

## THE EFFECTS OF DIAGENESIS ON LITHIUM ISOTOPE RATIOS OF SHALLOW MARINE CARBONATES

MATHIEU DELLINGER<sup>\*\*\*</sup>, DALTON S. HARDISTY<sup>§</sup>, NOAH J. PLANAVSKY<sup>\*\*\*\*</sup>, BENJAMIN C. GILL<sup>§§</sup>, BORIANA KALDERON-ASAEL<sup>\*\*\*</sup>, DAN ASAEL<sup>\*\*\*</sup>, THOMAS CROISSANT<sup>\*</sup>, PETER K. SWART<sup>§§§</sup>, and A. JOSHUA WEST<sup>\*\*</sup>

**ABSTRACT.** In this study, we present new data on the  $\delta^7\text{Li}$  values and  $\text{Li}/(\text{Ca}+\text{Mg})$  ratios of carbonate cores from the Great Bahama Bank (Clino, Unda), a deep water core off of the bank top (ODP Leg 166 Site 1007), and the coralline Key Largo Limestone. We use these samples to evaluate the influence of meteoric diagenesis, marine burial diagenesis, and dolomitization on the Li isotope system in carbonates. We find that recrystallization of aragonite to low-Mg calcite in the presence of meteoric fluids results in a systematic decrease of the  $\text{Li}/(\text{Ca}+\text{Mg})$  ratio in Clino, Unda and Key Largo samples, due to the lower  $\text{Li}/(\text{Ca}+\text{Mg})$  ratio in meteoric fluids compared to seawater. For Li isotopes, we observe that the  $\delta^7\text{Li}$  of meteorically altered low-Mg calcite is  $+22.0 \pm 3.8\text{‰}$  ( $n=28$ ,  $1\sigma$ ), which is coincidentally similar to the original aragonite-rich sediments ( $+22 \pm 1\text{‰}$  in the Bahamas,  $+18 \pm 1\text{‰}$  in Key Largo), but with a larger variability (from  $+15$  to  $+27\text{‰}$ ). We interpret these features as reflecting the overprinting of primary Li during meteoric alteration with a highly variable isotope signature that may be controlled by a combination of local porewater and/or global climatic conditions; in either case, meteoric diagenesis produces isotopic signatures that are unrelated to seawater composition. In contrast, marine burial diagenesis and dolomitization of Clino and Unda sediments under “fluid-buffered” conditions result in Li isotope composition that is similar ( $+30.2 \pm 1.5\text{‰}$ ,  $n=36$ ,  $1\sigma$ ) to modern seawater ( $+31\text{‰}$ ). For Site 1007, the  $\delta^7\text{Li}$  values range between  $+23$  permil and  $+31$  permil. We interpret this range as reflecting a combination of varying diagenesis style (fluid to sediment-buffered) and varying contribution of calcite derived from pelagic sediments, with distinct isotopic composition due to primary mineralogy. Altogether, our results show that diagenesis does not invalidate the use of bulk carbonates for deriving Li isotope paleo-records, but the reliability of past carbonates as recorders of seawater  $\delta^7\text{Li}$  values will depend on carefully characterizing their diagenetic history.

Keywords: Bahamas, diagenesis, lithium isotopes, carbonates, dolomite

### 1. INTRODUCTION

The lithium (Li) isotope composition ( $\delta^7\text{Li}$ ) of ancient carbonate rocks has emerged as a promising proxy for tracing past weathering and hydrothermal processes (Hathorne and James, 2006; Misra and Froelich, 2012; Pogge von Strandmann and others, 2013). Lithium has two stable isotopes,  $^7\text{Li}$  and  $^6\text{Li}$ , that are strongly fractionated during water-rock interaction, with the lighter isotope,  $^6\text{Li}$ , usually preferentially incorporated into secondary minerals relative to the heavy isotope,  $^7\text{Li}$  (Chan and others, 1992; Huh and others, 1998; Dellinger and others, 2015). Interest in applying this proxy has led to the publication of Li isotope records from past carbonate, using specific organisms like foraminifera (Misra and Froelich, 2012), brachiopods (Pogge

\* Department of Geography, Durham University, South Road, Durham, DH1 3LE, United Kingdom

\*\* Department of Earth Sciences, University of Southern California, 3651 Trousdale Pkwy, Los Angeles, California 90089, USA

\*\*\* Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06511, USA

§ Department of Earth and Environmental Sciences, Michigan State University, 288 Farm Lane, East Lansing, Michigan 48824, USA

§§ Department of Geosciences, Virginia Polytechnic and State University, Blacksburg, Virginia, USA

§§§ Department of Marine Geosciences, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149, USA

Corresponding author: mathieu.dellinger@durham.ac.uk

von Strandmann and others, 2017) and belemnites (Ullmann and others, 2013), as well as bulk shallow- and deep-water carbonates (Pogge von Strandmann and others, 2013, 2019; Lechler and others, 2015). These studies have documented significant Li isotope variations during geologically short warming (Lechler and others, 2015; Pogge von Strandmann and others, 2013; Lechler and others, 2015) and cooling events (Pogge von Strandmann and others, 2017) as well as long-term gradual changes in the  $\delta^7\text{Li}$  value of the ocean (Misra and Froelich, 2012). These changes have been interpreted as resulting predominately from variations in continental and reverse weathering over time, providing new insights into the evolution and operation of the long-term global carbon cycle. However, the reliability of the Li isotope proxy in carbonate depends upon the extent to which the initial  $\delta^7\text{Li}$  value of seawater is influenced by isotope effects during carbonate precipitation (for example, mineralogy, vital effects, ocean environmental parameters) and subsequently by diagenetic processes. Several studies have documented Li isotope effects during carbonate formation, both for abiogenic (Marriott and others, 2004a, 2004b; Taylor and others, 2019) as well as biogenic carbonates (Hathorne and James 2006; Rollion-bard and others, 2009; Misra and Froelich, 2012; Dellinger and others, 2018). Yet so far, very little is known about the behavior of Li isotopes during diagenesis—despite some evidence for potentially significant post-depositional alteration of primary values (Ullman and others, 2013).

There are a wide range of diagenetic processes that can influence the geochemical composition of carbonates (Brand and Veizer, 1980; Lohmann, 1988; Swart, 2015; Hood and others, 2018). Meteoric diagenesis occurs via interaction between meteoric or groundwater fluids and carbonates, primarily when carbonates are exposed to the atmosphere during seawater low-stands or by tectonic uplift (James and Choquette, 1984; Lohmann, 1988). Meteoric fluids generally have low to neutral pH and are undersaturated with respect to carbonate phases. These fluids dissolve primarily aragonite and high-Mg calcite (HMC) which are the most soluble phases, eventually reach calcite saturation, and then precipitate low-Mg calcite (LMC) that is stable under meteoric conditions (Lohmann, 1988; Swart, 2015). The composition of the meteoric fluids is influenced by chemical processes within the open systems of the soil vadose zones (Moore and Wade, 2013a), and therefore these fluids may have different  $\delta^7\text{Li}$  values and Li/Ca ratios relative to the original composition of carbonates (Pogge von Strandmann and others, 2017).

In addition to meteoric diagenesis, marine burial diagenesis can lead to the mineralogical transformation of primary carbonate, and, depending in part of fluid-to-rock ratios, can alter the primary chemical signature of carbonates in the process (Banner and Hanson, 1990). This type of diagenesis takes place in the marine environment and can occur below the meteoric diagenesis zone. In this process, primary aragonitic carbonates are dissolved by marine pore fluids, and secondary low-Mg calcite and/or dolomite are precipitated (Moore and Wade, 2013b). Marine pore fluids usually have seawater-like composition but can also be influenced by reactions with silicates if present, or by mixing with fresh groundwater fluids. The style of marine burial diagenesis is controlled by the permeability of the sediments and the fluid advection rate (Melim and others, 2001; Fantle and others, 2010; Higgins and others, 2018). When diagenesis occurs in a closed system (for example, for low rates of fluid advection and low permeability), the composition of the diagenetic carbonates is primarily determined by the original composition of the sediments (“sediment-buffered” diagenesis; Higgins and others, 2018). For high fluid flow rates and permeability, open-system diagenesis can lead to the precipitation of diagenetic carbonate with composition reflecting that of the fluid rather than the original carbonate (“fluid-buffered” diagenesis).

The goal of this study is to investigate how the Li isotope composition of marine carbonates, and in particular shallow water platform carbonates that are abundant in the geological record, are affected by both meteoric and marine burial diagenesis. We begin with quantitative theoretical consideration, including discussion of published experimentally-derived partition coefficient values and isotopic fractionation factors in order to evaluate the extent to which we expect  $\delta^7\text{Li}$  values and Li/Ca ratios to be affected by diagenesis under different conditions (section 2). Then, in sections 3–7, we present and discuss new measurements of the Li isotope composition and Li/(Ca+Mg) ratios of carbonate sediments from the Clino, Unda and 1007 cores from the Great Bahama Banks (GBB), along with altered corals from the Key Largo Limestone. Finally, in section 8, we use these data to assess the behavior of Li isotopes during diagenesis and provide guidelines for interpreting the  $\delta^7\text{Li}$  of ancient carbonates. These results have important implications for understanding the past Li isotope record of platform carbonate sediments.

