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1 **Assessing bulk carbonates as archives for seawater Li isotope ratios**

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18 Abstract

19 Silicate weathering is a primary control on the carbon cycle and therefore long-term

20 climate. Tracing silicate weathering in the geological record has been a challenge for

21 decades, with a number of proxies proposed and their limits determined. Recently

22 lithium isotopes in marine carbonates have emerged as a potential tracer. Bulk

23 carbonates are increasingly being used as a Li isotope archive, though with limited tests

24 thus far of the robustness of this approach in the modern ocean. As the bulk composition

25 of marine pelagic carbonates has changed through time and geographically, assessing

26 the fidelity of bulk carbonate as proxy carrier is fundamental. To address the impact of
27 compositional variability in bulk carbonate on Li isotopes, we examine 27 Bahamian
28 aragonitic bulk carbonates and 16 Atlantic largely calcitic core-top sediment samples.
29 Two core-tops only have trace (<10%) carbonate, and are analysed to test whether
30 carbonates in such sections are still a viable archive. We selectively extract the
31 exchangeable and carbonate fractions from the core-top samples. The exchangeable
32 fraction contains ~2% of the total Li and has a fairly constant offset from seawater of
33 $16.5 \pm 0.8\%$. When leaching silicate-containing carbonates, acetic acid buffered with
34 sodium acetate appears a more robust method of solely attacking carbonates compared
35 to dilute HCl, which may also liberate some silicate-bound Li. Carbonates from samples
36 that do not contain aragonite have the isotopic fractionation of seawater of $\Delta^7\text{Li}_{\text{seawater-}}$
37 $\text{calcite} = 6.1 \pm 1.3\%$ (2sd), which is not affected by latitude or the water depth the sample
38 was deposited at. The pure aragonite bulk carbonates from the Bahamas have a
39 fractionation of $\Delta^7\text{Li}_{\text{seawater-aragonite}} = 9.6 \pm 0.6\%$. A sediment sample from the Galician
40 coast that mostly consists of quartz is highly offset from seawater by ~20‰ and also
41 has relatively high Li/Ca ratios. These high values are not due to leaching of silicate
42 material directly (Al/Ca ratios are low). We interpret this addition via cation exchange
43 of Li from silicate during recrystallisation. Overall bulk carbonates from the open ocean
44 are a reliable archive of seawater $\delta^7\text{Li}$, but care must be taken with carbonate
45 mineralogy and low-carbonate samples. Overall, therefore, any examination of the
46 palaeo-seawater $\delta^7\text{Li}$ record must be reproduced in different global settings (e.g.
47 multiple global cores) before it can be considered robust.

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52 1.0 Introduction

53 Continental silicate weathering is considered to be a fundamental control on the
54 long-term carbon cycle and climate (Chamberlin, 1899; Walker et al., 1981) as
55 weathering provides nutrients for organic carbon formation in the oceans, clay particles
56 to help that organic carbon sink (Hawley et al., 2017), and alkalinity and cations such
57 as Ca and Mg for formation of oceanic carbonate (Berner, 2003). As such, considerable
58 effort has gone into developing methods to reconstruct palaeo-weathering behaviour,
59 to determine the effect it may have on the Earth's short- and long-term climate. Several
60 tracers have been used, but most suffer from not unambiguously being able to
61 distinguish between carbonate and silicate weathering (where only silicate weathering
62 sequesters CO₂), and/or being fractionated by biology (e.g. ⁸⁷Sr/⁸⁶Sr (Oliver et al., 2003)
63 or stable Ca, Mg or Si isotopes (Fantle and Tipper, 2014; Opfergelt et al., 2010; Pogge
64 von Strandmann et al., 2014)).

65 One tracer that is gaining increasing interest, as it is unaffected by these
66 processes, is lithium isotopes. Firstly, lithium is concentrated by several orders of
67 magnitude in silicates over carbonates. Consequently, carbonate weathering, even in
68 carbonate-dominated catchments, exerts no influence on riverine Li (Dellinger et al.,
69 2015; Kisakürek et al., 2005; Millot et al., 2010; Pogge von Strandmann et al., 2017b).
70 Secondly, Li isotopes are not fractionated during uptake into plants or phytoplankton
71 (diatoms, cyanobacteria and green algae) (Lemarchand et al., 2010; Pogge von
72 Strandmann et al., 2016).

73 Riverine $\delta^7\text{Li}$ values range between 2–44‰, with a global mean of 23‰
74 (Dellinger et al., 2015; Huh et al., 2001; Huh et al., 1998; Kisakürek et al., 2005; Pistiner
75 and Henderson, 2003; Pogge von Strandmann et al., 2010; Pogge von Strandmann et

76 al., 2006; Pogge von Strandmann et al., 2017b), compared to primary silicate rock $\delta^7\text{Li}$
77 values for the continental crust of 0‰ (Sauzéat et al., 2015), and of 3–5‰ for basalt
78 (Elliott et al., 2006). Primary rock dissolution does not cause isotope fractionation, but
79 secondary minerals preferentially take up ^6Li , driving residual waters isotopically
80 heavier (Pistiner and Henderson, 2003; Vigier et al., 2008; Wimpenny et al., 2015;
81 Wimpenny et al., 2010).

82 Therefore, in surface waters, Li isotopes provide information on the ratio of
83 primary mineral dissolution (low $\delta^7\text{Li}$), relative to secondary mineral formation
84 (driving $\delta^7\text{Li}$ high). This ratio is known as the weathering congruency, where congruent
85 weathering involves complete dissolution of the primary rock, and incongruent
86 weathering involves secondary mineral formation (Misra and Froelich, 2012; Pogge
87 von Strandmann and Henderson, 2015). Weathering congruency may be a tracer for the
88 weathering intensity, defined as the ratio of the weathering rate to denudation rate
89 (Dellinger et al., 2017; Dellinger et al., 2015; Pogge von Strandmann et al., 2017b).

90 In the modern oceans, riverine Li makes up approximately 50% of the Li input,
91 with the other half derived from hydrothermal fluids (Chan and Edmond, 1988; Chan
92 et al., 1994; Hathorne and James, 2006). Removal of Li from seawater comes from
93 uptake of Li into altered oceanic crust and authigenic clays, which cumulatively impose
94 a fractionation of around 15‰, driving modern seawater to 31‰. It follows that
95 changes in the riverine Li flux and/or isotope composition due to global weathering
96 changes would leave a fingerprint in the oceans.

97 A number of studies have used Li isotopes in different types of marine
98 carbonates to reconstruct palaeo-weathering conditions (Hall et al., 2005; Hathorne and
99 James, 2006; Lechler et al., 2015; Misra and Froelich, 2012; Pogge von Strandmann et
100 al., 2017a; Pogge von Strandmann et al., 2013; Ullmann et al., 2013). Some of these

101 studies used foraminifera as an archive, but they exhibit species-specific vital effects
102 on Li isotope fractionation, potentially controlled by pH, DIC or temperature (Hall et
103 al., 2005; Hathorne and James, 2006; Misra and Froelich, 2009; Roberts et al., 2018;
104 Vigier et al., 2015). The Cenozoic record of Misra and Froelich (2012) also exhibits
105 significant scatter of $>3\%$ at single points in time, with error widths of over 6%.
106 Therefore, increasingly, bulk carbonates are being used to reduce the time of sample
107 processing, and the amount of initial material required. Using bulk material was thought
108 to be viable, because all biogenic and inorganic calcites were thought to impose similar
109 fractionation factors on Li isotopes, of 0–5‰ (Marriott et al., 2004a; Marriott et al.,
110 2004b; Misra and Froelich, 2009; Pogge von Strandmann et al., 2013; Rollion-Bard et
111 al., 2009). Equally, inorganic and biogenic aragonites also exhibit similar fractionation
112 factors of $\sim 11\%$ (Dellinger et al., 2018; Marriott et al., 2004a; Marriott et al., 2004b).
113 However, a recent study of biogenic carbonates has exhibited greater, species-specific,
114 variability (Dellinger et al., 2018). Especially modern calcitic molluscs (scallops,
115 clams, mussels and oysters) exhibit $\delta^7\text{Li}$ values both higher and lower than modern
116 seawater ($\Delta^7\text{Li}_{\text{seawater-carb}} = -10$ to $+9\%$), although brachiopods show a narrow range of
117 fractionation ($\Delta^7\text{Li}_{\text{seawater-carb}} = 3.5$ – 5.5%) that is similar to inorganic fractionation
118 (Dellinger et al., 2018). Evolutionary changes in the composition from a
119 coccolithophore dominated carbonate in the Paleogene to a more equal share between
120 coccolithophores and foraminifers today (Schiebel, 2002) raise questions about the
121 potential impact on bulk carbonate derived isotopes. Combined with the geographic
122 differences in their importance for carbonate production and the differential
123 preservation potential of the two main carbonate producers it is imperative to assess the
124 importance of these processes on Li isotope composition.

