed significantly as well.

If foraminiferal $\delta^7\text{Li}$ tracks DIC, then perhaps it can be used in this aspect of studying the carbon cycle.

Shifts in carbon dioxide in the ocean has many implications for marine chemical balances. One direct effect is on pH; an increase in carbon dioxide allows creation of carbonic acid, which releases protons into solution, and a decrease does the opposite. Carbon dioxide also affects the ability of calcareous organisms to make shells, with more inorganic carbon present allowing more ease of shell formation. The presence of carbon dioxide in the atmosphere affects global temperatures which also itself alters the concentration of carbon dioxide in the ocean.

The marine carbonate system is fundamental to understanding ancient ocean environments from a geochemical perspective. Many variables included in the carbonate system are crucial to widely varying aspects of paleoenvironmental study, from the use of atmospheric $p\text{CO}_2$ levels to reconstruct global temperatures to the use of pH and $[\text{CO}_3^{2-}]$ to understand carbonate saturation state. Many issues, including global warming and ocean acidification, are not limited to the geologic record but affect the modern ocean as well. Unraveling how past marine chemistry evolved over time is fundamental to analyzing the marine geochemical system today.

Because of the various forms that carbon dioxide can take in solution, the marine carbonate system is far more complex than the atmospheric one. The three main forms of aqueous inorganic carbon are aqueous carbon dioxide ($\text{CO}_{2(\text{aq})}$), bicarbonate ion (HCO_3^-), and (CO_3^{2-}). Because aqueous carbon dioxide is in equilibrium with carbonic acid (H_2CO_3 , a small percentage of the total), the two will be subsequently grouped together following Zeebe (2012) into the variable $[\text{CO}_2]$. $[\text{CO}_2]$, $[\text{HCO}_3^-]$, and $[\text{CO}_3^{2-}]$ together make up the four forms of carbon dioxide in water. The distribution of these components within the system is also determined by three other factors: pH ($=-\log([\text{H}^+])$), total alkalinity (TA), and total dissolved inorganic carbon (DIC). TA is a measure of how much acid the given solution can neutralize, and it is functionally the sum of the weak bases in solution (see below). Total dissolved inorganic carbon is known by many names, including TCO_2 and ΣCO_2 , and it is the sum of all inorganic carbon species in solution (see below). The chemical system of different states of inorganic carbon in the ocean can be determined by a series of equilibrium equations adapted from Zeebe (2012) as follows:

The conversion of $\text{CO}_{2(\text{g})}$ in solution to $\text{CO}_{2(\text{aq})}$: $\text{CO}_{2(\text{g})} \leftrightarrow \text{CO}_{2(\text{aq})}$

The conversion of CO _{2(aq)} to carbonic acid:	$\text{H}_2\text{O} + \text{CO}_{2(\text{aq})} \leftrightarrow \text{H}_2\text{CO}_3$
The dissociation of carbonic acid:	$\text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+$ (governed by K ₁)
The dissociation of bicarbonate:	$\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$ (governed by K ₂)
The definition of DIC:	$\text{DIC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$
The definition of total alkalinity:	$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+] + \text{minor compounds.}$

The carbonate system can be thought of in terms of four variables: *p*CO₂, TA, pH, DIC (Dickson et al., 2007). The system of equations and the interrelation of these terms is such that there are only two degrees of freedom (Tyrrell and Zeebe, 2004), and therefore only two of these four parameters are needed to constrain all the variables of the entire system for a given temperature, salinity, and pressure (Zeebe, 2012; Dickson et al., 2007).

In an effort to constrain the carbonate system, it is crucial to find proxies for these different parameters. Foraminiferal boron ($\delta^{11}\text{B}$) as a pH proxy has been the focus of many recent studies (e.g. Hennehan et al., 2013). Because of the pH-dependent speciation of boron between B(OH)₄⁻ and B(OH)₃ and the fractionation in boron as it converts from one form to the other, then the $\delta^{11}\text{B}$ of B(OH)₄⁻ incorporated in foraminiferal calcite should directly correspond to pH. While in the past, the reliability of the boron proxy has been debated (e.g. Pagani et al., 2005; Hönisch et al., 2007), many of the issues in the boron proxy method have been improved in recent years. Analytical uncertainties in boron isotope measurements were improved with MC-ICP-MS in Foster (2008). Uncertainties in the boron fractionation factor were improved through empirical study in Klochko et al. (2006). Interspecific differences in isotopic values has also been studied and further constrained (Hennehan et al., 2013). Rae et al. (2011) applied improvements in MC-ICP-MS analysis of boron to benthic foraminifera, showing high predictability of pH through boron isotopes and the potential for future application to the record.

Because one parameter is not enough to constrain the carbonate system, the single-proxy method for reconstructing past climate is incomplete. Frequently, a second parameter is estimated (Henehan et al., 2013; Tyrrell and Zeebe, 2004), but the estimation of this second parameter introduces error. However, once the second degree of freedom is constrained with a more high-resolution proxy, then the system may be fully understood. The power of a two-proxy method partly motivates this study of the potential of the lithium isotopic system. Several factors come into picking a suitable proxy. For example, the proxy must represent (or be constrained to represent) a single parameter of the carbonate system, the proxy should be high resolution, and the proxy must be reliable over long periods of time. In Vigier et al. (2015), $\delta^7\text{Li}$ did not vary with temperature or pH, only varying with DIC. If $\delta^7\text{Li}$ can be used as a DIC proxy following that study, then the $\delta^7\text{Li}$ record will be reasonably sensitive to DIC changes; for each per mil variation in $\delta^7\text{Li}$ comes 80 $\mu\text{mol/kg}$ in DIC. For comparison, the Misra and Froelich (2012) record has a 9‰ increase in $\delta^7\text{Li}$ from the Paleocene to the present. In terms of DIC, this is significant variation in oceanic terms (the modern varies from 1800 to 2400 $\mu\text{mol/kg}$ DIC; Vigier et al., 2015).

If lithium is a proxy for DIC or another variable representing the local environment, it should also be recording some weathering signal since the seawater $\delta^7\text{Li}$ value (without vital effects) is likely weathering-driven (Misra and Froelich, 2012). For variation in the recent past, i.e. within one residence time of lithium (e.g. ~ 1.2 Ma to present), the DIC reconstructed from $\delta^7\text{Li}$ and pH reconstructed from $\delta^{11}\text{B}$ may be robust enough to constrain the carbonate system. Past 1.2 Ma, the weathering-driven variation in seawater $\delta^7\text{Li}$ values must be taken into consideration. If another variable can be found to be strictly a weathering proxy, then lithium and boron isotopes would be able to constrain the carbonate system throughout the Cenozoic. The converse is also true: if $\delta^7\text{Li}$ responds to DIC and another proxy is found for DIC, then the carbonate system may be constrained along with the power of $\delta^7\text{Li}$ as a silicate weathering intensity proxy.

Further complicating the $\delta^7\text{Li}$ record, DIC is expected to increase across the K-Pg boundary based on LOSCAR carbonate system models (Henehan et al., 2016; Zeebe et al., 2008). An increase in DIC would cause an increase in foraminiferal $\delta^7\text{Li}$, the opposite of what is seen in the Misra and Froelich (2012) curve. Vigier et al. (2015) have shown the potential for environmental influences to affect foraminiferal $\delta^7\text{Li}$ uptake, and as such this study will expand

beyond studies of only DIC. There are two main implications for this environmental variation. Firstly, the temporal variation in lithium isotopes cannot be interpreted as only weathering-related. Secondly, lithium isotopes may actually work as a proxy of other environmental variables. The potential for $\delta^7\text{Li}$ as a DIC proxy was proposed in Vigier et al. (2015) based on lab culture experiments, but it is unclear if lab cultures correspond to scenarios in practice. In this study we test both assertions by performing an analysis of coretop foraminifera from around the world, examining the relationship between foraminiferal $\delta^7\text{Li}$ and the carbonate system.