## 2. THEORETICAL INFLUENCE OF DIAGENESIS ON $\delta^7\text{Li}$ AND Li/Ca RATIOS

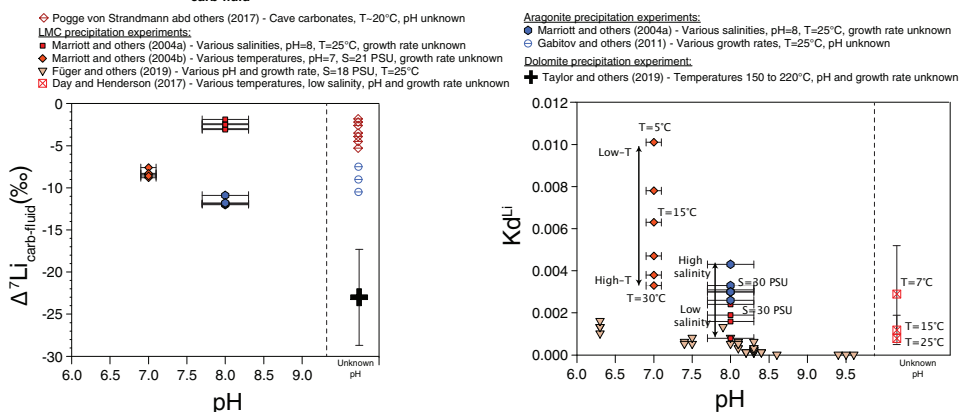
Prior work on carbonate diagenesis informs our approach to studying the effects on lithium specifically. In a series of seminal papers, Brand and Veizer identified general controls on the isotopic and trace element composition of diagenetic carbonates (Brand and Veizer, 1980, 1981). In the context of Li, these are: i) the partitioning coefficient of Li between secondary carbonate and fluids ( $Kd^{\text{Li}}$ ) and the Li isotope fractionation factor between the diagenetic carbonate and the fluid ( $\Delta^{\text{Li}}_{\text{carb-fluid}}$ ), ii) the composition of the initial diagenetic fluid, both elemental and isotopic, that is,  $(\text{Li}/\text{Ca})_{\text{fluid } 0}$  and  $\delta^7\text{Li}_{\text{fluid } 0}$ , respectively, iii) the elemental and isotopic composition of the original solid,  $(\text{Li}/\text{Ca})_{\text{prim}}$  and  $\delta^7\text{Li}_{\text{prim}}$ , and iv) the extent to which diagenesis is fluid-buffered (open system) or sediment-buffered (closed system). In the following sections, we consider each of these factors in sequence.

In sections 2.1–2.3, we follow the approach of Brand and Veizer (1980) and summarize what is known about key controls from field and experimental data. We then use this foundational understanding about how Li and its isotopes behave during water-carbonate interactions to make general predictions for how Li/Ca and  $\delta^7\text{Li}$  in carbonates may be affected by diagenesis, in section 2.4. In section 2.5, we turn to consider the role of fluid-buffered vs. sediment-buffered diagenetic conditions. The actual composition of the diagenetic carbonates will depend on the extent of fluid-rock interaction, and we adopt a mass balance model to quantify this effect (Banner and Hanson, 1990; Ahm and others, 2018). This model also allows us to compare the predicted behavior of Li with other carbonate geochemical signatures (in section 2.6). Taken together, this background information sets the foundation for our study of Li isotope compositions in Bahamian carbonates. Because most experimental data for LMC have been reported in terms of Li/Ca, we use this notation here, but later in the manuscript we use the Li/(Ca+Mg) ratio value in order to avoid biases when comparing ratios between LMC and dolomites ( $\text{Li}/\text{Ca} \sim \text{Li}/(\text{Ca}+\text{Mg})$  for LMC, but not for dolomite). Also, because diagenetic influence is element-specific, in the following, we refer to fluid- or sediment-buffered as being with respect to Li in the carbonate, unless otherwise specified.

### 2.1. Li Partition Coefficient and Fractionation Factor Between Carbonates and Fluid: $Kd^{\text{Li}}$ and $\Delta^7\text{Li}_{\text{carb-fluid}}$

A handful of experimental studies (Marriott and others, 2004a; Marriott and others, 2004b; Day and Henderson, 2013; Föger and others, 2019) have determined the apparent partition coefficient of Li ( $Kd^{\text{Li}}$ ) between fluids and both abiogenic LMC and aragonite (see compilation in fig. 1). Overall, the total range of possible  $Kd^{\text{Li}}$  values for typical natural waters is low ( $Kd^{\text{Li}}$  of  $10^{-4}$  to  $10^{-2}$ ), which means that Li is

### A. $Kd^{Li}$ and $\Delta^7Li_{carb-fluid}$ (section 2.1)



### B. $(Li/Ca)_{fluid 0}$ and $\delta^7Li_{fluid 0}$ (section 2.2)



Fig. 1. Partitioning of Li and fractionation of its isotopes during carbonate formation, and typical fluid compositions. (A) Summary of published experimental Li isotope fractionation factors ( $\Delta^7Li_{carb-fluid}$ ) and partition coefficients ( $Kd^{Li}$ ) between carbonates and fluid as a function of pH. (B)  $\delta^7Li$  and  $Li/Ca$  and supplementary data table, <http://earth.geology.yale.edu/~7eajs/SupplementaryData/2020/Dellinger/>, seawater (Misra and Froelich, 2012) and range of  $Li/Ca$  in carbonate and silicate rocks.

strongly partitioned in favor of the fluid rather than calcite during inorganic LMC precipitation. While there is uncertainty in terms of what controls the  $Kd^{Li}$  value, the available data suggest that the  $Kd^{Li}$  of LMC decreases with increasing temperature and pH but increases with increasing salinity and growth rate. Importantly, it appears that for a similar set of typical marine conditions, the  $Kd^{Li}$  of inorganic aragonite is higher ( $Kd^{Li} \sim 0.0025$  to  $0.0035$ ) than for inorganic LMC ( $Kd^{Li} \sim 0.0005$  to  $0.0020$ ).

Experimental studies have shown that the Li isotope fractionation factor for aragonite ( $\Delta^7Li_{Aragonite-fluid}$ ) ranges from  $-12$  to  $-8$  permil (fig. 1A) and may be controlled by crystal growth rate (Marriott and others, 2004b; Gabitov and others, 2011). In comparison, the Li isotope fractionation factor for LMC is lower than for aragonite ( $\Delta^7Li_{LMC-fluid} = -8$  to  $-1$ ‰) and unlike the  $Kd^{Li}$ , is not significantly influenced by temperature or salinity (Marriott and others, 2004a; Marriott and others, 2004b). It has been suggested (Coogan and others, 2016) that there might be a strong control by pH as the  $\Delta^7Li_{LMC-fluid}$  determined at  $pH = 8$  ( $\Delta^7Li_{LMC-fluid} = -2.5 \pm 1.5$ ‰) is significantly higher than that at  $pH = 7$  ( $\Delta^7Li_{LMC-fluid} = -8 \pm 1$ ‰). Similarly, an influence of pH on the  $\delta^7Li$  of biogenic LMC such as benthic foraminiferal tests has also been proposed (Roberts and others, 2018). A speleothem study by Pogge von Strandmann and others (2017) measured a field-based fractionation factor of  $\Delta^7Li_{LMC-fluid} = -3 \pm 2$ ‰, in good agreement with experimental results at  $pH = 8$  (Marriott and others, 2004a). For dolomite, a recent study reported a Li isotope fractionation factor between dolomites and fluids ( $\Delta^7Li_{Dolomite-fluid} = -23 \pm 5.8$ ‰ at  $25$  °C) much larger than  $\Delta^7Li_{Aragonite-fluid}$  and  $\Delta^7Li_{LMC-fluid}$  (Taylor and others, 2019),

though this value is an extrapolation from experiments done at high temperature (150 °C to 220 °C). While  $\Delta^7\text{Li}_{\text{Dolomite-fluid}}$  remains least well constrained, overall it appears that there is a strong mineralogical control on the Li isotope fractionation factor between inorganic carbonates and fluids.

### 2.2. Composition of the Diagenetic Fluid: $(\text{Li}/\text{Ca})_{\text{fluid } 0}$ and $\delta^7\text{Li}_{\text{fluid } 0}$

Given that we expect the Li in carbonates to be influenced by the composition of diagenetic fluids in many settings, understanding the controls on fluid composition will be important for interpreting carbonate isotopic signatures. Where diagenesis takes place through interaction with meteoric fluids (that is, “meteoric diagenesis”), we expect the fluid composition to reflect reactions in overlying weathering zones and thus have a  $\delta^7\text{Li}$  value in between that of the original carbonate (typically  $\delta^7\text{Li}$  in the range of  $\sim 15\text{--}30\text{‰}$  in the present-day; Misra and Froelich, 2012; Pogge von Strandmann and others, 2013 and 2017) and weathering of other phases, including detrital and dust sources (typically  $\sim 0\text{--}5\text{‰}$ , characteristic of silicate rocks; Sauzéat and others, 2015). Since carbonates contain much less Li (0–5 ppm, Li/Ca in the range of 1–200  $\mu\text{mol}\cdot\text{mol}^{-1}$ ) than silicates (5–100 ppm, Li/Ca of 8000–200000  $\mu\text{mol}\cdot\text{mol}^{-1}$ ; Teng and others, 2004; Sauzéat and others, 2015; Dellinger and others, 2018), even small amounts of silicates can dominate the dissolved Li budget and consequently control the isotope composition of fluids (as seen in karst settings by Pogge von Strandmann and others, 2017). The range of Li/Ca and  $\delta^7\text{Li}$  of rivers draining carbonate terranes (that is, an analogue to diagenetic meteoric fluids) are respectively 7–700  $\mu\text{mol}\cdot\text{mol}^{-1}$  and +10 to +26 permil (fig. 1B). In the case of diagenesis taking place through interaction with marine porewaters (that is, “marine burial diagenesis”), fluid  $\delta^7\text{Li}$  may be close to seawater isotope composition, perhaps modified by diffusion or reaction with carbonates or other phases in pore waters (Scholz and others, 2010).