125 We examine the Li isotope composition of core tops from several different
126 geographic locations in the Atlantic, as well as some shallow-water aragonitic sites
127 from the Bahamas. The aim is to determine whether bulk carbonate is a viable archive
128 for seawater Li isotopes, and if not, to determine the circumstances when it is not.

129

130 2.0 Samples

131 The Atlantic core-top samples used are largely taken from Geo Bremen cruises
132 of the research vessel RV Meteor between 1988 and 2000. The samples span the North
133 and South Atlantic from 70° north to 44° south (Fig. 1), relatively close to the shore
134 (~50km in the sample GeoB 11024-1 from the Galician continental margin, and ~180
135 km in the S. Atlantic sample 1719-5), as well as deep ocean sites. We also examine a
136 decarbonated samples from the Ocean Drilling Programme Site 980, on the Feni Drift
137 in the NE Atlantic, and a clay sample from GeoB 6409-2 from the central South
138 Atlantic. Sample depths range from 930 to 5389 m below sea-level (Table 1 and 2).

139 Of the 16 core-tops analysed, 7 consist largely of foraminiferal ooze with other
140 common carbonate particles and some opaline components, such as diatoms (Table 3).
141 Five core-tops (Table 3) contain optically trace amounts of aragonite, while two further
142 ones (GeoB 1724-3 and GeoB 11024-1) dominantly consist of quartz grains, with only
143 relatively little carbonate. These two latter core-tops were analysed to test whether
144 sections with trace-level carbonate (<10%) are still a viable seawater archive.

145 The Bahamian surface samples were collected from a several km² area near the
146 Exuma Cays on the eastern side of the Great Bahama Bank (Fig. 2), which is typically
147 considered the ‘type’ modern shallow water carbonate depositional analogue (Schlager
148 and Ginsburg, 1981). This relatively small geographic area in the Bahamas provides
149 multiple facies and different carbonate factories. This region has been used previously

150 to study B and U isotope behaviour in shallow water carbonates (Romaniello et al.,
151 2013; Zhang et al., 2017). Depth of the samples ranged from roughly 2–12 meters, with
152 depth varying on a daily basis with the tides. There is rapid exchange of water with tidal
153 cycles in the Exumas, with Atlantic surface water coming onto the bank-top and warmer
154 and slightly more saline waters coming off the bank-top. There have been multiple
155 papers describing the sediments and marine cements present in Exumas (Ginsburg and
156 Planavsky, 2008; Planavsky and Ginsburg, 2009; Whittle et al., 1993) and, therefore,
157 we provide only a brief description of the environment and samples. The sediment types
158 and environmental setting for each sample are listed in Table 2. Sediment grain size
159 varies from predominantly micrite (carbonate mud) to coarse grainstones. All
160 sediments are dominated by aragonite, but there may be trace amounts of high and low
161 Mg calcite (Zhang et al., 2017). The fine-grained material is typically derived from
162 green algae whereas the grainstones are a mix of algae and metazoan clasts and
163 nonskeletal grains (Wright and Burgess, 2005) We also analysed a marine hardground
164 and a stromatolite, which in the Bahamas are basically peloidal grainstones cemented
165 together (predominantly by botryoidal aragonite cements (Ginsburg and Planavsky,
166 2008)).

167

168 3.0 Methods

169 To determine the relative importance of coarse versus fine carbonate material,
170 which in the open ocean approximates the contribution of foraminifers versus
171 coccolithophores, bulk samples were washed and filtered at 20 microns. The carbonate
172 content (weight percent) of each sample was calculated based on total carbon (TC) and
173 total organic carbon (TOC) contents measured using a LECO-CS 200 element analyzer.
174 The calculation was made according to the equation $\text{CaCO}_3\% = 8.33 * (\text{TC}\% - \text{TOC}\%)$.

175 X-ray diffraction analysis was used to determine aragonite contents in two of the
176 samples. The sand fraction $> 63 \mu\text{m}$ was analysed microscopically for major sediment
177 contributors. The decarbonated sample was treated by addition of 12.5g HCl.

178 For the Atlantic samples the exchangeable fraction of the samples was leached
179 using 1M sodium acetate for 1 hour at room temperature (Tessier et al., 1979). The bulk
180 carbonate fraction of the samples was leached by two different methods. The first used
181 0.1M HCl for 1 hour at room temperature (Pogge von Strandmann et al., 2013). This
182 method has the advantage that no additional cation matrix is added to the sample, but
183 the potential drawback of using a strong acid is that any silicate fraction could also be
184 leached. Therefore, we also used a Tessier leaching method, where acetic acid was
185 buffered with sodium acetate to pH5 (Tessier et al., 1979). This method should attack
186 silicates less, but has the disadvantage of adding significant amounts of Na to the
187 sample, which the cation exchange columns have to deal with.

188 In both cases, the leached carbonate samples were analysed for trace element
189 ratios using a quadrupole ICP-MS, with calibration standards and samples matrix-
190 matched to $10 \mu\text{g/g}$ Ca (and also to Na content in the case of Na-acetate leaches). This
191 is important to determine whether silicates have been inadvertently leached, by
192 examining ratios such as Al/Ca and Mn/Ca (Pogge von Strandmann et al., 2013). The
193 international reference standard JLs-1 was used to assess accuracy and precision, which
194 is within 5% for all elements analysed.

195 The residual fractions (after the exchangeable and carbonate fractions were
196 removed) were dissolved in concentrated HF-HNO₃-HClO₄, followed by concentrated
197 HNO₃ and 6M HCl.

198 Lithium isotopes of the Atlantic samples were purified using a two-step cation
199 exchange method, which has been detailed for carbonates in numerous studies (Pogge

200 von Strandmann et al., 2017a; Pogge von Strandmann and Henderson, 2015; Pogge von
201 Strandmann et al., 2013). Analyses were performed on a Nu Instruments HR MC-ICP-
202 MS at the University of Oxford. Secondary standards run include seawater ($\delta^7\text{Li} = 31.3$
203 $\pm 0.6\text{‰}$, 2sd, n=62), USGS basalt BCR-2 ($\delta^7\text{Li} = 2.6 \pm 0.5\text{‰}$, 2sd, n=5) and shale SGR-
204 1 ($\delta^7\text{Li} = 3.6 \pm 0.4\text{‰}$, 2sd, n=3). SGR-1 was also leached for its carbonate and residual
205 fractions. The residual and bulk $\delta^7\text{Li}$ values of SGR-1 are identical (3.5 vs. 3.4‰,
206 respectively). Repeats of the samples analysed here also reproduce with an uncertainty
207 of $\pm 0.6\text{‰}$ (Table 1 and 2).