METHODS

Foraminifera were picked from the top of 15 cores selected for a wide range of expected DIC (Table 1) in an effort to expand on the results of Vigier et al. (2015). The DIC measurements were taken from the database of Takahashi et al. (2009), which constrains the entire carbonate system for more than three million points across the global ocean. Using these values for specific latitudes and longitudes, carbonate system parameters were constrained according to the methodology of Henehan et al. (2013) using `co2sys.m` (Van Heuven et al., 2011). The values for the surface ocean carbonate system parameters for each core were then approximated using interpolation of up to four data points from the database. Coretop samples were sieved to discrete size fractions between 212 μm to 500 μm in hole diameter. Particular emphasis was placed on picking *Globigerinoides ruber* as these foraminifera live in a narrowly constrained depth range such that vertical DIC gradients would not need to be constrained. Three sets of white and eight sets of mixed pink/white *G. ruber* were picked with this objective in mind. In order to observe larger trends and species effects, eight samples of *Orbulina universa*, four samples of *Globigerina bulloides*, and one sample of *Neogloboquadrina pachyderma* were picked. For *G. ruber*, *O. universa*, and *G. bulloides*, multiple size fractions were picked to observe any size/"growth" effects.

Sample number	Core name	Depth	Latitude (°)	Longitude (°)	Species	Size fraction	Temp. (°C)	Salinity (psu)	DIC (μmol/kg)
1	MC420	0-0.5cm	17.04	-66	<i>ruber</i> (pink)	250-300	27.6	35.5	1926.0
2	MC420	0-0.5cm	17.04	-66	<i>ruber</i> (pink)	300-355	27.6	35.5	1926.0
3	MC497	0-0.5cm	23.53	63.31	<i>ruber</i> (white)	250-300	26.9	36.4	1970.2
4	MC497	0-0.5cm	23.53	63.31	<i>ruber</i> (white)	300-355	26.9	36.4	1970.2
5	MC497	0-0.5cm	23.53	63.31	<i>bulloides</i>	250-300	26.9	36.4	1970.2
6	TAN1106/50-N7	tow	-49.69	165.07	<i>universa</i>	300-355	9.0	34.4	2100.9
7	MC577-17b	0-0.5cm	45.57	-17.40	<i>universa</i>	>355	15.3	35.7	2037.8
8	CH75/2/31/21	0-2cm	13	-45.96	<i>ruber</i> (pink)	250-300	26.7	36.0	1943.0
9	CH75/2/31/21	0-2cm	13	-45.96	<i>ruber</i> (pink)	300-355	26.7	36.0	1943.0
10	CH75/2/31/21	0-2cm	13	-45.96	<i>ruber</i> (pink)	>355	26.7	36.0	1943.0
11	All/42/17/16	0-2cm	19.56	-46.13	<i>ruber</i> (pink)	250-300	26.0	36.9	1987.4
12	All/42/17/16	0-2cm	19.56	-46.13	<i>ruber</i> (pink)	300-355	26.0	36.9	1987.4
13	All/42/17/16	0-2cm	19.56	-46.13	<i>ruber</i> (pink)	>355	26.0	36.9	1987.4
14	All/42/17/16	0-2cm	19.56	-46.13	<i>universa</i>	>355	26.0	36.9	1987.4
15	mv99-38	0-2cm	22.60	-111	<i>ruber</i> (white)	212-355	23.9	34.4	1921.1
16	mv99-38	0-2cm	22.60	-111	<i>bulloides</i>	212-355	23.9	34.4	1921.1
17	EW9303-18	0-2cm	-45.03	58.02	<i>bulloides</i>	250-300	4.7	34.5	2084.9
18	EW9303-18	0-2cm	-45.03	58.02	<i>bulloides</i>	300-355	4.7	34.5	2084.9
19	EW9303-18	0-2cm	-45.03	58.02	<i>pachyderma</i>	250-300	4.7	34.5	2084.9
20	OC476-SR223	0-2cm	-33.53	166.53	<i>universa</i>	>300	19.3	35.7	1995.1
21	T329	0-2cm	-12.96	173.57	<i>universa</i>	>500	28.6	34.8	1876.2
22	MC439	0-0.5cm	-20.03	59.46	<i>universa</i>	>355	10.1	35.2	2059.4
23	MC439	0-0.5cm	-20.03	59.46	<i>universa</i>	>355	10.1	35.2	2059.4

Table 1: all samples selected for analysis, arranged by species and core name.

As the presence of sodium during MC-ICP-MS analysis obscures the response of the ICP-MS to lithium through interference in the plasma (Misra and Froelich, 2009; Jeffcoate et al., 2004), it is necessary to put each column through chromatographic columns filled with ion exchange resin in order to separate the lithium and sodium (Dellinger et al., 2014; James and Palmer, 2000). The elution process as described in Dellinger et al. (2014) and adapted by Kalderon-Asael (personal communication) is illustrated in Figure 4.

Foraminifera were cleaned following the procedures of Henehan et al. (2013) as adapted from Rae et al. (2011). Each set of picked foraminifera was imaged for recordkeeping and then crushed between two glass slides such that all chambers of each foraminifera were broken and exposed. Samples were then rinsed and sonicated repeatedly using Milli-Q ultrapure water

(18.2M Ω) to remove clay contamination, since clay contamination may bias lithium towards light values (Misra and Froelich, 2012). The samples were treated via intensive oxidative cleaning (3 \times 20–30 min treatments of 250 μ l 1% H₂O₂+0.1 M NH₄OH₄ at 80 °C). Six samples (2, 4, 5, 11, 12, and 13 as numbered in Table 1) underwent additional reductive cleaning because of clay-contaminated appearance. The reductive cleaning step was taken from the cleaning for neodymium isotope analysis preparation done by Kraft et al. (2013). Samples then underwent a brief weak acid leach (0.0005M HNO₃) and then dissolved in 0.5N HNO₃.

The cleaned sample solutions were dried down and eluted through 2.7 ml AG-50W-X12 resin using 0.2N HCl, following Dellinger et al. (2014) and James and Palmer (2000). Each column was cleaned twice using 10ml 6N HCl and 10ml MQ2 water and then conditioned in 5ml 0.2N HCl. After sample introduction, 1.5ml MQ2 water was used to wash the remnants of each sample into the column. 16ml was eluted through the columns into waste containers, and then 24ml was collected (see Figure 4 for divisions between elutions). The elutions were then dried down and redissolved in 5% HNO₃. A 50 μ l split was taken of each sample to check for concentrations. Samples were subsequently diluted with 5% HNO₃ to appropriate concentrations or dried down and redissolved in 5% HNO₃ if concentrations were too low. Samples were analyzed for ⁶Li and ⁷Li using a Thermo Neptune MC-ICP-MS calibrated against L-SVEC.

Using this column procedure, the columns were calibrated using 2 \times 3.5ml splits during the second 7ml phase (the last phase not collected) and 8 \times 3ml splits during the 24ml collection phase. The results for lithium are shown below. The split test was done to examine i) the separation of lithium and sodium in the peaks and ii) to test the effects of different buffers on the response of the matrix solution in order to see if boron post-column solutions can be run through lithium columns. Each test ran 5ppb L-SVEC through the columns and each test was duplicated (shown below). The sodium peaks for each of these tests was not seen except when the sodium acetate buffer was used. In this case, the beginning of the sodium peak was visible in the final 3ml stage. This was not the case for the ammonium acetate buffer. In order to further future research of lithium and boron co-analysis of the same samples, from this point onward sodium acetate buffer were avoided in favor of ammonium acetate buffer in preparation for boron columns. Sodium levels were low in all of this study's foraminiferal samples, so the Na/Li ratio is not expected to have affected Li isotope measurements.