### 2.3. Composition of the Original Solid

In the modern oceans, we would expect primary abiotic aragonite to have  $\delta^7\text{Li} \sim 19$  to 24 permil and Li/Ca  $\sim 7$  to 12  $\mu\text{mol}\cdot\text{mol}^{-1}$ , based on modern seawater  $\delta^7\text{Li}$  of 31 permil and Li/Ca of 2500  $\mu\text{mol}\cdot\text{mol}^{-1}$ , and the partition coefficients and fractionation factors described in section 2.1, above. However, abiotic primary aragonite is scarce in the modern ocean, and even when non-skeletal carbonate forms (for example, as pelloids and ooids), it is often associated with fecal pellets, fossil fragments, and other material (Schlager, 2005). Moreover, platform and peri-platform carbonates can include abundant biogenic carbonates, and these have very wide-ranging Li compositions partly but not only determined by their mineralogy (Dellinger and others, 2018). Despite all of this potential complexity, measurements of bulk modern carbonates from the GBB (Zhang and others, 2017; Pogge von Strandmann and others, 2019) paint a picture that is relatively simple and consistent with the experimental partitioning coefficients and fractionation factors.

Present-day GBB platform carbonates (as described by Reijmer and others, 2009) are composed mostly of non-skeletal (peloids and ooids) aragonite (between 60 and 100%, average of 93%) with a minor component of HMC (average of 7%) and almost no LMC (<1%). The Li/(Ca+Mg) ratio of modern GBB sediments from Zhang and others (2017) ranges from 8 to 12  $\mu\text{mol}\cdot\text{mol}^{-1}$  (average  $10.2 \pm 1.6 \mu\text{mol}\cdot\text{mol}^{-1}$ ), while the Li/(Ca+Mg) ratios reported by Pogge von Strandmann and others (2019) are higher and range from 12 to 28  $\mu\text{mol}\cdot\text{mol}^{-1}$  (average  $18.6 \pm 4 \mu\text{mol}\cdot\text{mol}^{-1}$ ). These differences can be ascribed to different concentrations of HMC; indeed, the relationship between Li/(Ca+Mg) and Mg/(Ca+Mg) ratios in these samples systematic trends that we interpret as mixing between aragonite and HMC (fig. 2A). This mixing trend arises because the Li/(Ca+Mg) ratio of HMC is generally much higher than the Li/(Ca+Mg) ratio of aragonite (Darrenougue and others, 2014; Dellinger



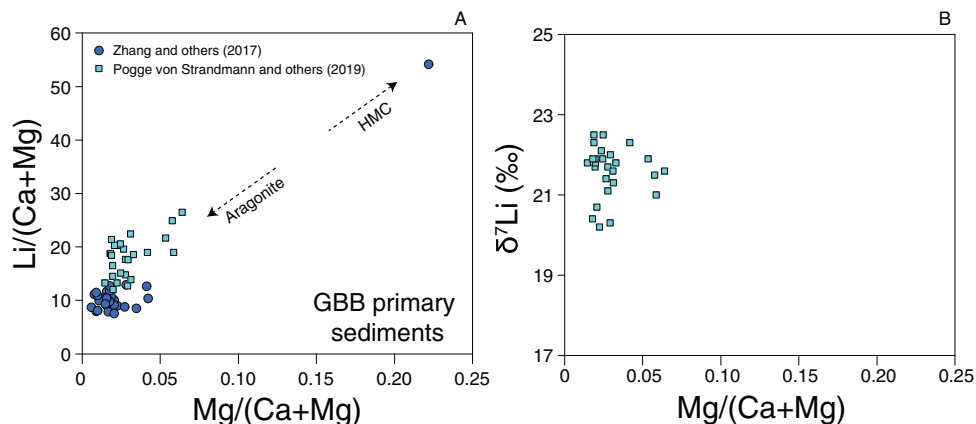


Fig. 2. Composition of unaltered Great Bahama Banks sediments. (A)  $\text{Li}/(\text{Ca}+\text{Mg})$  ratio (in  $\mu\text{mol}\cdot\text{mol}^{-1}$ ) and (B)  $\delta^7\text{Li}$  as a function of the  $\text{Mg}/(\text{Ca}+\text{Mg})$  ratio (in  $\text{mol}\cdot\text{mol}^{-1}$ ). Data are from Zhang and others (2017) and Pogge von Strandmann and others (2019). Note that Zhang and others (2017) did not report isotopic data for their samples.

and others, 2018). Interestingly, the mean HMC proportion in the Zhang and others (2017) sample set (17%) is higher than the average HMC content in GBB sediments (7%) determined by Reijmer and others (2009) from a much larger number of samples, so even the Zhang and others (2017) data reflects a mixed composition that does not, on its own, represent bulk unaltered GBB sediments. The aragonite-rich end-member defined by the correlation in figure 2A has a  $\text{Li}/(\text{Ca}+\text{Mg})$  of  $9\pm 1 \mu\text{mol}\cdot\text{mol}^{-1}$ , compatible with the expected composition of abiotic aragonite precipitating from present-day seawater ( $7.5\pm 1.0 \mu\text{mol}\cdot\text{mol}^{-1}$ ), as deduced from the experimental  $\text{Kd}^{\text{Li}}$  values discussed above. We see this  $\text{Li}/(\text{Ca}+\text{Mg})$  value as representative of primary unaltered aragonite.

The  $\delta^7\text{Li}$  of GBB sediments from Pogge von Strandmann and others (2019) is  $\sim 22\pm 1$  permil and shows no relationship with  $\text{Mg}/(\text{Ca}+\text{Mg})$  (fig. 2B), suggesting that the  $\delta^7\text{Li}$  of HMC in the Bahamas is not significantly different from aragonite. Hence, we can consider the  $\delta^7\text{Li}$  of GBB sediments from Pogge von Strandmann and others (2019) as representative of GBB primary unaltered sediments. This  $\delta^7\text{Li}$  value is within the range (19–24‰) expected for precipitation from seawater assuming the experimentally-determined inorganic aragonite fractionation factor.

We have focused here on primary carbonate compositions from the GBB, since modern bulk data are available. Importantly, the diagenetically altered samples we have studied are also from this region (see section 3), so we can be confident in assigning the unaltered end-member for our samples on the basis of these data. Additional work on modern bulk carbonates from other settings would help to establish whether the primary aragonite compositions inferred here are globally applicable. In any case, we adopt these compositions for the general consideration that follows.

#### 2.4. Expected Effects of Diagenesis on Bulk Carbonate $\delta^7\text{Li}_{\text{dCarb}}$ and $(\text{Li}/\text{Ca})_{\text{dCarb}}$ Ratios

Based on the experimental data on partition coefficients and fractionation factors from section 2.1, together with expectations of fluid and original solid compositions from sections 2.2 and 2.3, we can predict the change in  $\delta^7\text{Li}$  and  $\text{Li}/\text{Ca}$  during diagenetic conversion of aragonite to LMC or dolomite in the context of shallow marine carbonates, such as those in the Bahamas. Here we focus on fluid-buffered

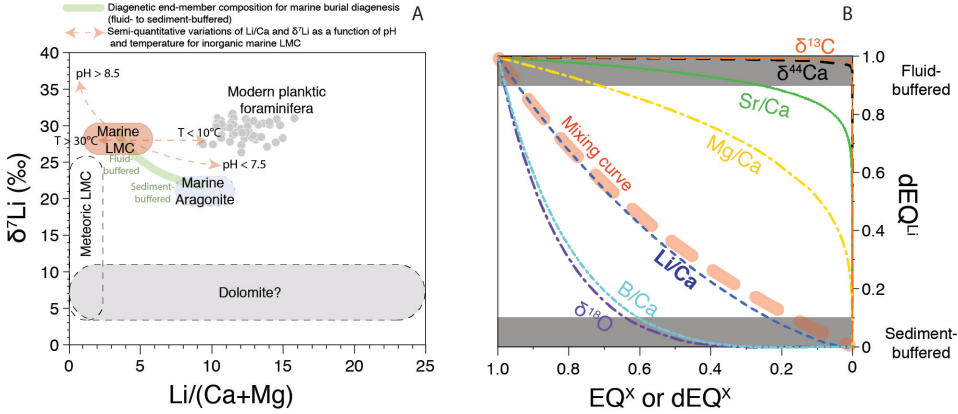


Fig. 3. (A) Expected effects of diagenesis on Li isotopes and  $\text{Li}/(\text{Ca}+\text{Mg})$  ratios (in  $\mu\text{mol}\cdot\text{mol}^{-1}$ ). The composition of marine aragonite is from section 2.3. The other compositions (for example, marine LMC, meteoric LMC) are based on fluid-buffered diagenesis, following equations 1 and 2. The green curve showing the expected trajectory between fluid- and sediment-buffered conditions is determined using the diagenesis model equations from Appendix 1. Note that we shift here and in the remainder of this paper to using  $\text{Li}/(\text{Ca}+\text{Mg})$ , rather than  $\text{Li}/\text{Ca}$  as in figure 1, in order to compare the elemental compositions of calcite and dolomite. (B) Carbonate compositions expected to result from alteration of aragonite to LMC in reaction with seawater fluid with modern composition for several geochemical proxies, calculated using the diagenesis model equations from Appendix 1. The black horizontal bars correspond to fluid-buffered ( $d\text{EQ}^{\text{Li}} > 0.9$ ) and sediment-buffered compositions ( $d\text{EQ}^{\text{Li}} < 0.1$ ) in regard to Li isotopes. The red dotted curve corresponds to the mixture between fluid-buffered (for all elements,  $\text{EQ}^x$  and  $d\text{EQ}^x > 0.9$ ) and sediment-buffered LMC ( $\text{EQ}^x$  and  $d\text{EQ}^x < 0.1$ ).