208 For the Bahamian samples the exchangeable fraction was removed with a
209 roughly one hour 1M ammonium acetate leach. The carbonate was dissolved in 0.05 M
210 HCl. Concentration analyses on the carbonate leaches were performed using a Thermo
211 Finnigan Element XR. Analytical uncertainty was less than 5% based on sample
212 duplicates and measurements of the USGS standard BHVO. A sample split of the acid
213 digest was brought up in 0.2N HCl and loaded Bio-Rad AG50W-X12 (200-400 mesh)
214 cation exchange resin pre-cleaned with 6N HCl. Matrix elements were eluted with 0.2N
215 HCl and then Li was eluted with 0.5N HCl (Dellinger et al., 2017). Li and Na
216 concentrations were analysed after column work, prior to Li isotope analysis. The Li
217 and Na post-column concentrations and the Li isotopic composition were measured
218 with a Thermo Finnigan Neptune Plus MC-ICP-MS at Yale Metal Geochemistry Center
219 using an ESI Apex-IR desolvating nebulizer. Li isotope data was collected at low
220 resolution in 1 block with 50 cycles per block. L-SVEC standard and an in-house Li
221 solution ($\delta^7\text{Li} = 43.5\text{‰} \pm 0.31\text{‰}$ relative to L-SVEC, 2sd, n = 50) was used to monitor
222 the long-term reproducibility of Li isotope analyses. The overall reproducibility and
223 accuracy of the Li procedure (sample digestion, Li separation, and Li isotope analysis)
224 were checked by repeated measurements of OSIL seawater ($\delta^7\text{Li} = 30.7\text{‰} \pm 0.5\text{‰}$

225 relative to L-SVEC, 2sd, n = 7) and BHVO-2 ($\delta^7\text{Li} = 4.4\text{‰} \pm 0.3\text{‰}$ relative to L-SVEC,
226 2sd, n = 7 digestions).

227

228 4.0 Results

229 *4.1 Atlantic Core-tops*

230 Examination of the carbonate mineralogy of the samples shows that the bulk
231 CaCO_3 composition varies between ~4 and 85%, and total organic carbon between ~0.2
232 and 2.4% (Table 3). At least one sample (GeoB 4315-1) also contains significant
233 (~17%) aragonite. By means of the bulk carbonate $>20\mu\text{m}$ CaCO_3 data and the
234 proportion of that grain size in the total sediment (Table 3), it is possible to calculate
235 the foraminifer carbonate content in the total sediment, and then assume that the
236 difference is coccolith carbonate ($<20\mu\text{m}$). As shown in Table 3, some samples are
237 dominated by foraminiferal carbonate, while others are more dominated by coccolith
238 carbonate.

239 The exchangeable fraction's $\delta^7\text{Li}$ for all samples ranges between 13.8 and
240 16.7‰, with the clay samples' exchangeable $\delta^7\text{Li}$ within that range (14.2–14.4‰). The
241 resulting $\Delta^7\text{Li}_{\text{seawater-exch}}$ is 14.6–17.5‰, close to the theoretical value of 15–16‰ of
242 authigenic clays required to balance seawater $\delta^7\text{Li}$ (Chan et al., 1992; Hathorne and
243 James, 2006; Misra and Froelich, 2012).

244 Carbonate leaches have $\delta^7\text{Li}$ ranging between 10.5 and 26.8‰, with no
245 relationship between $\delta^7\text{Li}$ and the fraction of carbonate in the sample or total organic
246 carbon (Table 1). The carbonate leach of SGR-1 also has a $\delta^7\text{Li}$ of 22.4‰. Generally,
247 the Al/Ca and Mn/Ca of the HCl leaches are higher than those of the Na acetate leaches
248 (Table 1), although all are below the calculated nominal cutoff value above which
249 silicate Li would begin to affect total $\delta^7\text{Li}$ (Pogge von Strandmann et al., 2013).

250 Generally, the $\delta^7\text{Li}$ values of both leaches are similar for each sample, with the average
251 difference 0.11‰, and a maximum difference of 2.6‰ (Fig. 3).

252 The silicate residues have $\delta^7\text{Li}$ values of -1.8 to 2.6‰, with an average of 0.8‰,
253 generally similar to the values of the upper continental crust (Sauzéat et al., 2015), and
254 to marine sediments (Chan et al., 2006). The Li concentrations in these fractions are
255 quite variable (4.1–72 $\mu\text{g/g}$), and between 2.3 and 36% of total Li in these samples is
256 located in the carbonate fractions, clearly demonstrating how important a clean leach
257 of the carbonate fraction is.

258

259 *4.2 Bahamas surface samples*

260 The Bahamian aragonite samples have a relatively narrow range in Li/Ca (18.6
261 ± 4 $\mu\text{mol/mol}$) (Table 1). As would be expected, given aragonite mineralogy, their
262 Sr/Ca is also significantly higher than the dominantly calcitic core-tops: $\sim 10 \pm 1$
263 mmol/mol , compared to ~ 1.5 mmol/mol in the core-tops. The $\delta^7\text{Li}$ varies between 20.2
264 and 22.5‰, and the average $\Delta^7\text{Li}_{\text{seawater-arag}} = 9.6 \pm 0.6$ ‰.

265

266 5.0 Discussion

267 *5.1 Bahamas samples*

268 There is no correlation between elemental ratios such as Li/Ca, Mg/Ca or Sr/Ca
269 and the narrow range in $\delta^7\text{Li}$ in these samples. The key observation from these entirely
270 aragonitic samples is that the $\Delta^7\text{Li}_{\text{seawater-sample}}$ of 9.6 ± 0.6 ‰ (Fig. 4) is within the range
271 shown for inorganic aragonites (11.7 ± 0.5 ‰ (Marriott et al., 2004b)), given the ± 1.0 ‰
272 uncertainty of the latter study. Biogenic aragonites, from molluscs (clams) and corals,
273 exhibit a wider scatter of ~ 8 – 16 ‰ (Dellinger et al., 2018; Marriott et al., 2004a;
274 Rollion-Bard et al., 2009). Therefore, this study's bulk aragonites exhibit a very narrow

275 range in $\Delta^7\text{Li}$, which is entirely consistent with inorganic and biogenic aragonites (Fig.
276 4). Samples from this area have shown variations in boron isotopes between different
277 carbonate types (e.g. ooids, cements, carbonate muds and micrite (Zhang et al., 2017)),
278 which is thought to result from microbially-mediated carbonate precipitation. The
279 relative invariance of our Li isotope data suggest that, in aragonites at least, the Li
280 isotope fractionation factor is relatively constant in all these different carbonate types.
281 Assuming limited diagenetic effects, it appears that bulk aragonites can be used to track
282 past seawater $\delta^7\text{Li}$ values.

283

284 *5.2 Core-top Li/Ca ratios*

285 The Li/Ca ratios of the core-top carbonate leaches ranges between 21 and 71
286 $\mu\text{mol/mol}$. There is no trend between Li/Ca and the proportion or weight of the fine vs.
287 the coarse carbonate fraction, suggesting no trend with the foraminifer to coccolith
288 ratio. However, the Li/Ca range of samples that are dominated by foraminiferal ooze
289 (average 25 $\mu\text{mol/mol}$) are only slightly higher than modern and Holocene foraminifera
290 (<18.5 (Hall and Chan, 2004; Hathorne and James, 2006; Marriott et al., 2004b; Misra
291 and Froelich, 2009). In contrast, samples that are largely agglutinated abiotic carbonate,
292 combined with aragonites and other particles (Table 3), tend to have higher Li/Ca ratios,
293 averaging ~ 34 $\mu\text{mol/mol}$. Some biogenic carbonates have much higher Li/Ca values,
294 with molluscs ranging from ~ 20 – 60 $\mu\text{mol/mol}$ and high-Mg calcites, such as
295 echinoderms, with values close to 100 $\mu\text{mol/mol}$ (Dellinger et al., 2018). In contrast,
296 benthic foraminifera, corals and aragonitic molluscs have Li/Ca values of ~ 2 – 20
297 $\mu\text{mol/mol}$ (Dellinger et al., 2018). Bulk carbonates from the geologic record have Li/Ca
298 ratios that have a larger spread from 0.9 to 46 $\mu\text{mol/mol}$ (Lechler et al., 2015; Pogge
299 von Strandmann et al., 2017a; Pogge von Strandmann et al., 2013). Hence, the type of

300 carbonate mineralogy and the mixture of calcifying organisms is likely controlling
301 significant parts of the variation in Li/Ca. The two samples dominated by quartz, with
302 only little carbonate, have an average of $\sim 59 \mu\text{mol/mol}$. This is unlikely to stem directly
303 from leaching of quartz or opal, because ratios such as Al/Ca, Mn/Ca and Sr/Ca are still
304 low. However, it is possible that cation exchange occurred between the silicates and
305 trace carbonates, increasing the concentration of some elements, especially Li.