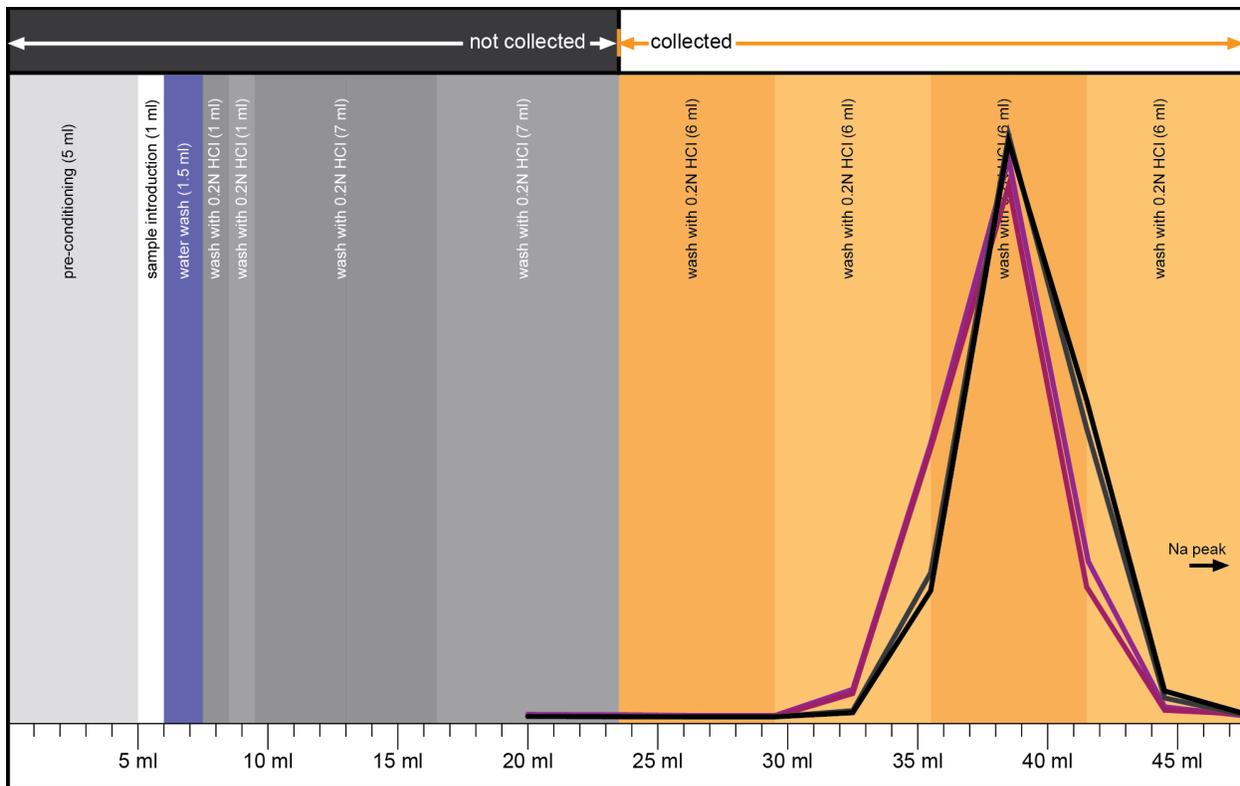


Figure 4: elution graph for lithium columns as described above. Concentrations are relative and therefore omitted. The two black lines connect measurements from elutions of L-SVEC. The two purple lines connect measurements from splits of L-SVEC combined with ammonium acetate buffer.

RESULTS

All sites, species, and data values from this study can be found in Table 2. The measurement of the geostandard BHVO-2 in this study was $5.78 \pm 0.25\%$, while the published literature value is generally around 4.6% ($4.7 \pm 0.22\%$ in Jeffcoate et al., 2004; $4.55 \pm 0.29\%$ in Magna et al., 2004). The results in this study were corrected using the difference between the literature BHVO-2 value and the produced BHVO-2 value so as to make any comparisons with Hathorne and James (2006) and Vigier et al. (2015) data more meaningful. SBC-1, another geostandard used as an in-house standard, had values of $0.28 \pm 0.24\%$ compared to the typical in-house value of around -0.9% . However, there is significant internal variation in SBC-1 (Kalderon-Asael, personal communication), so it is disregarded in correction calculation. Further column analysis revealed a bias in standards of approximately $0.8\text{-}1.2\%$ for different

concentrations of samples of BHVO-2 and L-SVEC; this research is currently in progress. Al/Ca ratios will also be revealed in that research, showing which samples were clay-contaminated, if any.

Output files from each sample were checked to verify that samples had not dried out or that the MC-ICP-MS intake tip made contact with the sample. In several cases, the output files for many of the samples had anomalous isotope measurements due to too much solution having evaporated. Many of these files were corrected and subsequently reintroduced. The samples that underwent 50 cycles were never reduced lower than 36, and only one was reduced to fewer than 40 cycles. The values corrected for mis-sampling due to evaporation are believed to be correct.

The corrected $\delta^7\text{Li}$ values of our samples varied from 27.2‰ to 32.8‰ with an average of 30.7‰ ($2\sigma=1.5\%$). In examining the data we compared $\delta^7\text{Li}$ values to both aspects of the foraminifera picked and carbonate system parameters based on location of the coretop. Interpolating between the geographically nearest two to four points of from Takahashi et al. (2009) for each coretop latitude and longitude, six different parameters were determined: temperature, salinity, DIC, TA, pH, and $p\text{CO}_2$. Three samples of *O. universa* were also taken from the Hathorne and James (2006) dataset and analyzed alongside our own samples of the same species.

VARIATION WITH SIZE FRACTION

Many different sites had multiple sizes of certain species picked. For two separate coretop sites (CH75/2/31/21 and AII/42/17/16), we picked three different size fractions of *G. ruber*. Little correlation was found here between size fraction and $\delta^7\text{Li}$, rounding size fraction down to the lower sieve used; any difference between size fractions was obscured by internal error. For other sites where the same species was picked at different size fractions, there is no consistent trend. *O. universa* across all the sites indicated no correlation with size fraction ($r^2=0.08$, not controlling for other trends).

VARIATION WITH TEMPERATURE AND SALINITY

Little significant correlation with salinity was observed ($r^2=0.35$). An overall positive correlation was observed between temperature and $\delta^7\text{Li}$ ($r^2=0.61$). The overall correlation with temperature is dominated by the three samples from the lowest-temperature site (4.7°C, off the coast of Greenland). When divided by species, the correlations varied. The species were clustered in different regions of the plot as shown in Figure 4.

VARIATION WITH CARBONATE SYSTEM PARAMETERS

Alkalinity ($r^2=0.24$), pH ($r^2=0.04$), and $p\text{CO}_2$ ($r^2=0.02$) show little correlation with $\delta^7\text{Li}$. DIC shows some negative correlation with $\delta^7\text{Li}$ ($r^2=0.40$). $[\text{CO}_3^{2-}]$ shows positive correlation with $\delta^7\text{Li}$ ($r^2=0.61$). The results for alkalinity, pH, and $p\text{CO}_2$ agree with those of Vigier et al. (2015). However, the correlation with DIC is the opposite of that study, and the correlation with $[\text{CO}_3^{2-}]$ is not seen in that study altogether.

VARIATION WITH SPECIES

The four species picked were difficult to distinguish between in trends with all variables. Differences between species averages are significant, though for some species, the environmental ranges of these samples are small, and for this reason the interspecies variation may be overpowered by internal error. Using linear multiple regression, we compared a fit with carbonate and species with a fit of species only, reflecting the significance of carbonate ($p=0.00011$). In order to increase the pool of species, we looked at the $\delta^7\text{Li}$ for recent foraminifera in Hathorne and James (2006). Using a linear multiple regression model, we compared the results of a fit with $[\text{CO}_3^{2-}]$ and species a fit with $[\text{CO}_3^{2-}]$ alone. Comparing the two fits with an ANOVA test, species significantly affected the $\delta^7\text{Li}$ response ($p=3.5\text{E}-7$). The low p-value is largely influenced by the variation with species in a single site evident visually upon inspection of the Hathorne and James dataset (**FIGURE 5**). Using our data alone, there was insufficient significance ($p=0.31$).