diagenesis, and we consider the effect of sediment-buffered conditions in the next section (section 2.5). For fluid-buffered diagenesis, the  $\text{Li}/\text{Ca}$  ratio of diagenetic carbonates  $(\text{Li}/\text{Ca})_{d\text{Carb}}$  can be expressed as:

$$\left(\frac{\text{Li}}{\text{Ca}}\right)_{d\text{Carb}}^{\text{fluid-buffered}} = \text{Kd}^{\text{Li}} \times \left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{fluid } 0} \quad (1)$$

where  $(\text{Li}/\text{Ca})_{\text{fluid } 0}$  is the  $\text{Li}/\text{Ca}$  ratio of the initial advecting fluid and  $\text{Kd}^{\text{Li}}$  is the apparent partition coefficient of Li between carbonate and fluid ( $\text{Kd}^{\text{Li}} = (\text{Li}/\text{Ca})_{\text{carb}}/(\text{Li}/\text{Ca})_{\text{fluid}}$ ). Similarly, the  $\delta^7\text{Li}_{d\text{Carb}}$  of fluid-buffered carbonates can be expressed as:

$$\delta^7\text{Li}_{d\text{Carb}}^{\text{fluid-buffered}} = \delta^7\text{Li}_{\text{fluid } 0} + \Delta^7\text{Li}_{\text{carb-fluid}} \quad (2)$$

where  $(\delta^7\text{Li})_{\text{fluid } 0}$  is the  $\delta^7\text{Li}$  value of the initial advecting fluid and  $\Delta^7\text{Li}_{\text{carb-fluid}}$  is the Li isotopic fractionation factor between the carbonate and fluid ( $\Delta^7\text{Li}_{\text{carb-fluid}} \sim 1000 \ln(\alpha_{\text{carb-fluid}}^{\text{Li}})$ ).

So, what does all of this mean, considering what we know about the respective partition coefficients and fractionation factors (section 2.1)? Predicted changes in composition as a result of transformation of aragonite to LMC and dolomite are shown in figure 3A. The inorganic  $\text{Kd}^{\text{Li}}$  of LMC is lower than that for inorganic or biogenic aragonite (Marriott and others, 2004a, 2004b; Hathorne and others, 2013), so transformation of aragonite to calcite should result in lowering of the  $\text{Li}/\text{Ca}$  of limestones (fig. 3A) if the fluid composition and temperature are the same, as expected for marine pore waters. Meanwhile, we expect that  $\delta^7\text{Li}$  would increase, because of the smaller fractionation factor into calcite than aragonite. Altogether, for typical marine pH (7.5–8.5) and Bahamian temperature and salinity, the  $\text{Li}/\text{Ca}$  of fluid-buffered diagenetic LMC should be  $\sim 1$  to  $6 \mu\text{mol}\cdot\text{mol}^{-1}$  and  $\delta^7\text{Li}$  should be +26 to +30 permil

(marine LMC region in fig. 3A). If the diagenetic transformation of aragonite to calcite takes place at lower temperatures (for example,  $T < 10\text{ }^\circ\text{C}$ ) or lower pH (for example,  $\text{pH} < 7.5$ ) than aragonite formation, the expected compositions might differ both in terms of elemental and isotopic ratios (illustrated by dashed arrows in fig. 3A). Specifically, the  $K_d^{\text{Li}}$  of calcite increases with decreasing temperature (Marriott and others, 2004a, 2004b) and decreasing pH (Füger and others, 2019), so lower  $T$  and lower pH both may yield Li/Ca ratios of LMC higher than primary inorganic aragonite ( $> 10\text{ }\mu\text{mol}\cdot\text{mol}^{-1}$ ). Temperature of diagenetic reactions is not likely to affect  $\delta^7\text{Li}$ , but pH might, and diagenesis at  $\text{pH} \sim 7.5$  might produce  $\delta^7\text{Li} < 23$  permil according to experimental  $\Delta^7\text{Li}_{\text{carb-fluid}}$  at  $\text{pH}=7$  (Marriott and others, 2004a).

For the formation of dolomite during marine diagenesis, the Li isotope fractionation inferred from experiments (Taylor and others, 2019) predicts diagenetic dolomite  $\delta^7\text{Li}$  significantly lower than  $\delta^7\text{Li}$  values for aragonite, LMC and seawater (dolomite region in fig. 3A). However, if the fractionation factor for dolomite is more similar to that for calcite, we would expect higher  $\delta^7\text{Li}$  values than shown in figure 3A. In the absence of any experimental or other constraints on the  $K_d^{\text{Li}}$  for dolomite, it is not possible to make any prediction on the Li/(Ca+Mg) for dolomites.

For meteoric diagenesis, we expect an even larger decrease in carbonate Li/Ca ( $< 2\text{ }\mu\text{mol}\cdot\text{mol}^{-1}$ ) relative to primary aragonite than for marine diagenesis, because the Li/Ca of meteoric fluids (for example, rivers in fig. 2B) tends to be lower than that of seawater-derived carbonates (fig. 1B), and because the Li partition coefficient ( $K_d^{\text{Li}}$ ) is lower in inorganic LMC compared to either primary aragonite or biogenic calcite (fig. 1A). Considering the range of  $\delta^7\text{Li}$  in modern rivers draining limestones (fig. 1B), we expect a  $\delta^7\text{Li}$  in meteoric LMC in the range of +5 to +25 permil, lower than present-day oceanic  $\delta^7\text{Li}$  value (meteoric LMC region in fig. 3A).

### 2.5. The Effect of Fluid vs. Sediment Buffered Conditions

Thus far, we have considered predictions for fluid-buffered conditions. However, as noted above, actual diagenetic transformations occur across a range of conditions that vary from fluid- to sediment-buffered, and these conditions can strongly affect the composition of carbonate that forms (Brand and Veizer, 1980). The composition of carbonate precipitated in fluid-buffered conditions has been described in section 2.4, above. For carbonate precipitation in sediment-buffered conditions, the geochemical and isotopic composition of diagenetic carbonates will be unchanged relative to the primary aragonite carbonates, so  $(\text{Li}/\text{Ca})_{\text{dCarb}} = (\text{Li}/\text{Ca})_{\text{prim}}$  and  $\delta^7\text{Li}_{\text{dCarb}} = \delta^7\text{Li}_{\text{prim}}$ . In between these two diagenetic end-members, the composition of the diagenetic carbonates has intermediate values depending on the extent of fluid-rock interaction (Banner and Hanson, 1990). To capture the range of predicted compositions, we also need to account for the evolution of fluid chemistry with the extent of reaction (Fantle and others, 2010). We can do this by following recent work (Ahm and others, 2018) in combining mass-balance calculations (Banner and Hanson, 1990) with 1-D reactive-transport calculations corresponding to a reaction between a downward advecting fluid and sediments. In this way, we can calculate the range of expected composition for diagenetic carbonates depending on specific chemical and physical parameters (for example, depth of diagenetic reactions, fluid advection rates, reaction rates), and using the background information for Li established in sections 2.1-2.3. In Appendix (1), we provide a full expression for the diagenetic effects on LMC based on a 1-D mass-balance reactive-transport framework (Pogge von Strandmann and others, 2014; Ahm and others, 2018). Here and in figure 3, we report a summary of the predictions for marine diagenesis.

The predicted effect of shifting from sediment- to fluid-buffered conditions is relatively straightforward: the compositional range of predicted diagenetic LMC (sediment-buffered to fluid-buffered) displays a negative curve in  $\delta^7\text{Li}\text{-Li}/(\text{Ca}+\text{Mg})$



space (green curve in fig. 3A). We expect diagenetic carbonates to fall along a similar trajectory, depending on the specific conditions. It is readily apparent from this analysis that there is a potentially large range of carbonate compositions, both in terms of  $\delta^7\text{Li}$  and  $\text{Li}/(\text{Ca}+\text{Mg})$ , that can result depending on whether reactions are fluid- or sediment-buffered (for example,  $\sim 10\%$  range in  $\delta^7\text{Li}$  along this trajectory in fig. 3A). Thus, accurately interpreting the Li isotope composition of marine carbonates will depend on identifying the diagenetic conditions—not just whether the carbonates are altered diagenetically, and not just whether that was by meteoric or marine fluids, but also the extent to which marine diagenesis was fluid or sediment buffered.