306 Early stage diagenesis in carbonates is sometimes monitored by comparing
307 Sr/Ca ratios to Mn or Mn/Ca, where diagenesis should decrease Sr/Ca and increase Mn
308 (Korte et al., 2005; van Geldern et al., 2006). In our samples, there is no trend between
309 Sr/Ca (or Li/Ca) and Mn/Ca or $\delta^7\text{Li}$. Further, Sr/Ca ratios are uniformly higher than
310 nominally diagenetic cutoff values (Brand and Veizer, 1980; Korte et al., 2005),
311 suggesting that these samples have not been resolvably diagenetically perturbed.

312 There is no simple trend in our carbonates with latitude (Fig. 6), suggesting no
313 direct controlling influence by temperature, nor with depth (Fig. 7), although inorganic
314 carbonate Li/Ca ratios are inversely correlated with temperature, with values decreasing
315 by a factor of ~ 3 for a 30°C increase in temperature (Marriott et al., 2004a; Marriott et
316 al., 2004b). This may suggest that there is an overarching biological control on Li/Ca,
317 especially given that more Li/Ca variation exists at high latitudes, which may mean that
318 there is a secondary control on Li/Ca, via a temperature and location control on the
319 types of carbonate growing in those waters (Fig. 6).

320 There is also no obvious offset in Li/Ca (or Sr/Ca) in core-top samples that have
321 aragonite, compared to those that do not (Fig. 6), in contrast to the pure aragonitic
322 samples from the Bahamas. The geographic difference of the aragonite saturation
323 horizon in the Atlantic with higher saturation in the North Atlantic than the South
324 Atlantic (Jiang et al., 2015) should have resulted in a geographic bias if the trace

325 amounts of aragonite in these core-tops would significantly affect the bulk mass
326 balance. Hence, in detail, elemental ratios are likely to be controlled by the mix of
327 carbonate mineralogy and biogenic carbonate producer at each site, modified by
328 external parameters such as temperature. This is not unexpected, and highlights why
329 foraminifera are generally the archive of choice for reconstruction of past Li/Ca ratios
330 (Lear et al., 2010; Lear and Rosenthal, 2006).

331

332 *5.3 Core-top exchangeable fractions*

333 In principle, Li from seawater will be adsorbed onto the exchangeable fraction,
334 with an inherent isotope fractionation. Whether there is a fractionation difference
335 between adsorbed and structurally bound Li in silicate clays has never been fully
336 addressed. There is potentially a mineralogical effect on the fractionation factor (Millot
337 and Girard, 2007; Pistiner and Henderson, 2003; Vigier et al., 2009; Wimpenny et al.,
338 2015; Wimpenny et al., 2010), although the minerals withdrawing Li from seawater by
339 sorption are expected to have a broadly similar fractionation as during authigenic clay
340 neoformation, of ~15‰ (Chan et al., 1992; Hathorne and James, 2006; Pogge von
341 Strandmann et al., 2008).

342 The data from the core-top exchangeable fractions leached during this study
343 suggest a narrow range in $\delta^7\text{Li}$, on average $16.5 \pm 0.8\text{‰}$ lower than seawater (Fig. 8).
344 The exchangeable fraction from the decarbonated sample has a similar $\delta^7\text{Li}$ (~14‰),
345 suggesting that the exchangeable sites in all samples are on the silicate portion of each
346 sample. In other words, there is apparently no exchangeable uptake onto carbonate
347 surfaces, or if there is, it imposes the same fractionation factor.

348 Another unknown factor in the behaviour of lithium in the oceans is how much
349 Li is taken up into exchangeable sites. Mass balance of Li in the exchangeable leach

350 compared to the residual and carbonate samples suggests that $2.0 \pm 0.6\%$ is sorbed onto
351 silicate exchangeable sites. This is approximately a factor of four less Li than is being
352 taken into carbonates in these samples, suggesting that sorbed Li is an insignificant sink
353 from the global oceans. Until laboratory experiments are conducted, though, it will be
354 unknown how long the exchangeable isotope ratio can be preserved for, and hence
355 whether this phase can be used as an archive of past seawater $\delta^7\text{Li}$ values.

356

357 *5.4 Core-top carbonate fractions*

358 Generally, the two different carbonate leaching methods employed yield the
359 same $\delta^7\text{Li}$ values. There are some samples where the difference between the two
360 leaches is up to $\sim 2.5\%$, easily resolvable outside of analytical uncertainty. In most of
361 these cases, the Na acetate leach is isotopically heavier, and has slightly lower Al/Ca,
362 Mn/Ca and Li/Ca values. Given that leaching of silicates would drive $\delta^7\text{Li}$ lower and
363 element/Ca ratios higher, it seems likely that the difference in $\delta^7\text{Li}$ is due to the addition
364 of Li (and other elements) leached from silicates during attack with dilute HCl.
365 Therefore, while the values are generally similar (Fig. 3), leaching with Na acetate is
366 likely a more robust method for attaining Li from the carbonate fraction only.

367 In samples that contain no aragonite, the $\Delta^7\text{Li}_{\text{seawater-carbonate}}$ is $6.1 \pm 1.3\%$ (2sd)
368 (Fig. 5). There is no trend with latitude or ocean depth similar to the Li/Ca ratio (Fig.
369 7). This isotopic range is similar to the range suggested by inorganic calcite
370 precipitation from seawater of $\sim 3\text{--}5\%$ (Marriott et al., 2004b), albeit those experiments
371 used Li concentrations ~ 10 times higher than seawater. The fractionation factor
372 observed is less than calcite grown from pure water without other trace elements ($\sim 8\%$
373 (Marriott et al., 2004a)). Planktic foraminifera exhibit a species-specific fractionation
374 factor of $0\text{--}4\%$ (Hall et al., 2005; Hathorne and James, 2006), while benthic

375 foraminifera (*Uvigerina* spp.) show fractionation of 4–10‰ (Marriott et al., 2004b).
376 Brachiopods incur ~3.5–5.5‰ fractionation (Dellinger et al., 2018). In contrast,
377 molluscs, especially oysters, are highly variable, with $\Delta^7\text{Li}_{\text{seawater-carbonate}} \sim -10$ to +8‰,
378 with large differences within even mono-mineralic shells, thought to be due to both
379 environmental and calcification effects (Dellinger et al., 2018). Overall, our relatively
380 deep marine samples are within the ranges for inorganic and foraminiferal calcite, albeit
381 with a slightly higher average. There is also no relationship between $\delta^7\text{Li}$ (or Li/Ca)
382 and the % the fine fraction makes up of each sample (Table 3), which can be used as a
383 first order approximation of the ratio of foraminifera to coccoliths.