Site	Species	Size fraction	Temp.	Temp. (2SD)	Sal.	Alkalinity (umol/kg)	Alk. (2SD)	pH (NBS scale)	pH (2SD)	CO3		DIC		pCO2 (uatm)	pCO2 (per 2SD)	d7LI (per mil)	corr. d7LI (per mil)	d7LI (2SD)	Na (ppb)	
										(umol/ kg)	CO3 (2SD)	(umol/ kg)	DIC (2SD)							
MC497	<i>Globigerina bulloides</i>	250-300	26.9	3.6	36.4	0.2	2375.7	13.2	8.2	0.0	281.4	27.4	1970.2	39.3	295.1	18.1	33.6	33.6	0.3	0.0
mv99-36	<i>Globigerina bulloides</i>	212-355	23.9	4.4	34.4	0.2	2265.1	12.7	8.1	0.1	239.6	13.8	1921.3	21.4	299.0	38.4	29.9	29.9	0.3	0.0
EW9303-18	<i>Globigerina bulloides</i>	250-300	4.7	3.8	34.5	0.4	2308.3	25.6	8.2	0.0	154.7	23.3	2084.9	57.6	252.6	21.4	29.1	29.1	0.2	0.0
EW9303-18	<i>Globigerina bulloides</i>	300-355	4.7	3.8	34.5	0.4	2308.3	25.6	8.2	0.0	154.7	23.3	2084.9	57.6	252.6	21.4	28.3	28.3	0.3	0.0
EW9303-18	<i>Neoglobobulimina pachyderma</i>	250-300	4.7	3.8	34.5	0.4	2308.3	25.6	8.2	0.0	154.7	23.3	2084.9	57.6	252.6	21.4	30.3	30.3	0.3	0.1
MC497	<i>Globigerinoides ruber, white</i>	250-300	26.9	3.6	36.4	0.2	2375.7	13.2	8.2	0.0	281.4	27.4	1970.2	39.3	295.1	18.1	32.6	32.6	0.2	0.7
MC497	<i>Globigerinoides ruber, white</i>	300-355	26.9	3.6	36.4	0.2	2375.7	13.2	8.2	0.0	281.4	27.4	1970.2	39.3	295.1	18.1	32.9	32.9	0.2	0.0
mv99-36	<i>Globigerinoides ruber, white</i>	212-355	23.9	4.4	34.4	0.2	2265.1	12.7	8.1	0.1	239.6	13.8	1921.3	21.4	299.0	38.4	31.1	31.1	0.2	0.0
MC420	<i>Globigerinoides ruber, pink</i>	250-300	27.6	1.1	35.5	0.5	2337.9	25.5	8.2	0.0	285.9	4.1	1926.0	20.2	277.5	8.4	33.1	33.1	0.2	0.7
MC420	<i>Globigerinoides ruber, pink</i>	300-355	27.6	1.1	35.5	0.5	2337.9	25.5	8.2	0.0	285.9	4.1	1926.0	20.2	277.5	8.4	33.8	33.8	0.2	0.0
CH75/2/31/2 1	<i>Globigerinoides ruber, pink</i>	250-300	26.7	1.9	36.0	0.6	2361.2	35.9	8.2	0.0	288.1	10.7	1943.0	35.2	278.2	26.4	32.0	32.0	0.3	0.2
CH75/2/31/2 1	<i>Globigerinoides ruber, pink</i>	300-355	26.7	1.9	36.0	0.6	2361.2	35.9	8.2	0.0	288.1	10.7	1943.0	35.2	278.2	26.4	32.0	32.0	0.2	0.4
CH75/2/31/2 1	<i>Globigerinoides ruber, pink</i>	>355	26.7	1.9	36.0	0.6	2361.2	35.9	8.2	0.0	288.1	10.7	1943.0	35.2	278.2	26.4	31.9	31.9	0.2	0.0
All/42/17/16	<i>Globigerinoides ruber, pink</i>	250-300	26.0	2.2	36.9	0.2	2421.0	11.2	8.2	0.0	299.0	7.4	1987.4	13.7	275.4	15.1	32.4	32.4	0.2	0.1
All/42/17/16	<i>Globigerinoides ruber, pink</i>	300-355	26.0	2.2	36.9	0.2	2421.0	11.2	8.2	0.0	299.0	7.4	1987.4	13.7	275.4	15.1	32.4	32.4	0.2	0.9
All/42/17/16	<i>Globigerinoides ruber, pink</i>	>355	26.0	2.2	36.9	0.2	2421.0	11.2	8.2	0.0	299.0	7.4	1987.4	13.7	275.4	15.1	32.3	32.3	0.2	0.4
TAN1106/50-N7	<i>Orbulina universa</i>	300-355	9.0	-	34.4	-	2282.3	-	8.0	-	133.3	-	2100.9	-	396.4	-	31.2	31.2	0.2	0.1
MC577-17b	<i>Orbulina universa</i>	>355	15.3	4.8	35.7	0.1	2348.4	2.2	8.2	0.0	214.4	29.6	2037.8	43.7	274.0	0.8	30.2	30.2	0.2	0.9
All/42/17/16	<i>Orbulina universa</i>	>355	26.0	2.2	36.9	0.2	2421.0	11.2	8.2	0.0	299.0	7.4	1987.4	13.7	275.4	15.1	33.2	33.2	0.2	0.0
OC476-SR223	<i>Orbulina universa</i>	>300	19.3	3.7	35.7	0.1	2352.7	8.8	8.2	0.0	248.1	16.0	1995.1	21.5	262.2	7.9	32.5	32.5	0.2	0.2
T329	<i>Orbulina universa</i>	>500	28.6	1.4	34.8	0.2	2287.7	16.1	8.2	0.0	284.7	6.0	1876.2	10.3	270.3	17.1	33.9	33.9	0.2	0.8
MC439	<i>Orbulina universa</i>	>355	10.1	3.1	35.2	0.1	2324.8	4.9	8.2	0.0	182.9	16.1	2059.4	26.7	265.0	14.3	30.8	30.8	0.2	0.2
MC439	<i>Orbulina universa</i>	>355	10.1	3.1	35.2	0.1	2324.8	4.9	8.2	0.0	182.9	16.1	2059.4	26.7	265.0	14.3	30.9	30.9	0.2	0.9
M35010-2	<i>Orbulina universa</i>	>710	27.1	2.7	36.3	0.2	2379.1	14.1	8.1	0.0	284.2	20.7	1967.7	30.0	298.4	23.6	30.7	30.7	0.2	-
M35010-2	<i>Orbulina universa</i>	500-710	27.1	2.7	36.3	0.2	2379.1	14.1	8.1	0.0	284.2	20.7	1967.7	30.0	298.4	23.6	31.1	31.1	0.2	-
GIK15672-2	<i>Orbulina universa</i>	>500	19.3	4.1	36.4	0.2	2394.4	7.2	8.2	0.0	252.6	14.1	2028.0	17.4	267.7	34.5	31.4	31.4	0.2	-

Table 2: all results from this study.