### 2.6. Contextual Information From Other Geochemical Proxies in Diagenetic Carbonates

It is usually a challenge to know the extent of fluid advection (that is, the cumulative fluid-rock ratio) through ancient carbonate sediments, as would be needed to assess whether the diagenetic carbonate composition is fluid or sediment-buffered. But it may still be possible to constrain the degree of diagenetic resetting of ancient carbonate rocks by comparing between chemical proxies (for example,  $\text{Sr}/\text{Ca}$ ,  $\text{Mg}/\text{Ca}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{44}\text{Ca}$  and others; Brand and Veizer, 1980). Because the original signature (prior to diagenesis) of mineralogical phases of different proxies can vary in space and time, we follow Banner and Hanson (1990) and define the  $\text{EQ}^{\text{X}}$  parameter which corresponds to the extent to which the concentration of the element X in the diagenetic product is fluid-buffered ( $\text{EQ}^{\text{X}} > 0.9$ ) or sediment-buffered ( $\text{EQ}^{\text{X}} < 0.1$ ):

$$\text{EQ}^{\text{X}} = \frac{[\text{X}]_{\text{dCarb}} - [\text{X}]_{\text{prim}}}{[\text{X}]_{\text{fluid-buffered}} - [\text{X}]_{\text{prim}}} \quad (3)$$

Similarly, we can define the  $\text{dEQ}^{\text{X}}$  for isotope ratios ( $\delta^{\text{Y}}\text{X}$ ):

$$\text{dEQ}^{\text{X}} = \frac{\delta^{\text{Y}}\text{X}_{\text{dCarb}} - \delta^{\text{Y}}\text{X}_{\text{prim}}}{\delta^{\text{Y}}\text{X}_{\text{fluid-buffered}} - \delta^{\text{Y}}\text{X}_{\text{prim}}} \quad (4)$$

with  $[\text{X}]_{\text{dCarb}}$ ,  $[\text{X}]_{\text{prim}}$ ,  $[\text{X}]_{\text{fluid-buffered}}$  and  $\delta^{\text{Y}}\text{X}_{\text{dCarb}}$ ,  $\delta^{\text{Y}}\text{X}_{\text{prim}}$ ,  $\delta^{\text{Y}}\text{X}_{\text{fluid-buffered}}$  respectively the concentration and isotope composition of the element X in diagenetic, primary and fluid-buffered carbonates. The advantage of this notation is that, for a given fluid composition and fluid-rock ratio, the  $\text{EQ}^{\text{X}}$  value for any element is independent of the concentration in the initial solid and fluid. Different chemical elements will have distinct EQ values as the latter is then only controlled by the partition coefficient of a given element (Banner and Hanson, 1990; Jacobsen and Kaufman, 1999). Thus, comparison between elements provides a method to estimate the degree of fluid and sediment buffered diagenesis of ancient limestones.

An example of a diagenetic end-member calculation for several geochemical proxies is shown for diagenetic transformation of aragonite to LMC in modern-type seawater fluid in figure 3B (using equations from Appendix A1, and modern seawater compositions for the fluids). We observe that for a given set of conditions,  $\text{Li}/\text{Ca}$  ratios and  $\delta^7\text{Li}$  values have lower EQ and dEQ values than  $\text{B}/\text{Ca}$  and oxygen isotopes and higher values than  $\text{Mg}/\text{Ca}$ ,  $\text{Sr}/\text{Ca}$ , calcium and carbon isotopes. This analysis is important for several reasons. First, evidence for preservation of the  $\delta^{18}\text{O}$  or  $\text{B}/\text{Ca}$  primary composition in ancient carbonates (that is, sediment buffered composition for  $\delta^{18}\text{O}$  and B,  $\text{EQ}^{\text{O}}$  and  $\text{EQ}^{\text{B}} < 0.1$ ) implies that the  $\text{Li}/\text{Ca}$  and  $\delta^7\text{Li}$  are also likely to be sediment-buffered ( $\text{dEQ}^{\text{Li}} \sim 0$ ). Second, evidence that Sr, C, Mg or Ca have fluid-buffered compositions ( $\text{EQ} \sim 1$ ) would indicate that Li will also be reset to fluid values by diagenetic reactions ( $\text{dEQ}^{\text{Li}} \sim 1$ ). Third, the diagenetic LMC end-members define specific trends in cross-plots between  $\delta^7\text{Li}$  and other geochemical proxies (fig. 3B), and these trends can be used to discriminate fluid-buffered and sediment-buffered

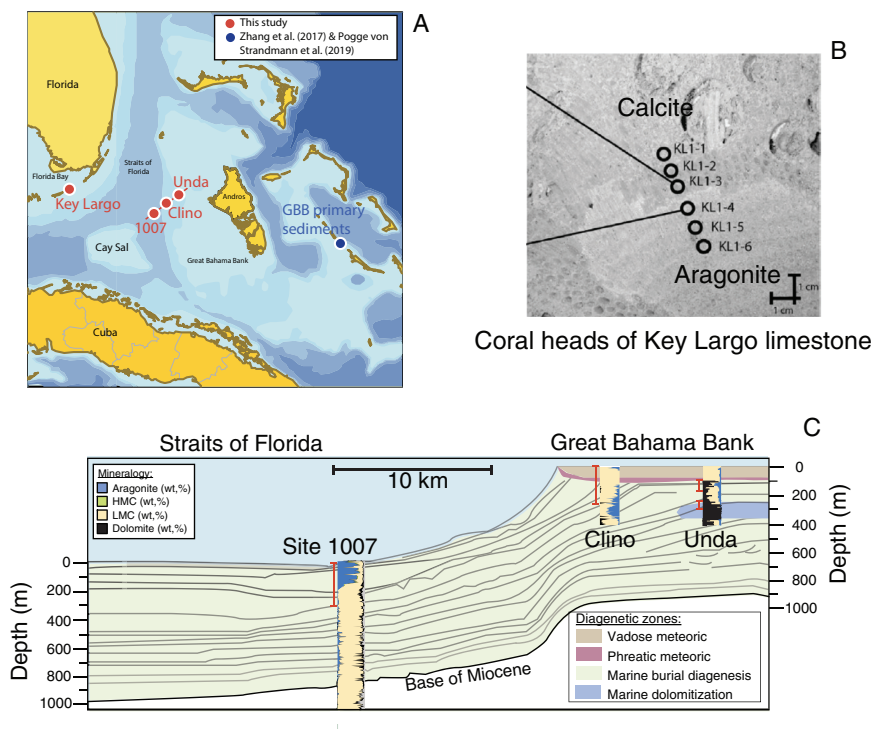


Fig. 4. Location and characteristics of sample sites from this study. (A) Map with the location of Clino, Unda, Key Largo and 1007 core (modified from Swart, 2015). (B) Photograph of KL1 sample transect from the Key Largo Limestone and location of the samples analyzed in this study. (C) Cross section of the GBB and location of Clino, Unda, and 1007 cores. The red vertical lines indicates sample areas from this study.

diagenesis. Fourth, as shown for other proxies (Ahm and others, 2018), a fluid-buffered Li isotope composition ( $dEQ^{Li} \sim 1$ ) corresponds a large range of Sr/Ca,  $\delta^{13}C$  and  $\delta^{44}Ca$  values. Fifth, diagenetic trends are distinct from mixing trends (of diagenetic end-members, except in the  $\delta^7Li$ -Li/Ca space) making it possible to discriminate diagenetic paths relative to mineral mixing (fig. 3B). Note that these results might vary for a different set of parameter values (for example, different fluid composition, fractionation factor, or partition coefficient value), but it is beyond the scope of this study to explore the total range of possible values of Li/Ca,  $\delta^7Li$ , and other proxies resulting from diagenetic processes.

The key point is that theoretical calculations informed by experimental data on Li partitioning and isotope fractionation allow us to make predictions about Li isotope effects under different diagenetic conditions. These suggest potentially significant diagenetic effects that vary as a function of diagenetic process and environmental conditions, and we may be able to tease apart the specific conditions by comparing to other element and isotope systems. These predictions set the stage for our analysis of Bahamas carbonate samples.

### 3. SAMPLES

In this study, we have analyzed shallow water platform carbonates from the Florida Keys and the Great Bahama Bank, specifically from the Clino, Unda, and ODP 1007 cores (fig. 4). The locations and number of samples measured in this study are indicated in table (1). These samples represent primary GBB carbonates (as described

TABLE 1  
*Diagenetic conditions and main characteristics of the samples from this study*

Diagenetic setting	References	Depositional Setting	Location	Age	Core depth	Mineralogy	Number of samples	Symbol in the figures
<i>Bahamas platform</i>								
Initial deposition	Zhang and others, (2017); Pogge von Strandmann and others. (2019)	Bank top	Little Darby and Lee Stocking Islands, Bahamas	Modern	-	Aragonite > HMC	23 and 26	○ and □
Meteoritic	This study	Platform top Platform top	Clino Unda	Pleistocene Pleistocene	23-150 m 90-107 m	LMC >> Aragonite LMC	16 6	○
Marine burial	This study	Platform top Platform top Platform top Toe of slope Toe of slope	Clino Unda Unda 1007 site 1007 site	Pleistocene Pleistocene Pliocene Pleistocene - Late Pliocene Early Pliocene - Late Miocene	155-250 m 110-150 m 274-292 m 23-150 m 200-350 m	LMC > aragonite LMC > dolomite Dolomite > LMC Aragonite > LMC LMC >> Aragonite	7 17 12 14 8	□ □ □ △ △
<i>Key Largo</i>								
Initial deposition	This study	Reef	Key Largo	Pleistocene	-	Aragonite	6	◇
Meteoritic	This study	Reef	Key Largo	Pleistocene	-	LMC >> Aragonite	14	◇

in section 2.3) that have been altered by different types of diagenesis (meteoric and marine) and in environments characterized by different fluid advection rates (Melim and others, 1995; Caspard and others, 2004; Swart and Oehlert, 2018). One additional difference between the different cores is that the modern to mid-Pliocene sediments found within Clino and Unda are predominantly platform facies with minor pelagic components (foraminifera and coccoliths), while the sediments from the peri-platform facies from core 1007 contain a higher proportion of pelagic material (and thus some contribution from primary low-Mg calcite, with distinct Li systematics, for example, see fig. 4).