384 In comparison, inorganic aragonite imparts a higher fractionation of $\Delta^7\text{Li}_{\text{seawater-}}$
385 $\text{carbonate} \sim 11\%$ (Marriott et al., 2004b), similar to our Bahamian aragonitic samples.
386 Equally, aragonitic molluscs and corals impart greater fractionation of 8–16‰
387 (Dellinger et al., 2018). Our core-top carbonate samples that contain some aragonite
388 (Table 3) have a much greater $\Delta^7\text{Li}$ variability of 4.7 to 20.3‰, albeit this range is
389 dominated by the exceptionally light and anomalous sample from the Galician coast
390 discussed below. The Atlantic samples with trace aragonite range from 4.7 to 6.4‰
391 (average $5.4 \pm 0.7\%$), effectively indistinguishable from the calcitic samples. This is
392 not necessarily unexpected, given the only trace levels of aragonite. Sample GeoB4315-
393 1, however, contains around 17% aragonite, and exhibits a $\Delta^7\text{Li}_{\text{seawater-carbonate}} = 6.1\%$.
394 Assuming the observed average distribution of Li between calcite and aragonite, and
395 their fractionation factors, this proportion should yield a fractionation of ~6.7‰, within
396 uncertainty of that observed. Hence, the presence of aragonite can perturb the carbonate
397 $\delta^7\text{Li}$, but in these core-top samples the proportion of aragonite to calcite is too small to
398 have a significant effect. Extrapolating this mass balance suggests that the aragonite
399 content would have to be >35% before the bulk $\Delta^7\text{Li}$ composition would be resolvably

400 affected. Modern open marine sediments are consistently dominated by calcite, and
401 rarely have >10% aragonite, meaning that open marine core-tops should consistently
402 be uniformly isotopically offset from seawater.

403 Two of our core-top samples (GeoB1724-4 and 11024-1) predominantly consist
404 of quartz, with some volcanic ash and opaline organisms, and were analysed to test
405 whether trace carbonates in sections are still viable seawater archives. The former
406 sample has a “normal” calcite $\delta^7\text{Li}$ value, whereas the latter has the lowest $\delta^7\text{Li}$
407 measured here. 1724-4 contains some detrital carbonate, and, given the low Al/Ca and
408 Mn/Ca ratios and carbonate-like $\delta^7\text{Li}$, it seems likely that this was the only phase
409 leached by the Na acetate method. Thus, this leaching method appears to be able to be
410 applied to some modern very carbonate-poor samples (4.2% carbonate).

411 Sample 11024-1 is from the Galician continental margin, and has $\delta^7\text{Li}$ values of
412 $\sim 11\text{‰}$. This sample also exhibits higher Li/Ca than other samples (Fig. 6). Given that
413 the sample also has low Al/Ca, these higher Li/Ca values are unlikely to stem from
414 silicate dissolution. The $\Delta^7\text{Li}$ value of $\sim 20\text{‰}$ is considerably greater than even from the
415 pure aragonitic Bahamian samples, and therefore additional processes must be lowering
416 the $\delta^7\text{Li}$. While very low $\delta^7\text{Li}$ values ($\sim 5\text{‰}$) have been reported from the (radiolarian-
417 rich) core-top carbonates of ODP Site 851B (eastern equatorial Pacific) (You et al.,
418 2003), no trace element data were included in that study, and hence it is possible that
419 radiolarian silicates were partially leached, lowering the bulk $\delta^7\text{Li}$.

420 There are therefore two possibilities to explain the low $\delta^7\text{Li}$ in the sample from
421 the Galician coast: 1) recrystallisation of the carbonate and incorporation of Li from the
422 silicate fraction; 2) localised incorporation of Li from anthropogenic sources such as
423 fertiliser, given this is a relatively near-shore site. The latter possibility is unlikely,
424 however, given that this is still an open ocean site. We note that this sample has the

425 highest proportion of Li in silicates relative to carbonates (only ~2.3% of the total Li is
426 in the carbonate fraction). Data from such carbonate-poor samples must therefore be
427 treated with a degree of caution when reconstructing past seawater $\delta^7\text{Li}$.

428

429 6.0 Conclusions

430 In this study we determined the bulk Li isotope composition of carbonate from
431 27 Bahamian aragonitic samples, and the exchangeable, carbonate and residual phases
432 for Li isotopes of 16 Atlantic core-top sediments, to determine whether bulk carbonates
433 can serve as a reliable archive of seawater Li isotope ratios.

434 Around 2% of the total Li is situated in the exchangeable fractions, which has a
435 ~16.5‰ fractionation from seawater. Carbonate leaching techniques using dilute HCl
436 and acetic acid buffered with Na acetate are compared. While $\delta^7\text{Li}$ values are similar,
437 the Na acetate method yields slightly lower Al/Ca and Mn/Ca values and higher $\delta^7\text{Li}$.
438 These results suggest that the HCl method can weakly leach the silicate fractions of the
439 sediments. We therefore recommend that bulk carbonates, if there is siliciclastic
440 material in the sample, are leached using acetic acid buffered with Na acetate.

441 Bulk carbonate samples that only contain calcite have a uniform and constant
442 offset from seawater of $\Delta^7\text{Li}_{\text{seawater-carbonate}} = 6.1 \pm 1.3\text{‰}$ (2sd), close to that exhibited by
443 inorganic and several biogenic calcites. Five core-tops contain trace amounts of
444 aragonite, but exhibit no difference in their $\Delta^7\text{Li}_{\text{seawater-carbonate}}$. Mass balance agrees with
445 our analyses, and that even the most aragonite-rich core-top, with 17% aragonite, would
446 only see 0.6‰ more fractionation due to this difference in mineralogy when compared
447 to a pure calcite sample.

448 In contrast, the pure aragonite samples from the Bahamas have $\Delta^7\text{Li}_{\text{seawater-}}$
449 $\text{carbonate} = 9.6 \pm 0.6\text{‰}$, in keeping with inorganic aragonite fractionation experiments.

450 Two core-top samples have <10% carbonate contents, and were analysed to test
451 whether trace carbonates are still a viable seawater archive. The calcite in one of these
452 samples (GeoB 1724-4) has a similar carbonate $\delta^7\text{Li}$ to the carbonate-rich core-tops,
453 while the other sample (from the Galician coast) has a very low carbonate $\delta^7\text{Li}$
454 ($\Delta^7\text{Li}_{\text{seawater-carbonate}} = 20\text{‰}$) that cannot be explained by any known carbonate
455 fractionation factors. This sample also has slightly higher Li/Ca values and could be
456 explained either by localised addition of anthropogenic Li, or, more likely by
457 recrystallisation of the carbonate, gaining Li from the silicate portion, which in this
458 sample is particularly enriched in Li.

459 Overall, core-top bulk carbonates (both calcites and aragonites) from the open
460 ocean are a reliable archive for seawater $\delta^7\text{Li}$. The lack of correlation between bulk
461 carbonate $\delta^7\text{Li}$ and latitude, depth or carbonate make-up suggests that bulk carbonates
462 may be a more robust archive than foraminifera, where vital effects may complicate the
463 signal. However, care must be taken concerning carbonate mineralogy, in that the
464 original carbonate type must be known before attempting to reconstruct seawater $\delta^7\text{Li}$
465 values. The potential effects of carbonate-poor samples must also be determined.
466 Overall using bulk carbonates as archives of palaeo-seawater $\delta^7\text{Li}$ clearly has high
467 potential, but it must be stressed that any values should be reproduced in different global
468 sections, to avoid small mineralogical effects, or potentially larger effects of cation
469 exchange.