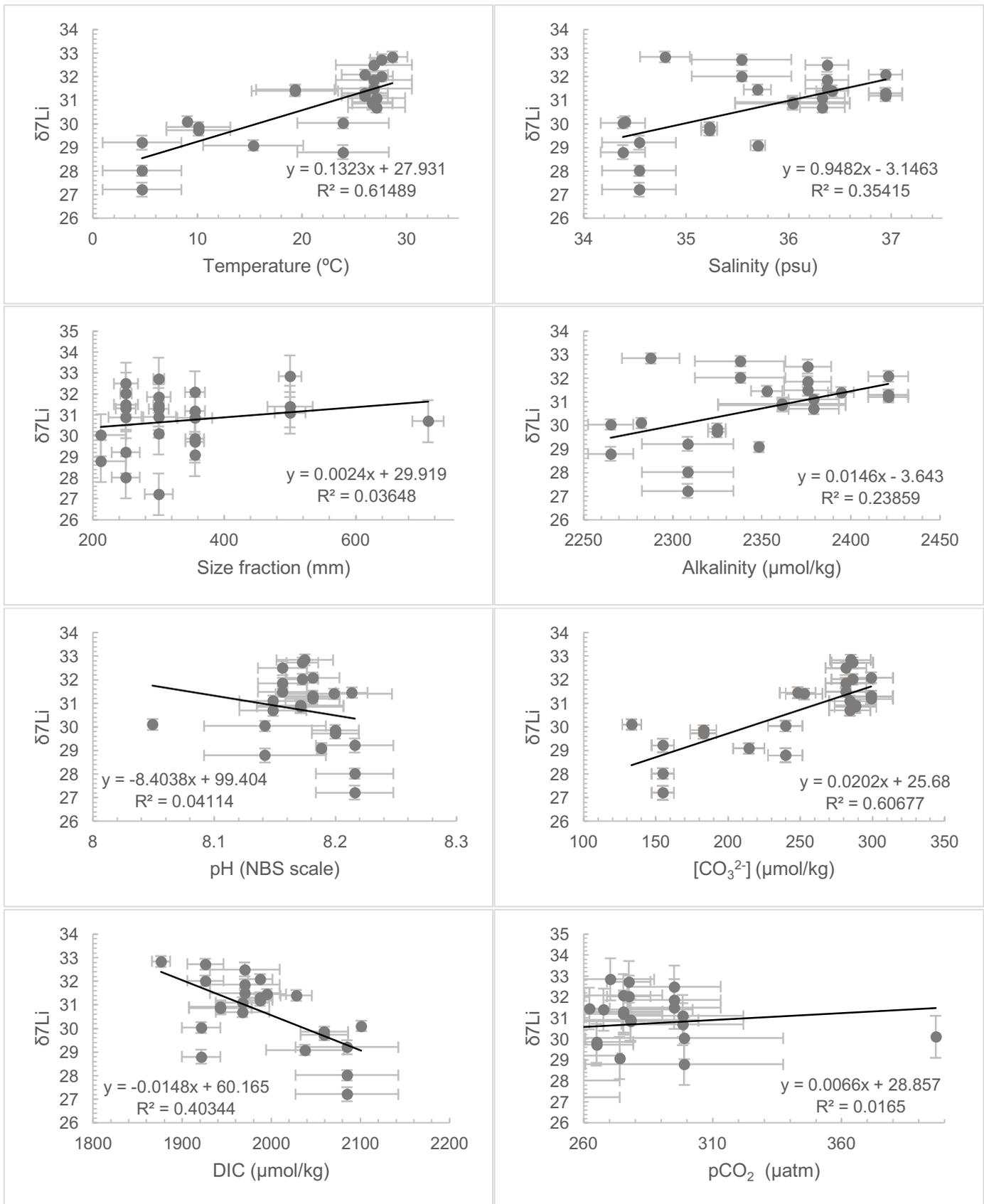


Figure 4: Correlation between various carbonate system parameters shown here. Top: $\delta^7\text{Li}$ versus temperature and salinity; upper middle: $\delta^7\text{Li}$ versus size fraction and alkalinity; lower middle: $\delta^7\text{Li}$ vs. pH and carbonate ion concentration (i.e. carbonate saturation state); bottom: $\delta^7\text{Li}$ versus DIC and pCO_2 . Horizontal error bars represent 2 S.D. uncertainty due to interpolation from Takahashi et al. (2009). The vertical error bars represent 2 S.D. uncertainty based on the number of uptake cycles run for each sample during MC-ICP-MS analysis; a run of standards was used to determine 2 S.D. uncertainty for each number of cycles used.

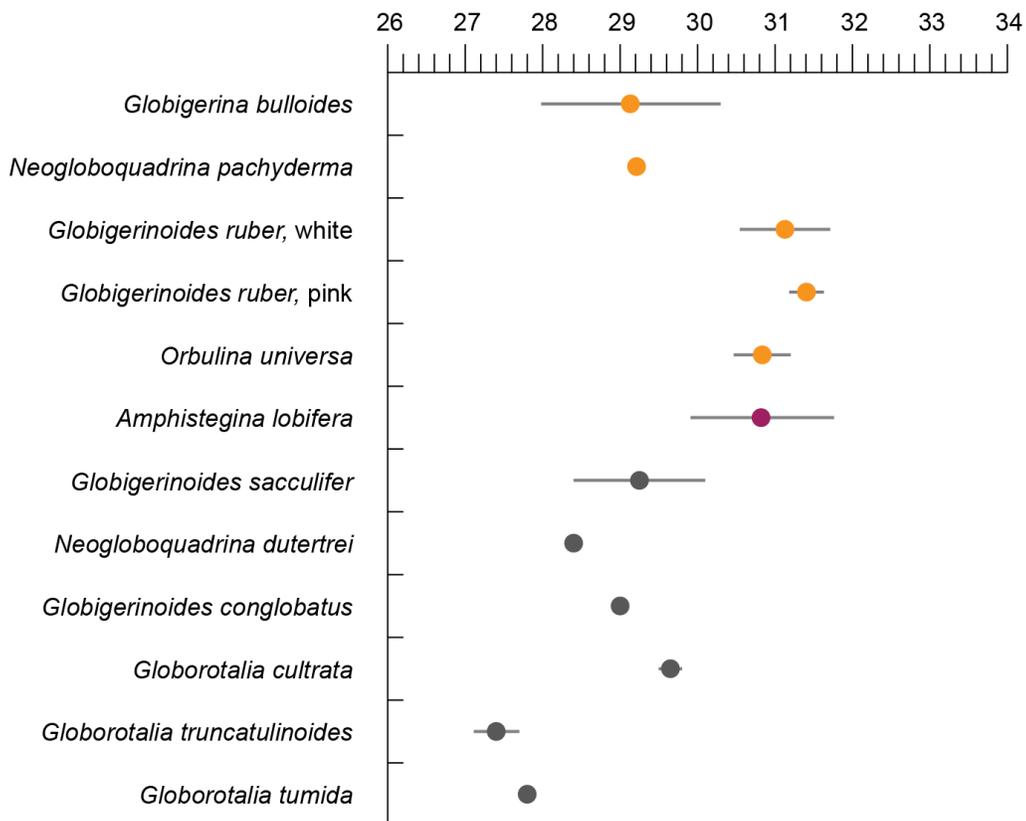
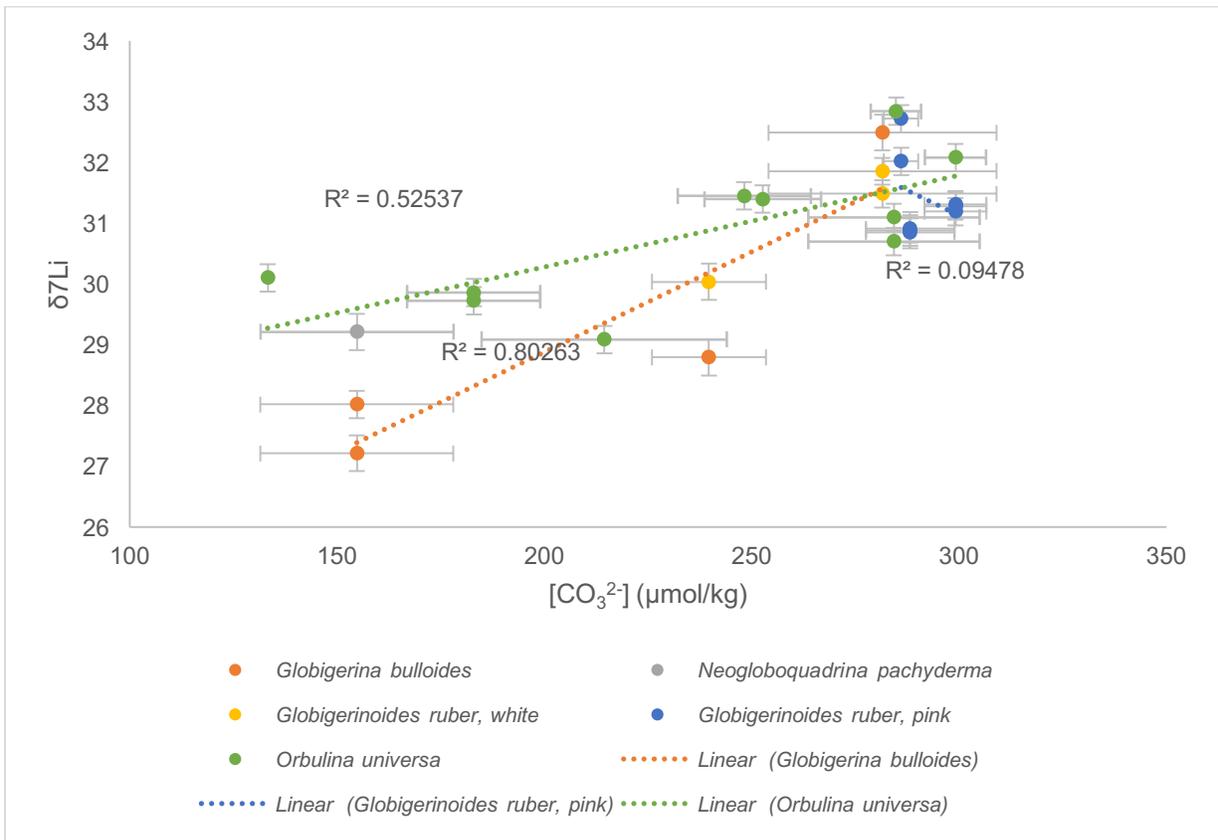