The samples we have analyzed correspond to those used in previous studies of diagenetic alterations to carbonate proxies, specifically for  $I/(Ca+Mg)$  (Hardisty and others, 2017),  $\delta^{238}U$  (Chen and others, 2018a), REEs (Liu and others, 2019), and carbonate-associated sulfate for Key Largo samples (Gill and others, 2008). The samples have also been previously characterized for  $\delta^{13}C$ ,  $\delta^{18}O$ , and mineralogy (Swart and Eberli, 2005; Gill and others, 2008; Hardisty and others, 2017). In addition,  $\delta^{44}Ca$ ,  $\delta^{26}Mg$ , and  $\delta^{11}B$  have been measured on the same Bahamian cores (although not the exact samples used here) as part of other previous studies (Stewart and others, 2015; Higgins and others, 2018). Altogether, these cores provide an ideal opportunity to characterize the influence of diagenesis on the Li isotope composition of platform carbonate sediments, typical of those preserved in the rock record. Moreover, all samples we study are younger than 8 Ma, and so formed during a period of time during which the  $\delta^7Li$  value of seawater is not thought to have varied significantly from today (Hathorne and James, 2006; Misra and Froelich, 2012).

### 3.1. Clino and Unda Cores

The Clino and Unda cores—collected in 1990 during the Bahama Drilling Project (Ginsburg, 2001)—recovered periplatform carbonate sediments that are part of the margin of the Great Bahama Bank (fig. 4) and cover a time period ranging from early Miocene (5.3 Ma) to the present-day. The original mineralogical composition of the carbonate is mainly aragonite (Reijmer and others, 2009), but the cores show well-defined meteoric diagenesis fronts, as well as deeper zones of dolomitization (table 1; Swart and Melim, 2000; Melim and others, 2001). Repeated Pleistocene sea-level changes exposed the upper 120m of the carbonate platforms to the infiltration of meteoric fluids and led to recrystallization of aragonite to meteoric LMC (Melim and others, 1995; Swart and Oehlert, 2018). Specifically, the uppermost 100 m in Clino and 60 m in Unda correspond to meteoric diagenesis in the vadose zone with dominantly meteoric LMC characterized by negative carbon and oxygen isotope excursions relative to the primary aragonite sediments in both cores (Melim and others, 1995; Stewart and others, 2015; Swart and Oehlert, 2018). The middle part (100–150 m for Clino, 60–107 m in Unda) corresponds to the meteoric phreatic zone with increasing carbon and oxygen isotope composition with depth. The zone below 160 m in Clino and below 100 m in Unda is characterized by marine burial diagenesis with no subaerial exposure. In the marine burial diagenesis zone, both cores remain dominated by LMC but with minor dolomite mostly in Unda (in general < 5%, referred as “background dolomite”, Swart and Melim, 2000) and up to 50 percent aragonite between 300 and 350m in Clino. Finally, between 250 and 350 m depth in Unda, there is a transition to a zone of pure dolomite of Pliocene age (referred as “massive dolomite”).

### 3.2. Site 1007

Ocean Drilling Program (ODP) core 1007 was drilled in 1990 in the western margin of the Great Bahama Bank as part of Leg 166 (fig. 4). It is located in a more distal part of the bank than the Clino and Unda cores, on the toe-of-slope of the

western GBB, under 647 m of water (Eberli and Swart, 1997). The core has a total depth of 1250 m, covering the entire Neogene and the early Oligocene. Contrary to Clino and Unda, the 1007 core has not been exposed to meteoric diagenesis. In the upper 150 to 200m, the mineralogy is dominated by aragonite (about 70–80%), but below this depth, the proportion of aragonite drops to less than 20 percent with most of the mineralogy being low-Mg calcite, with minor proportions of dolomite (fig. 4). We note that contrary to the Clino and Unda cores, there is a minor proportion of non-carbonate phases, mostly between 0 and 10 percent (median of 5%) with a few samples having more than 20 percent non-carbonate phases. The transition from aragonite- to LMC-dominated sediments is accompanied by a decrease of the carbon isotope composition from 4–5‰ at the top of the core to a minimum of 1 to 2 permil at 350m (Swart and Eberli, 2005), and this change has been interpreted as reflecting a change in the source of the sediments from dominantly LMC pelagic carbonates before the late Pliocene to aragonitic peri-platform sediments in the late Pliocene and Pleistocene (Swart and Eberli, 2005; Swart, 2008). Recent work investigating Ca and Mg isotopes on the same core (Higgins and others, 2018) temper these conclusions by highlighting that some of these mineralogical and geochemical changes are also the result of change in the diagenesis style, from sediment to fluid-buffered diagenesis. Here, we analyzed 22 samples between 23 and 350 m depth, all younger than 8 Myr.

### 3.3. Key Largo Limestone

The Key Largo Limestone occurs in the southern part of Florida and formed from patch reefs that started growth about 120,000 years ago, during the last interglacial (Multer and others 2002). This unit has been continuously exposed to meteoric fluids since the onset of the Wisconsinan regression, ~100,000 years ago, and shows varying degrees of aragonite-to-calcite alteration and variable calcite cementation (Multer and others 2002; Gill and others, 2008). The samples on which we measured the  $\delta^7\text{Li}$  are the same as those used by Gill and others (2008). The carbonate powder was collected by drilling the original aragonite and the secondary calcite on the coral heads of the species *Orbicella annularis* (formerly *Montastrea annularis*) (Gill and others, 2008). Previous characterization of these samples has shown that the geochemical alteration signature in Key Largo samples has evolved over time, likely in response to the evolution of the overlying vadose zone (Gill and others, 2008).

## 4. ANALYTICAL METHODS

For Clino, Unda and the Key Largo limestone we worked with the same carbonate powder samples as used in prior geochemical studies (Gill and others, 2008; Hardisty and others, 2017; Chen and others, 2018; Liu and others, 2019). About 10 to 20 mg of sample was pre-leached, following the same method as in Dellinger and others (2018), to remove exchangeable ions using 1N ammonium acetate followed by 3 rinses with 18.2 megaOhm (Millipore) water. The samples were then digested in dilute hydrochloric acid (HCl 0.05N) for 30 minutes to an hour. The volume of acid used for digestion was calculated to dissolve 30 to 95 percent of the sample (depending upon the silicate proportion) in order to minimize the leaching of non-carbonate phases. After the digestion, the supernatant was collected while the sample residue was weighed in order to determine the yield of the digestion. Ratios of trace elements relative to Ca were measured using a Thermo Scientific Element XR ICP-MS inductively coupled plasma mass spectrometer (ICP-MS) at the Yale Metal Geochemistry Center following a method adapted from Misra and others (2014). All samples and standards were measured at a Ca concentration of 50 ppm. The instrument was first conditioned for 1 hour with a solution of 50 ppm Ca. A set of 5 to 10 multi-elemental calibration standards was measured at the beginning of the run, and a bracketing standard solution was measured every 5 to 10 samples to correct for the drift of the signal.



Accuracy and precision of analyses were checked using the aragonite reference material FEBS-1 (NRC) and in-house prepared standard solutions matching typical calcium carbonate chemical composition. Analytical precision was between 5 and 15 percent, depending on the element and the concentration.

For the Li isotope analyses, Li was separated from the rest of the sample matrix chromatographically at the Yale Metal Geochemistry Center using 2.7 mL of AG50W-X12 resin following the method used in Dellinger and others (2014). A mass of 1 to 40 ng of Li was introduced into the column (in 0.5 mL 0.2N HCl) and Li was eluted with 40 mL of 0.2N HCl. The total procedural blank for Li isotope analysis was  $\sim 0.02$  ng Li ( $n=5$  blanks), which is insignificant compared to sample Li. Sodium concentration in the elution fraction was checked before every isotope analysis, and samples having Na/Li ratios higher than 5 were processed through a second column. Lithium isotope ratios were measured using a Thermo Scientific Neptune Plus multiple collector inductively coupled plasma mass spectrometer (MC-ICP-MS) using an APEX desolvation system at the Yale Metal Geochemistry Center. Most samples were successively measured 2 consecutive times within a standard-sample bracketing (SSB) sequence with ratios reported in delta notation relative to LSVEC. For each sample and bracketing standard,  $^7\text{Li}/^6\text{Li}$  ratios were measured for 50 cycles of 4 seconds each. With this setup, the sensitivity was 0.6V/ppb Li and measured samples had signal intensity ranging from 0.4 to 8.0 V (average of 3.5V), depending on the amount of Li in the sample. Background intensities (usually stable during a whole sequence of several hours) were measured before and after each bracketing standard, and sample intensities were corrected for the background signal. The blank intensity of the background was no more than 0.2 to 1 percent of the sample intensity. The internal standard error of sample measurements (average of  $\pm 0.08\text{‰}$ ,  $2\sigma$ ) was typically between  $\pm 0.05$  permil for high Li beam intensity to  $\pm 0.40\text{‰}$  ( $2\sigma$ ) for low beam intensity. Atlantic Seawater (OSIL) was measured as a reference standard to check the accuracy of the data and returned an average  $\delta^7\text{Li}$  value of  $31.2 \pm 0.6$  permil ( $2\sigma$ ,  $n=7$  different aliquots processed through column chemistry), in good agreement with average data from the literature. We also measured the  $\delta^7\text{Li}$  of the NRC carbonate standard FEBS-1 and obtained a  $\delta^7\text{Li}$  value of  $15.8 \pm 0.4$  permil ( $n=2$ ). Overall, we consider a maximum uncertainty of  $\pm 0.8$  permil ( $2\sigma$ ) on  $\delta^7\text{Li}$  for all samples.