470

471

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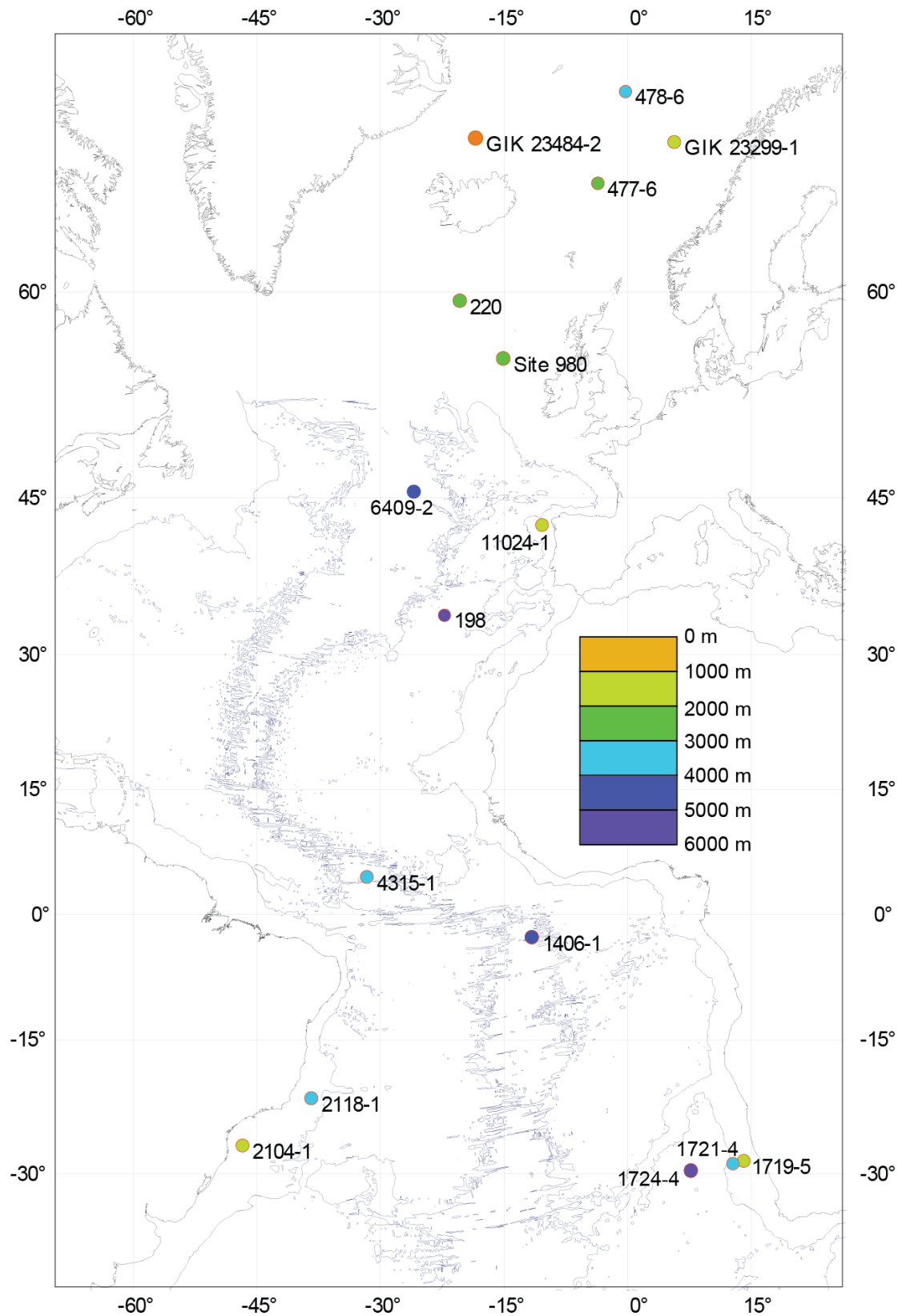
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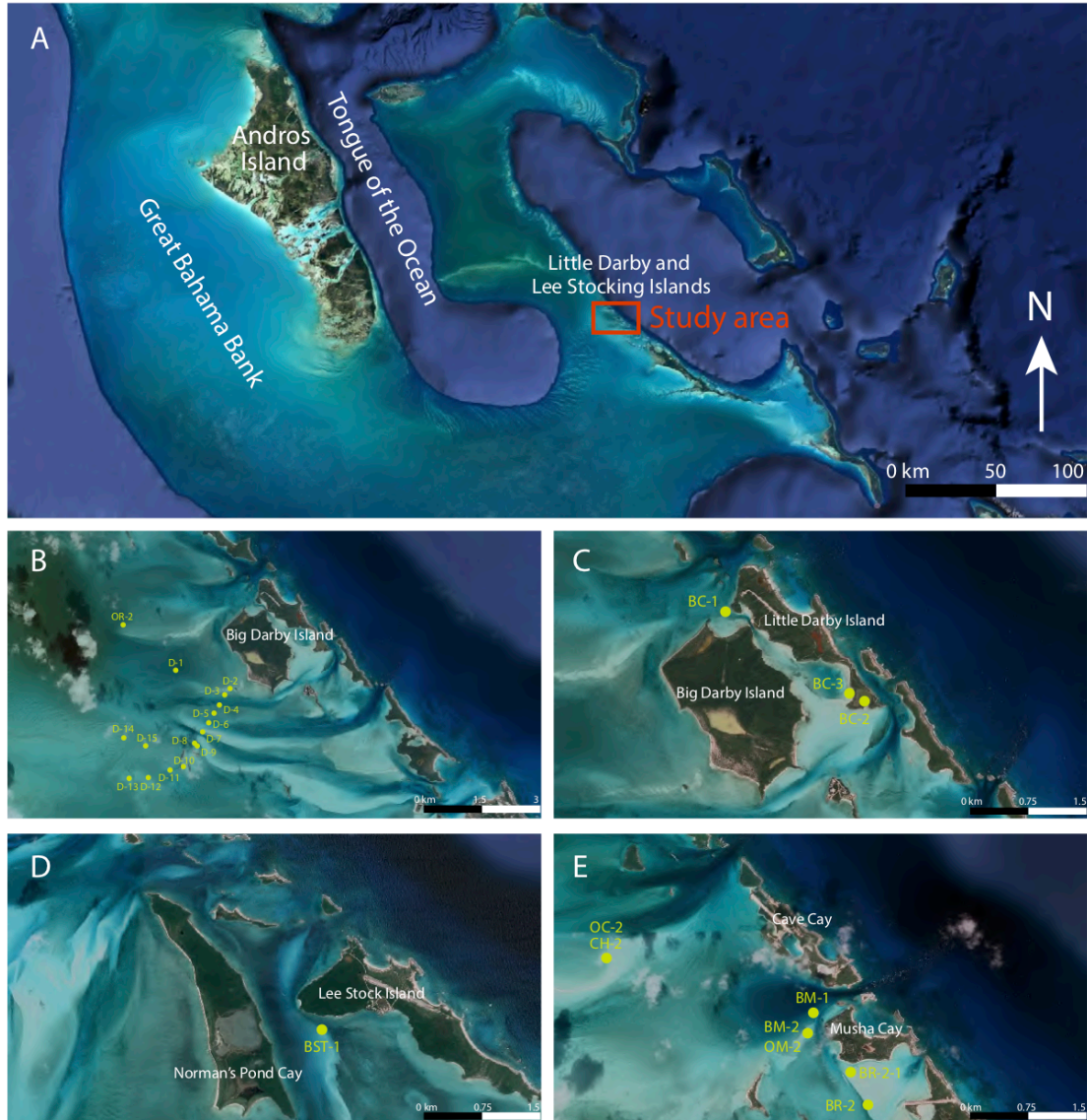
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676 Figure 1. Sample location map for the core tops. The 4000m contour is also shown.

677 Symbol colours represent the broad depth scale.

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680 Figure 2. Location of the examined surface samples from the Great Bahamas Bank.