Figure 5: a) $\delta^7\text{Li}$ versus carbonate ion concentration (gray bars represent 2 S.D.), separated by species. Correlations for *Globigerina bulloides* ($r^2=0.80$), *Orbulina universa* including Hathorne and James (2006) data ($r^2=0.53$), and *Globigerinoides ruber* (pink and white mixed, $r^2=0.09$). Correlations for *Globigerinoides ruber* (white) and *Neogloboquadrina pachyderma* omitted because of low sample number ($n=3$ and $n=1$, respectively). b) $\delta^7\text{Li}$ versus species (gray bars represent 2 S.D.). Data for *Globorotalia tumida*, *G. truncatulinoides*, *G. cultrata*, *Globigerinoides conglobatus*, *Neogloboquadrina dutertrei*, and *Globigerinoides sacculifer* are taken from Hathorne and James (2006). Data for *Amphistegina lobifera* from Vigier et al. (2015).

DISCUSSION

The range of 5.6‰ is supported by the observation of similar modern variation in other studies (Hathorne and James, 2006; Misra and Froelich, 2012). While a small amount of variation in dissolved $\delta^7\text{Li}$ is evident in today (Hall et al., 2005; Jeffcoate et al., 2003), the vast majority of this 5.6‰ variation is likely due to variation as lithium is incorporated into foraminifera. The fact that the foraminifera seem to fractionate only towards lighter values may support the importance of a metabolic process like that suggested in Vigier et al. (2015).

The results from the earlier study of the lab culture of *Amphistegina* suggested that DIC can be used as a proxy in the modern, where higher $\delta^7\text{Li}$ reflects higher DIC. However, the correlation for this study's dataset (whether split by species or combined) is negative and much weaker. There is also a significant correlation between the observed $\delta^7\text{Li}$ and the $[\text{CO}_3^{2-}]$. A strikingly similar correlation (regression line and r^2) is observed in Vigier et al. (2015) when that study varies DIC with constant pH but not when that study varies pH with constant DIC, rendering this comparison minimally useful. Lastly, there is a significant correlation with temperature which is not observed in other studies (Vigier et al., 2015; Vigier et al., 2007; Hathorne and James, 2006).

Combination of our dataset with the Hathorne and James (2006) dataset allows higher species resolution and indicates that there is significant variation in Li fractionation between species ($p=3.5\text{E-}7$). Because different species may live in different parts of the ocean whether longitudinally, latitudinally, or depthwise, it is necessary in the future to take into account spatial gradients in carbonate system parameters for given species. This is difficult to constrain for species that have already been deposited, but may be possible with live foram collection and analysis.

The effects of species obscure the relationship with carbonate system parameters (Figure 5a). Earlier studies claim no relationship between foraminiferal $\delta^7\text{Li}$ and temperature or $[\text{CO}_3^{2-}]$. Vigier et al. use different species in the genus *Amphistegina*, though there is evidence of *Amphistegina* having similar calcification methods to the planktonic foraminifera studied here (Erez 2003). The difference between the relationships found in that study and those found in this study may result from the use of lab culture conditions. The setup of the *Amphistegina* study uses a high constant flow of altered seawater through each culture, a constant supply of fresh nutrients

and food. These conditions including exposure to natural light may have allowed for maximum rates of metabolism (ter Kuile and Erez, 1984), under which the foraminifera may respond differently to various environmental changes. The potential for vital effects is seen in other isotope systems, like that of boron (e.g. Rollion-Bard and Erez, 2010). As discussed in Vigier et al. (2015), the symbiont-bearing foraminifera (like those of the genus *Amphistegina*) precipitate from their microenvironment. Foraminifera not bearing symbionts may have different pathways for calcification and therefore alternate species-specific effects on lithium uptake. Those bearing symbionts (i.e. *Globigerinoides sacculifer*, *Amphistegina lobifera*, *Orbulina universa*, and *Globorinoides ruber*) seem to have generally higher $\delta^7\text{Li}$ values than those of symbiont-lacking foraminifera. It is possible that the symbiont-influenced microenvironment alters how lithium is incorporated, but the reasons remain unclear.

Hathorne and James (2006) do not find a temperature correlation, but they also do not use more than three individuals of any particular species. Our pool alone shows a significant variation between *O. universa* $\delta^7\text{Li}$ and temperature ($r^2=0.78$), and when the three *universa* points from Hathorne and James (2006) are included, there remains a significant correlation ($r^2=0.53$). Because the Hathorne and James study uses several species of foraminifera from only two different coretops, observations of temperature or other carbonate system parameter effects may have been obscured by the different species assemblages and small number of sites to compare. The current study provides a larger number of sites in addition to those of Hathorne and James (2006). Inter-lab variability between lithium isotope measurements are recognized, and the BHVO-2 correction as mentioned above has been used to minimize this. As there is still potential for inter-lab variability, future communication and study is warranted.

The foraminifera that live deeper in the water column (e.g. *Globorotalia tumida* and *Globorotalia truncatulinoides*) also seem to have lower values for $\delta^7\text{Li}$. It is possible that some depth gradient is confounding comparison between species, since interspecies variation may actually be the result of different water column niches and therefore depth gradients. However, it is difficult to constrain the depth ranges of each species given that they may vary by latitude, and future analyses may reveal some greater trend whether species- or carbonate system-determined.