## 5. RESULTS

### 5.1. Meteoric Diagenesis Zone

Results for Li isotopes and Li, Ca, Mg, Sr, Mn, Al, and Fe contents are presented in table (2). The samples from the meteoric diagenesis zone of Clino and Unda have a range of  $\delta^7\text{Li}$  values that span 13‰, with values from +16 to +29 permil in Clino and from +21 to +29 permil for Unda (fig. 5). The bulk meteoric vadose zone  $\delta^7\text{Li}$  value is  $+22.1 \pm 3.0$  permil ( $1\sigma$ ,  $n=13$ ), indistinguishable from the inferred original  $\delta^7\text{Li}$  value of the GBB sediments ( $\delta^7\text{Li} = +22 \pm 1\text{‰}$ ; fig. 5) but showing a much wider range. The average  $\delta^7\text{Li}$  value in the phreatic zone ( $+24.4 \pm 3.7\text{‰}$ ;  $1\sigma$ ,  $n=9$ ) is slightly higher than in the vadose zone and increases with depth from a value of +17 permil to values of about +27 permil at higher depth. The average Li/(Ca+Mg) ratio of the vadose zone samples is  $4.9 \pm 1.1 \mu\text{mol}\cdot\text{mol}^{-1}$  ( $1\sigma$ ,  $n=13$ ), and  $3.3 \pm 1.3 \mu\text{mol}\cdot\text{mol}^{-1}$  ( $1\sigma$ ,  $n=10$ ) for the phreatic zone samples, both lower than the Li/(Ca+Mg) ratio of the unaltered platform carbonates ( $9 \pm 1 \mu\text{mol}\cdot\text{mol}^{-1}$ ). In Clino and Unda, the Li/(Ca+Mg) ratios decrease from about 4–5  $\mu\text{mol}\cdot\text{mol}^{-1}$  at the top of the phreatic zone to values of 1  $\mu\text{mol}\cdot\text{mol}^{-1}$  at the bottom, before increasing again at the transition to marine burial diagenesis. Measured Al/(Ca+Mg) ratios are generally low (0.01–0.25  $\text{mmol}\cdot\text{mol}^{-1}$ ) and on average only slightly higher than in the original GBB sediments (fig. 5).

TABLE 2A

*Li isotope, Li/Ca and other trace element ratios in the Clino and Unda cores*

Core	Sample	Depth (m)	$\delta^7\text{Li}$ (‰)	Li/Ca ( $\mu\text{mol/mol}$ )	Mg/Ca ( $\text{mol/mol}$ )	Al/Ca ( $\text{mmol/mol}$ )	Mn/Ca ( $\mu\text{mol/mol}$ )	Fe/Ca ( $\mu\text{mol/mol}$ )	Sr/Ca ( $\text{mmol/mol}$ )
Clino	Clino 70'6"	21.49	17.7	5.93	0.0070	0.11	1.8	55.6	5.77
Clino	Clino 83'	25.3	24.0	5.41	0.0124	0.07	3.5	70.0	4.26
Clino	Clino 90'	27.43	16.1	2.87	0.0111	0.13	2.0	49.5	2.02
Clino	Clino 103'6"(a)	31.55	25.8						
Clino	Clino 112'	34.19	20.4	4.85	0.0155	0.07	5.3	66.3	3.31
Clino	Clino 123'5"	37.62	21.9	5.92	0.0209	0.08	5.3	90.8	2.45
Clino	Clino 133'(a)	40.54	21.1	5.48	0.0135	0.10	4.2	134.2	2.27
Clino	Clino 192'7"	56.92	21.3	4.68	0.0165	0.15	6.7	153.8	1.71
Clino	Clino 211'8"	64.52	25.2	5.49	0.0186	0.06	3.8	92.7	1.42
Clino	Clino 244'11"	74.65	20.0	6.72	0.0145	0.21	11.2	206.6	1.87
Clino	Clino 252'2"	76.86	25.1	3.91	0.0166	0.05	10.2	93.9	1.49
Clino	Clino 277'.7"	84.61		3.78	0.0163	0.12	7.9	70.4	1.73
Clino	Clino 294'5"	89.74	23.7	5.44	0.0162	0.13	7.4	150.0	1.60
Clino	Clino 318'	96.93	24.8	4.11	0.0184	0.09	9.0	112.9	1.26
Clino	Clino 340'6"	103.78	17.1	4.07	0.0001	0.04	1.4	2.4	2.64
Clino	Clino 366'	111.56		0.94	0.0157	0.03	7.0	33.4	3.14
Clino	Clino 432'	131.67	26.8	1.85	0.0274	0.02	10.2	21.4	1.87
Clino	Clino 483'6"	147.37	28.0	5.26	0.0305	0.03	14.1	24.1	3.44
Clino	Clino 503'8"	155.55	30.5	6.79	0.0580	0.05	13.4	18.0	2.43
Clino	Clino 532'	162.15	31.2	5.61	0.0647	0.03	11.9	13.1	1.39
Clino	Clino 575'3"	175.34	30.3	6.44	0.0517	0.03	15.1	6.5	1.73
Clino	Clino 608'5"	185.45	30.2	9.77	0.0758	0.07	15.5	7.7	2.24
Clino	Clino 736'1"	224.36	24.6	8.52	0.0310	0.34	4.5	29.9	4.60
Clino	Clino 764'3.5"	232.96	24.3	6.10	0.0264	0.20	2.8	21.3	5.27
Clino	Clino 828'1"	252.4	30.5	8.40	0.0636	0.08	16.0	18.1	1.57
Unda	Unda 296'5"	90.4494	21.1	5.07	0.0141	0.24	8.4	158.5	1.68
Unda	Unda 309'5"	94.31	25.6	3.94	0.0175	0.19	12.1	115.1	1.94
Unda	Unda 313'	95.4	22.5	3.61	0.0190	0.19	8.0	126.7	1.55
Unda	Unda 321'5"	97.97	23.8	3.44	0.0186	0.14	16.1	146.8	1.92
Unda	Unda 343'5"	104.67	27.6	2.89	0.0182	0.08	23.4	71.1	1.93
Unda	Unda 350'6"	106.83	27.3	2.69	0.0231	0.10	30.7	85.2	2.39
Unda	Unda 359'2"	109.47	30.8	28.98	0.5479	0.75	26.7	424.4	1.33
Unda	Unda 360'	109.73	29.4	13.39	0.2131	0.36	17.0	161.5	1.77
Unda	Unda 369'1"	112.5	29.6	5.61	0.0574	0.04	15.9	94.6	2.29
Unda	Unda 377'2"	114.96	28.9	10.18	0.0977	0.05	11.9	106.3	1.98
Unda	Unda 386'1"	117.68	30.3	15.36	0.1609	0.17	13.9	144.2	1.98
Unda	Unda 396'6"	120.85	30.2	17.42	0.1553	0.06	11.6	132.6	2.45
Unda	Unda 403'73"	123.01	30.7	14.13	0.1120	0.08	9.8	69.9	2.27
Unda	Unda 411'4"	125.37	30.4	14.20	0.1739	0.25	13.6	68.3	1.46
Unda	Unda 428'10"	130.71	30.8	12.61	0.0865	0.06	14.6	36.9	1.73
Unda	Unda 433'10"	132.23	30.2	10.75	0.0504	0.04	14.9	27.2	1.89
Unda	Unda 442'1"	134.75		9.80	0.0641	0.07	16.8	38.8	1.48
Unda	Unda 450'6"	137.31	31.2	9.22	0.0679	0.08	16.5	18.4	1.39
Unda	Unda 458'8"	139.8	30.2	10.36	0.0665	0.16	12.1	21.9	1.92
Unda	Unda 466'10"	142.29	30.7	9.53	0.0866	0.09	28.6	16.6	1.56
Unda	Unda 476'4"	145.19	30.7	8.24	0.0858	0.08	9.4	16.7	1.68
Unda	Unda 485'8"	148.03	30.6	7.95	0.0799	0.10	9.0	18.2	1.68
Unda	Unda 493'2"	150.32		8.77	0.0823	0.13	9.3	16.5	1.61
Unda	Unda 901'	274.62	30.4	18.23	0.2778	0.34	29.0	109.0	0.62
Unda	Unda 904'4"	275.64	30.5	16.43	0.2546	0.26	23.3	81.3	0.62
Unda	Unda 910'	277.37	30.8	16.76	0.2525	0.25	23.5	99.6	0.61
Unda	Unda 915'10"	279.15	30.8	18.77	0.3348	0.33	23.6	58.0	0.64
Unda	Unda 920'	280.42	29.9	17.02	0.2443	0.31	19.2	79.0	0.61
Unda	Unda 925'2"	281.99	30.7	24.95	0.6743	0.57	29.9	87.3	0.50
Unda	Unda 931'5"	283.9	30.8	23.60	0.6885	0.53	28.1	96.3	0.50
Unda	Unda 936'9"	285.52	30.6	22.92	0.6697	0.60	28.8	115.4	0.48
Unda	Unda 941'	286.82	30.7	22.97	0.6688	0.64	28.3	97.6	0.48
Unda	Unda 944'8"	287.93	30.7	21.23	0.5647	0.68	28.6	83.5	0.55
Unda	Unda 950'2"	289.61	31.0	23.42	0.6825	0.82	35.0	117.3	0.46
Unda	Unda 955'2"	291.13	30.4	23.54	0.7177	0.73	36.6	137.0	0.42

In the Key Largo Limestone, the bulk average  $\delta^7\text{Li}$  value of the meteoric-altered samples is  $18.1 \pm 2.2$  permil ( $1\sigma$ ,  $n=6$ ) which is indistinguishable from the non-altered value of  $17.9 \pm 0.7$  permil ( $1\sigma$ ,  $n=5$ ), but the range and standard deviation are larger for the altered samples (fig. 6). The Li/(Ca+Mg) ratios of the unaltered aragonite