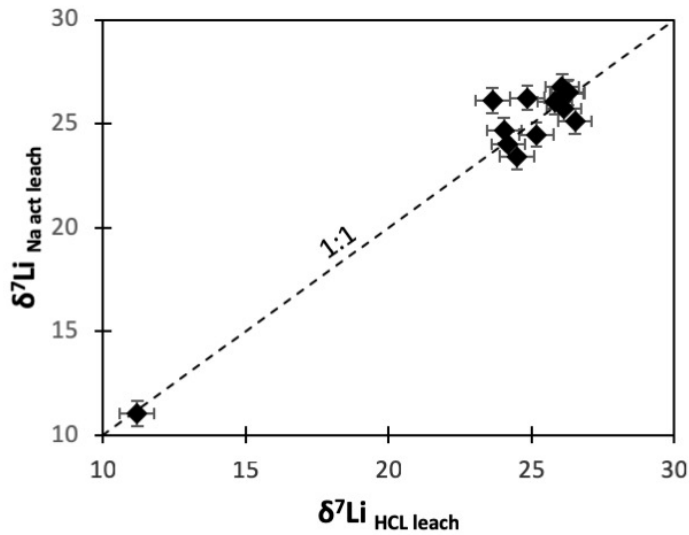
681 All samples are from the Exuma Cays on the eastern edge of the Great Bahamas Bank

682 (A). Samples are from active ooid shoals (white regions) and from regions covered by

683 sparse to dense green algae and seagrass (darker regions). Samples are dominated by

684 sand size grains except for the sites with seagrass cover shown in panel B.

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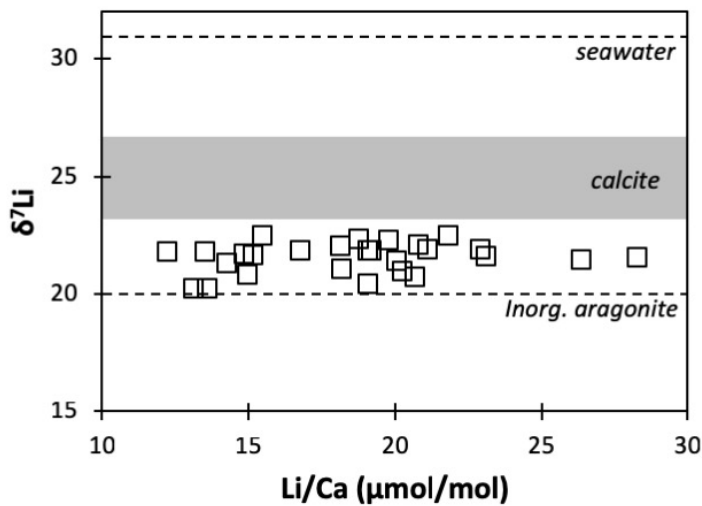


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688 Figure 3. Comparison of $\delta^7\text{Li}$ from carbonate fractions leached by dilute HCl,
 689 compared to those leached by acetic acid buffered with Na acetate. The dotted line
 690 represents a 1:1 gradient. See text for details.

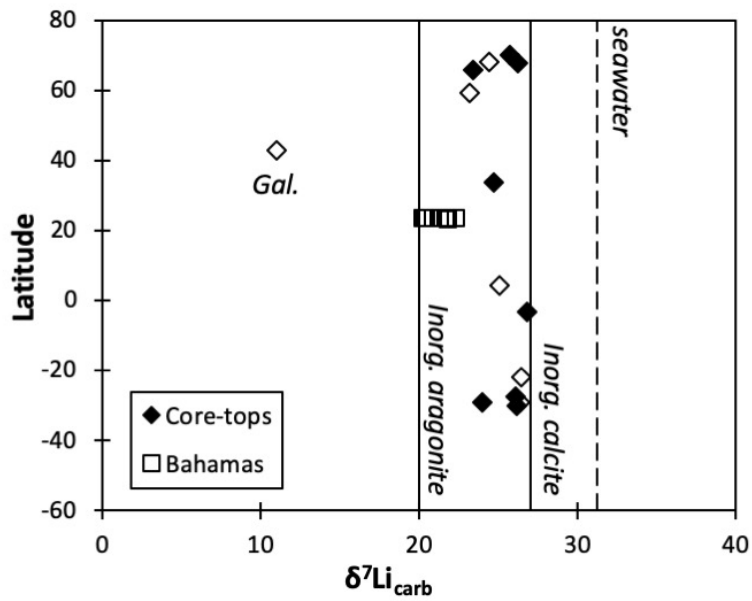
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693 Figure 4. Li isotope ratios and Li/Ca ratios for the Bahamian samples. Analytical
 694 uncertainty is smaller than the symbols. The grey box represents this study's core-top
 695 samples. Values for inorganic aragonite and calcite precipitated from seawater are
 696 from Marriott et al., 2004.

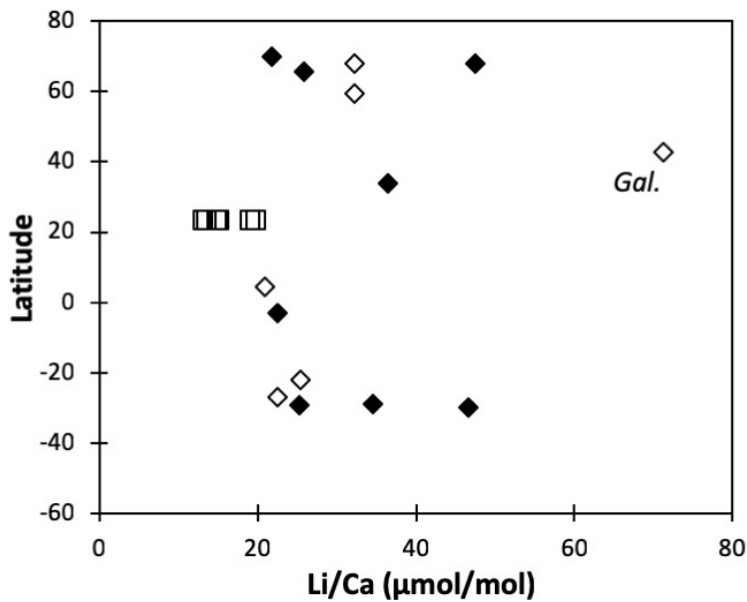
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699 Figure 5. Carbonate $\delta^7\text{Li}_{\text{carb}}$ values for core-tops and the Bahamas plotted against sample
 700 latitude. Open diamonds are samples with traces of aragonite. For the core-tops
 701 (diamonds), the Na acetate leach values are shown. Values for inorganic aragonite and
 702 calcite precipitated from seawater are from Marriott et al., 2004.

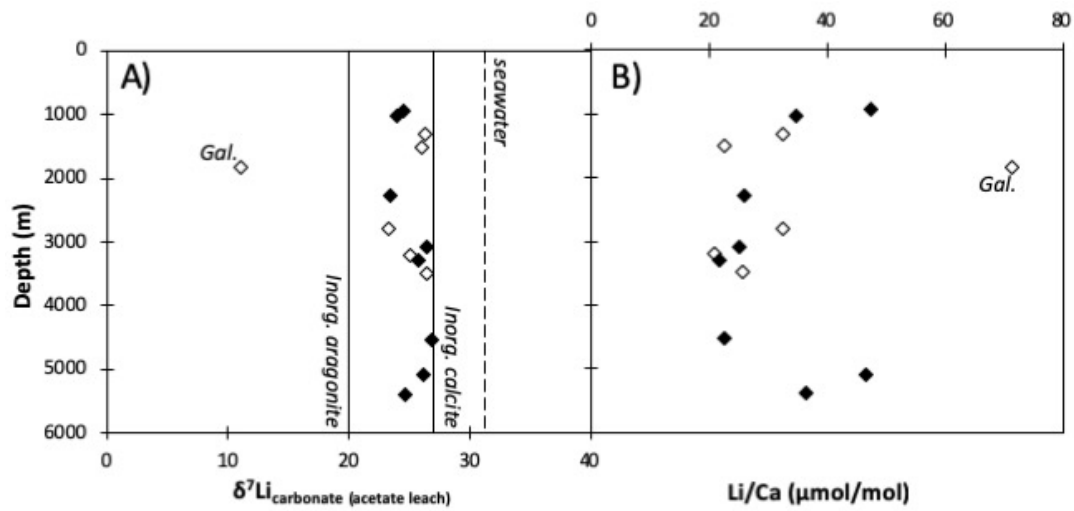
703



704

705 Figure 6. Carbonate Li/Ca ratios for the core-tops and the Bahamas plotted against
 706 sample latitude. Open diamonds are samples with traces of aragonite. The Galician
 707 coast sample GeoB 11024-1 is also highlighted.