The meaning of the correlations with DIC, $[\text{CO}_3^{2-}]$, and temperature remain a mystery. An increase in DIC implies an increase in carbonate ion concentration, yet the correlations are opposite each other. The temperature correlation may be inherent to direct affects on growth or

Li incorporation, or it may be confounded by the correlation with $[\text{CO}_3^{2-}]$. Because of the lack of definitive data on the influence of (or covariance with) different carbonate parameters, we do not speculate on any mechanisms.

Variation in both carbonate system parameters and species assemblage have the power to explain the mysteries of the Misra and Froelich (2012) record. As mentioned before, there is large short-term variation during a few periods in the Cenozoic that is difficult to explain in terms of variations in global seawater values. Perhaps this variation is actually due to changes in environmental parameters like DIC, temperature, or carbonate saturation state. These parameters may change on much shorter timescales, and for this reason they might be able to explain this short-term variation. An alternative explanation of the variation in the record is actually shifts in species assemblage. Notably, around 15-18 Ma in the original Misra and Froelich (2012) figure, there seems to be a gap between two foraminifera of the two sites. Despite temporal proximity, there may be different conditions and species between the two sites.

It is impossible to reconstruct a record from a single species across the Cenozoic because there are no species that exist in continuous cores over the last 65 Ma. As seen in the Misra and Froelich dataset, there are many shifts from site to site, and it is possible that the different species assemblages both spatially and temporally can explain some of the variation seen throughout the Cenozoic. The use of bulk foraminifera may track vital effects of different foraminifera weighted by their abundance, in some ways a proxy in itself. However, because different species may respond (and respond distinctly) to changes in the carbonate system parameters, it is difficult to disentangle these two effects and warrants further study.

The $\delta^7\text{Li}$ record also contains the previously mentioned large negative $\delta^7\text{Li}$ excursion across the K-Pg (Misra and Froelich, 2012). With large environmental changes and species assemblage turnover (e.g. Schulte et al., 2010), it is possible that the K-Pg $\delta^7\text{Li}$ excursion may not be caused by massive alterations in the global weathering signal but rather large shifts in the carbonate system state and in spatial/temporal distributions of different species. If different species have different vital effects in incorporation of Li, then the $\delta^7\text{Li}$ excursion is perhaps due to species alone; indeed, the single-species record across the K-Pg is discontinuous in Misra and Froelich (2012). The large turnover in species assemblage across the Cretaceous-Paleogene boundary (e.g. Arenillas et al., 2000) has large potential to explain the $\delta^7\text{Li}$ excursion in terms of

vital effects. Further information may be revealed by carbonate system studies of the K-Pg, including those using boron isotopes.

The original tentative suggestion in Misra and Froelich (2012) was the existence of K-Pg continental weathering on a large enough scale to perturb the lithium reservoir in the ocean. This interpretation of the K-Pg excursion assumes the long residence time of lithium in the ocean and foraminiferal $\delta^7\text{Li}$ record strictly following the weathering signal. However, the long residence time of lithium is perhaps the key to understanding shorter term variation in systems like species assemblage or carbonate system parameters. On timescales too short for the global signal to be perturbed, the variation in the $\delta^7\text{Li}$ isotope signal has the potential to be used as a proxy outside of silicate weathering intensity. It is possible that the interpretation of the K-Pg excursion may not be weathering variability at all but rather the significance of species effects or carbonate system evolution. Single-species records of $\delta^7\text{Li}$ from benthic foraminifera that survived the mass extinction (Schulte et al., 2010) may prove useful for future study of carbonate system changes.

The challenge of constraining the carbonate system still remains. However, if $\delta^7\text{Li}$ varies with carbonate ion concentration or DIC, then it has potential to be used in the future in tandem with boron isotopes. Variation on timescales shorter than 1.2 Ma has the potential for future study using a more constrained lithium isotope system alongside boron pH reconstructions. This may constrain the carbonate system over short periods of time where the changes may be unclear, including the K-Pg but also applicable anywhere in the record.

CONCLUSION

Given the large variation of $\delta^7\text{Li}$ values in the modern, foraminifera cannot be expected to strictly record the global seawater $\delta^7\text{Li}$ signal. As foraminifera fractionate lithium as they incorporate it from seawater, the foraminiferal $\delta^7\text{Li}$ values are thus reliant on both seawater values and species. There may also be a relationship with some environmental variable like temperature or carbonate ion concentration. The complexity based on this environmental variable requires further research for better understanding of how foraminiferal shells record $\delta^7\text{Li}$ values.

Due to these complications, the $\delta^7\text{Li}$ record as presented in Hathorne and James (2006) and Misra and Froelich (2012) can no longer be strictly interpreted as silicate weathering. The $\delta^7\text{Li}$ record may represent some form of carbonate system change superimposed on species effects and the weathering signal. Because carbonate system parameters can vary spatially at any given point in time (e.g. the modern), diachronic changes in $\delta^7\text{Li}$ are obscured, awaiting further study of this issue.

Lithium isotopic records across the K-Pg also attract further attention. Because of the large-scale environmental changes due to the eruption of the Deccan Traps and the contemporaneous Chicxulub bolide impact (Schulte et al., 2010), it is possible that the lithium cycle was seriously altered. However, as the foraminiferal record may not be strictly recording seawater $\delta^7\text{Li}$ values, the silicate weathering interpretation remains elusive. Further study of lithium isotopes and the evolution of the K-Pg carbonate system are needed to constrain this section of the $\delta^7\text{Li}$ record. Such study may reveal if the $\delta^7\text{Li}$ excursion was driven by local/global environmental variation or instead due to mass extinction and large species assemblage turnover. Similar observations may be made for other parts of the $\delta^7\text{Li}$ record.

While future research may not be able to rely on the $\delta^7\text{Li}$ record to study the processes of silicate weathering, we may still be able to study carbon cycling or ecological changes through the $\delta^7\text{Li}$ record (Figure 6), and there is promise for using single-species $\delta^7\text{Li}$ records together with boron and other proxies in carbonate system reconstruction.

SUMMARY

The interpretation of $\delta^7\text{Li}$ as a silicate weathering proxy has allowed for much study of this isotope system, most recently producing a $\delta^7\text{Li}$ record from 68 Ma to the present. Foraminiferal $\delta^7\text{Li}$ seems to represent three major components of environmental change. The first component is silicate weathering intensity, which alters the global seawater $\delta^7\text{Li}$ value and therefore seawater lithium reservoir from which foraminifera calcify. The second component is composed of species vital effects, in which different species incorporate marine lithium differently. The third is variation in in foraminiferal lithium incorporation with carbonate system parameters likely dependent on species. These effects superimposed complicate interpretation of the use of foraminiferal $\delta^7\text{Li}$ as a weathering intensity proxy. However, they also build potential in the use of foraminiferal $\delta^7\text{Li}$ beyond studying weathering intensity and instead studying short-term variation in carbon-cycling and ecological change, which may be applicable to illuminating massive short-scale climate and environmental alterations like those during the K-Pg extinction. Using lithium as a proxy for these three aspects of how the earth as a geochemical system has evolved in the past may illuminate the future of the complex environmental change that we see today.

REFERENCES

- Arenillas, I., Arz, J. A., Molina, E., & Dupuis, C. (2000). The Cretaceous/Paleogene (K/P) boundary at Ain Settara, Tunisia: sudden catastrophic mass extinction in planktic foraminifera. *The Journal of Foraminiferal Research*, 30(3), 202-218.
- Arrhenius, S. (1896). XXXI. On the influence of carbonic acid in the air upon the temperature of the ground. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 41(251), 237-276.
- Berner, R. A., Lasaga, A. C., & Garrels, R. M. (1983). The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Sci*, 283(7), 641-683.
- Broecker, W. S., Peng, T. H., & Beng, Z. (1982). *Tracers in the Sea*. Lamont-Doherty Geological Observatory, Columbia University.
- Caldeira, K. (1995). Long-term control of atmospheric carbon dioxide; low-temperature seafloor alteration or terrestrial silicate-rock weathering?. *American Journal of Science*, 295(9), 1077-1114.
- Chan, L.H., & Edmond, J. M. (1988). Variation of lithium isotope composition in the marine environment: a preliminary report. *Geochimica et Cosmochimica Acta*, 52(6), 1711-1717.
- Dellinger, M., Gaillardet, J., Bouchez, J., Calmels, D., Galy, V., Hilton, R. G., ... & France-Lanord, C. (2014). Lithium isotopes in large rivers reveal the cannibalistic nature of modern continental weathering and erosion. *Earth and Planetary Science Letters*, 401, 359-372.
- Dickson, A. G., Sabine, C. L., & Christian, J. R. (2007). *Guide to Best Practices for Ocean CO₂ Measurements*.
- Erez, J. (2003). The source of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies. *Reviews in mineralogy and geochemistry*, 54(1), 115-149.
- Foster, G. L. (2008). Seawater pH, pCO₂ and [CO₂-3] variations in the Caribbean Sea over the last 130 kyr: A boron isotope and B/Ca study of planktic foraminifera. *Earth and Planetary Science Letters*, 271(1), 254-266.
- Hathorne, E. C., & James, R. H. (2006). Temporal record of lithium in seawater: A tracer for silicate weathering?. *Earth and Planetary Science Letters*, 246(3), 393-406.
- Henehan, M. J., Rae, J. W., Foster, G. L., Erez, J., Prentice, K. C., Kucera, M., ... & Marshall, B. J. (2013). Calibration of the boron isotope proxy in the planktonic foraminifera *Globigerinoides ruber* for use in palaeo-CO₂ reconstruction. *Earth and Planetary Science Letters*, 364, 111-122.
- Huh, Y., Chan, L. H., Zhang, L., & Edmond, J. M. (1998). Lithium and its isotopes in major world rivers: implications for weathering and the oceanic budget. *Geochimica et Cosmochimica Acta*, 62(12), 2039-2051.
- Huh, Y., Chan, L. H., & Edmond, J. M. (2001). Lithium isotopes as a probe of weathering processes: Orinoco River. *Earth and Planetary Science Letters*, 194(1), 189-199.

- James, R. H., & Palmer, M. R. (2000). The lithium isotope composition of international rock standards. *Chemical Geology*, 166(3), 319-326.
- Jeffcoate, A. B., Elliott, T., Thomas, A., & Bouman, C. (2004). Precise/small sample size determinations of lithium isotopic compositions of geological reference materials and modern seawater by MC-ICP-MS. *Geostandards and Geoanalytical Research*, 28(1), 161-172.
- Kalderon-Asael, B. (2016). Personal communication.
- Kırsakürek, B., James, R. H., & Harris, N. B. (2005). Li and $\delta^7\text{Li}$ in Himalayan rivers: proxies for silicate weathering?. *Earth and Planetary Science Letters*, 237(3), 387-401.
- Klochko, K., Kaufman, A. J., Yao, W., Byrne, R. H., & Tossell, J. A. (2006). Experimental measurement of boron isotope fractionation in seawater. *Earth and Planetary Science Letters*, 248(1), 276-285.
- Kraft, S., Frank, M., Hathorne, E. C., & Weldeab, S. (2013). Assessment of seawater Nd isotope signatures extracted from foraminiferal shells and authigenic phases of Gulf of Guinea sediments. *Geochimica et Cosmochimica Acta*, 121, 414-435.
- Magna, T., Wiechert, U. H., & Halliday, A. N. (2004). Low-blank isotope ratio measurement of small samples of lithium using multiple-collector ICPMS. *International Journal of Mass Spectrometry*, 239(1), 67-76.
- Misra, S., & Froelich, P. N. (2012). Lithium isotope history of Cenozoic seawater: changes in silicate weathering and reverse weathering. *Science*, 335(6070), 818-823.
- Myrow, P. M., Hughes, N. C., Derry, L. A., McKenzie, N. R., Jiang, G., Webb, A. A. G., ... & Singh, B. P. (2015). Neogene marine isotopic evolution and the erosion of Lesser Himalayan strata: Implications for Cenozoic tectonic history. *Earth and Planetary Science Letters*, 417, 142-150.
- Palmer, M. R., & Edmond, J. M. (1992). Controls over the strontium isotope composition of river water. *Geochimica et Cosmochimica Acta*, 56(5), 2099-2111.
- Peucker-Ehrenbrink, B., & Ravizza, G. (2000). The marine osmium isotope record. *Terra Nova*, 12(5), 205-219.
- Rae, J. W., Foster, G. L., Schmidt, D. N., & Elliott, T. (2011). Boron isotopes and B/Ca in benthic foraminifera: Proxies for the deep ocean carbonate system. *Earth and Planetary Science Letters*, 302(3), 403-413.
- Rollion-Bard, C., & Erez, J. (2010). Intra-shell boron isotope ratios in the symbiont-bearing benthic foraminiferan *Amphistegina lobifera*: implications for $\delta^{11}\text{B}$ vital effects and paleo-pH reconstructions. *Geochimica et Cosmochimica Acta*, 74(5), 1530-1536.
- Schulte, P., Alegret, L., Arenillas, I., Arz, J. A., Barton, P. J., Bown, P. R., ... & Collins, G. S. (2010). The Chicxulub asteroid impact and mass extinction at the Cretaceous-Paleogene boundary. *Science*, 327(5970), 1214-1218.
- Takahashi, T., Sutherland, S. C., Wanninkhof, R., Sweeney, C., Feely, R. A., Chipman, D. W., ... & Watson, A. (2009). Climatological mean and decadal change in surface ocean pCO₂, and net sea-

- air CO₂ flux over the global oceans (vol 56, pg 554, 2009). *Deep Sea Research Part I: Oceanographic Research Papers*, 56, 2075-2076.
- ter Kuile, B., & Erez, J. (1984). In situ growth rate experiments on the symbiont-bearing foraminifera *Amphistegina lobifera* and *Amphisorus hemprichii*. *The Journal of Foraminiferal Research*, 14(4), 262-276.
- Tyrrell, T., & Zeebe, R. E. (2004). History of carbonate ion concentration over the last 100 million years. *Geochimica et Cosmochimica Acta*, 68(17), 3521-3530.
- Van Heuven, S., Pierrot, D., Lewis, E., & Wallace, D. W. R. (2011). CO₂SYST v 1.1: MATLAB program developed for CO₂ system calculations. *ORNL/CDIAC-105b, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee*.
- Vigier, N., Rollion-Bard, C., Spezzaferri, S., & Brunet, F. (2007). In situ measurements of Li isotopes in foraminifera. *Geochemistry, Geophysics, Geosystems*, 8(1).
- Vigier, N., Decarreau, A., Millot, R., Carignan, J., Petit, S., & France-Lanord, C. (2008). Quantifying Li isotope fractionation during smectite formation and implications for the Li cycle. *Geochimica et Cosmochimica Acta*, 72(3), 780-792.
- Vigier, N., Rollion-Bard, C., Levenson, Y., & Erez, J. (2015). Lithium isotopes in foraminifera shells as a novel proxy for the ocean dissolved inorganic carbon (DIC). *Comptes Rendus Geoscience*, 347(1), 43-51.
- von Strandmann, P. A. P., Jenkyns, H. C., & Woodfine, R. G. (2013). Lithium isotope evidence for enhanced weathering during Oceanic Anoxic Event 2. *Nature Geoscience*, 6(8), 668-672.
- Zeebe, R. E. (2012). History of seawater carbonate chemistry, atmospheric CO₂, and ocean acidification. *Annual Review of Earth and Planetary Sciences*, 40, 141-165.