708



709

710 Figure 7. A) Core-top carbonate $\delta^7\text{Li}$ plotted against sample depth below sea-level.

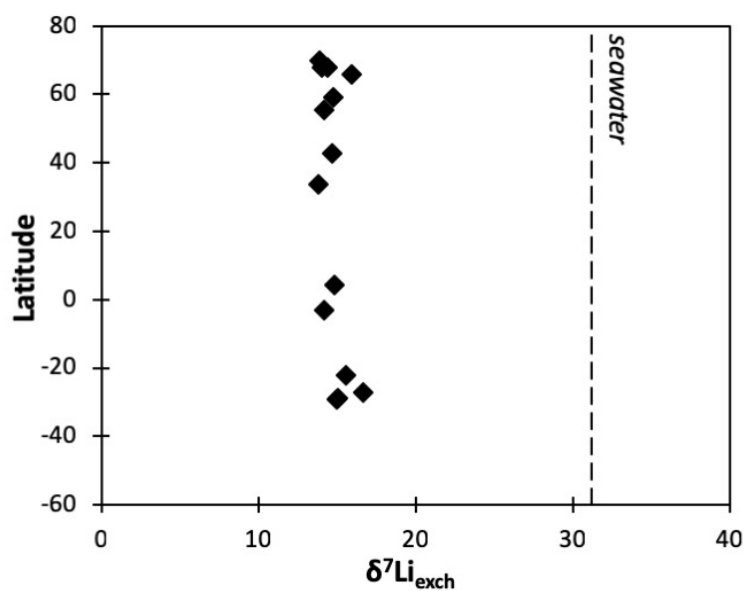
711 Open symbols are samples with traces of aragonite. The sample from the Galician

712 coast GeoB 11024-1 is also highlighted. Values for inorganic aragonite and calcite

713 precipitated from seawater are from Marriott et al., 2004. B) Li/Ca values from the

714 same samples.

715



716

717 Figure 8. Core-top exchangeable Li isotope ratios plotted against sample latitude.

718

Cruise	Carbonate (HCl)								$\delta^7\text{Li}$	2sd	Li/Ca $\mu\text{mol}/\text{mol}$
	$\delta^7\text{Li}$	2sd	Li $\mu\text{g}/\text{g}$	Li/Ca $\mu\text{mol}/\text{mol}$	Mg/Ca mmol/mol	Al/Ca mmol/mol	Mn/Ca mmol/mol	Sr/Ca mmol/mol			
M16-1	26.1	0.6	1.4	52.5	47.7	0.3	0.3	1.9	26.8	0.7	40.3
									25.9	0.2	43.1
M20-2	24.2	0.2	0.6	44.6	42.0	0.4	0.2	1.9	24.0	0.1	38.4
M20-2	26.2	0.2	0.6	35.2	36.8	0.1	0.5	1.1	26.4	0.3	35.4
M20-2	23.6	0.3	6.8	46.6	19.5	0.6	0.3	0.4	26.1	0.3	39.4
M23-2	25.8	0.2	1.3	22.5	14.6	0.1	0.2	0.8	26.1	0.2	20.4
									26.3	0.2	22.7
M23-2	26.3	0.3	1.2	35.5	31.3	0.3	0.2	1.4	26.5	0.1	36.1
											35.3
M38-1	26.5	0.6	1.0	30.9	43.3	0.2	0.3	1.7	25.1	0.5	28.8
M46-4											
Pos366-3	11.2	0.4	1.0	71.4	44.3	0.2	0.5	2.4	11.1	0.5	64.6
									11.7	0.5	60.2
M21-3	24.0	0.2	1.3	56.5	31.5	0.1	0.4	2.2	24.7	0.3	55.7
									25.5	0.1	56.2
M21-3	25.3	0.7	0.7	32.3	50.1	0.4	0.2	2.1	23.4	0.2	30.5
M26-2	24.5	0.5	0.8	45.9	17.3	0.3	0.2	2.1	23.4	0.8	45.1
M26-2	26.1	0.3	1.5	31.8	12.0	0.4	0.2	1.3	25.7	0.2	31.2
M7-3	24.8	0.4	1.1	32.3	12.4	0.4	0.3	1.4	26.2	0.4	31.9
M21-5	25.2	0.1	3.7	57.5	10.9	0.5	0.4	0.8	24.5	0.2	55.1
									24.1	0.2	53.1
ODP 162											

ples

719 B-Massha 2 20.9 0.1 15.0 18.5 0.5 10.6

720

Sample No.	Cruise	Lat	Long	Depth (m)	Remark	Residue $\delta^7\text{Li}$	2sd
1406-1	M16-1	-3.16	-11.23	4523		-1.8	0.1
rpt							
1719-5	M20-2	-28.93	14.17	1024		1.9	0.5
1721-4	M20-2	-29.18	13.09	3079		1.2	0.1
1724-4	M20-2	-29.98	8.04	5086		1.7	0.1
2104-1	M23-2	-27.29	-46.38	1505		-0.3	0.2
rpt							
2118-1	M23-2	-22.09	-38.02	3482		-0.4	0.2
rpt							
4315-1	M38-1	4.17	-31.28	3198		1.4	0.2
rpt							
6409-2	M46-4	-44.51	-21.72	4296	(clay)	0.2	0.5
11024-1	Pos366-3	42.70	9.76	1831	(<63 μm)	-1.5	0.2
rpt							
198	M21-3	33.81	-21.92	5389		1.9	0.1
rpt							
220	M21-3	59.26	-19.98	2797		1.2	0.4
477-6	M26-2	65.82	-3.27	2275		2.6	0.4
478-6	M26-2	70.00	0.06	3298		1.7	0.2
GIK 23299-1	M7-3	67.78	6.01	1305		1.2	0.2
GIK 23484-2	M21-5	67.94	-18.04	930		1.7	0.4
rpt							
Site 980	ODP 162	55.48	-14.70	2179	(decarbonated)	0.3	0.3

Bahamas samples

Site description

Sample

BM-2	B-Massha 2	23.541	-76.168	unvegetated shoals	superfi
BR-2-1	B-Rudder 2	23.535	-76.154	unvegetated shoals	superfi
OM-2	Ooid Massha 2	23.537	-76.161	unvegetated shoals	superfi
721 BC-2	B-core 2	23.505	-76.124	sparse green algae and seagrass	peloids

722

723

Cruise	CaCO ₃	TOC	Aragonite	Grain size		CaCO ₃	TOC	CaCO ₃	CaCO ₃	Fine fraction
	% bulk	%	wt.-%	% <20µm	% >20µm	% >20µm		% >20µm	% <20µm calc.	by weight %
M16-1	65.0	0.9		25.0	75.0	73.6	0.71	55.2	9.8	66.4
M20-2	76.4	2.4		24.7	75.3	93.2	0.32	70.2	6.2	67.3
M20-2	84.8	0.4								64.9
M20-2	4.2	0.5								41.5
M23-2	18.4	1.2								80.3
M23-2	66.8	0.2		32.6	67.4	76.5	0.17	51.5	15.3	40.6
M38-1	81.4		16.7	45.9	54.1	60.3	0.59	32.6	48.8	46.7
M46-4										
Pos366-3										65.0
M21-3	58.0	0.6		92.0	8.0	60.0	0.48	4.8	53.2	94.3
M21-3	69.2	0.3		36.7	63.3	79.6	0.25	50.4	18.8	41.1
M26-2	80.2	0.5		25.0	75.0	70.0	0.33	52.5	27.7	36.9
M26-2	48.3	1.1		78.6	21.4	44.3	1.10	9.5	38.9	89.9
M7-3	41.0	0.9		86.1	13.9	39.0	0.96	5.4	35.5	97.2
M21-5										72.1

Table 3. Carbonate mineralogy and observational contents of the core-top samples.