TABLE 2B

*Li isotope, Li/Ca and other trace element ratios in the Key Largo Limestone*

Transect	Sample	Distance (m)	$\delta^7\text{Li}$ (‰)	Li/Ca ( $\mu\text{mol/mol}$ )	Mg/Ca (mol/mol)	Al/Ca (mmol/mol)	Mn/Ca ( $\mu\text{mol/mol}$ )	Fe/Ca ( $\mu\text{mol/mol}$ )	Sr/Ca (mmol/mol)
KL1	KL 1-1	0.04	20.6						
KL1	KL 1-2	0.022	20.4						
KL1	KL 1-3	0.005	18.7	0.79	0.0029		0.2		1.69
KL1	KL 1-4	-0.015	17.5	5.15	0.0034		0.1		7.09
KL1	KL 1-6	-0.043	17.6	5.64	0.0035		0.2		7.30
KL11	KL 11-3	0.057		0.98	0.0035	0.01	1.0	4.6	2.58
KL11	KL 11-4	0.049		1.41	0.0035	0.02	0.9	6.5	4.84
KL11	KL 11-5	0.0405		0.28	0.0042	0.01	1.7	22.4	4.94
KL11	KL 11-6	0.033		2.06	0.0044	0.00	0.9	4.4	5.13
KL11	KL 11-8	0.015		1.42	0.0044	0.02	0.8	6.0	5.47
KL11	KL 11-12	-0.0215	19.1	6.50	0.0034	0.00	0.6	5.0	9.02
KL11	KL 11-14	-0.037		6.01	0.0037	0.02	1.0	7.5	8.80
KL12	KL 12-1	0.0575		0.54	0.0035	0.02	0.6	4.0	2.18
KL12	KL 12-2	0.049	15.0	0.84	0.0029	0.04	0.0	0.0	2.04
KL12	KL 12-3	0.0405		3.41	0.0029	0.02	0.4	4.2	1.66
KL12	KL 12-4	0.032		1.93	0.0037	0.01	0.5	6.0	2.08
KL12	KL 12-5	0.023	16.9	1.05	0.0036	0.02	0.6	4.4	2.09
KL12	KL 12-6	0.014		5.99	0.0032	0.02	0.5	4.3	2.63
KL12	KL 12-7	0.006	17.2	0.68	0.0030	0.01	0.6	5.5	2.45
KL12	KL 12-8	-0.0065	18.3	5.80	0.0036	0.03	0.5	5.2	9.10
KL12	KL 12-9	-0.0165		5.94	0.0038	0.05	0.7	12.8	9.01
KL12	KL 12-10	-0.0245	17.9	4.87	0.0037	0.01	0.4	3.1	8.94

TABLE 2C

*Li isotope, Li/Ca and other trace elements ratios in the ODP Site 1007*

Leg	Site	Hole	Core	Type	Sec	Upp	Low	Depth (mbsf)	$\delta^7\text{Li}$ (‰)	Li/Ca ( $\mu\text{mol/mol}$ )	Mg/Ca (mol/mol)	Al/Ca (mmol/mol)	Mn/Ca ( $\mu\text{mol/mol}$ )	Sr/Ca ( $\mu\text{mol/mol}$ )
166	1007	B	3	H	4	39	40	23.9	24.4	10.24	0.0133	0.09	17.9	8.68
166	1007	B	5	H	2	39	40	41.9	26.6	12.20	0.0140	0.16	91.9	7.72
166	1007	B	5	H	4	39	40	44.9	25.0	14.99	0.0184	1.26	269.2	3.31
166	1007	B	7	H	6	39	40	65.4	25.6	11.45	0.0156	0.16	72.9	8.11
166	1007	B	8	H	2	39	40	68.9	23.4	11.24	0.0115	0.12	10.8	10.80
166	1007	B	8	H	4	39	40	71.9	23.9	9.19	0.0123	0.10	9.8	9.88
166	1007	B	9	H	2	39	40	78.4	27.4	10.57	0.0097	0.07	2.7	10.40
166	1007	B	11	X	2	39	40	93.6	23.3	8.72	0.0066	0.07	5.6	10.05
166	1007	B	11	X	4	39	40	96.6	27.9	15.23	0.0432	0.46	88.1	3.35
166	1007	B	12	X	1	64	65	101.8	26.0	10.42	0.0179	0.13	7.7	8.83
166	1007	B	13	X	CC	40	41	111	22.6	9.20	0.0183	0.04	10.4	7.86
166	1007	B	16	X	2	39	40	140.4		8.99	0.0228	0.23	79.3	7.63
166	1007	B	17	X	2	39	40	149.3	26.4	9.71	0.0207	0.26	54.8	1.82
166	1007	B	17	X	4	39	40	152.3	26.6	11.53	0.0424	0.17	6.3	8.76
166	1007	B	23	X	6	39	40	211	25.7	15.41	0.0401	0.28	188.4	1.70
166	1007	B	24	X	4	39	40	217.3		21.36	0.0381	0.26	150.5	1.83
166	1007	B	25	X	4	39	40	226.4	28.4	11.46	0.0163	0.05	305.1	1.93
166	1007	B	26	X	4	39	40	235.5	28.4					
166	1007	B	28	X	2	39	40	251	28.1	10.18	0.0174	0.10	201.9	1.43
166	1007	B	34	X	1	62	63	304.9	28.9	13.79	0.0315	0.14	114.2	1.84
166	1007	B	36	X	1	14	15	322.9	29.0	7.97	0.0276	0.08	49.3	1.77
166	1007	B	38	X	1	13	14	341.2	27.3	6.10	0.0107	0.08	45.1	1.27

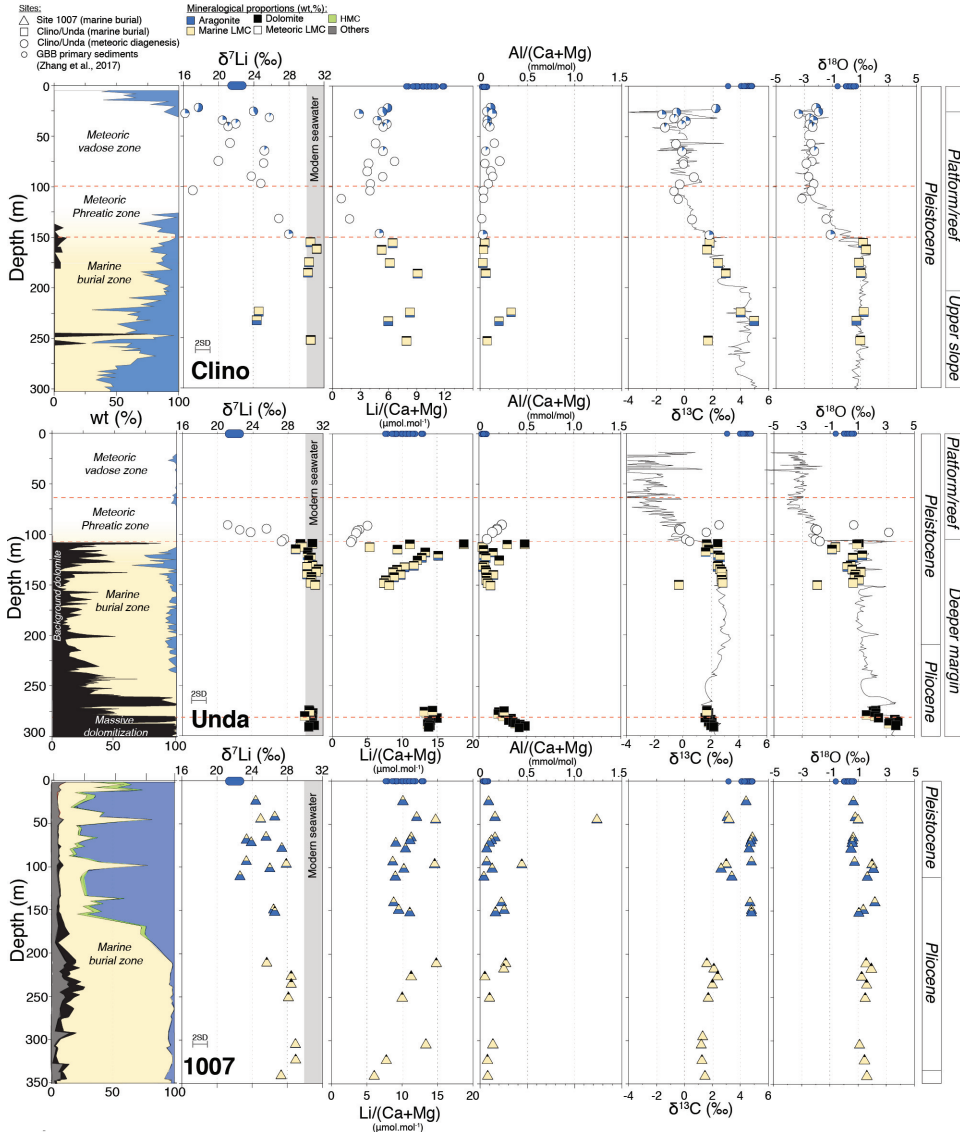


Fig. 5. Carbonate mineralogy,  $\delta^7\text{Li}$ , and  $\text{Li}/(\text{Ca}+\text{Mg})$ ,  $\text{Al}/(\text{Ca}+\text{Mg})$ ,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  versus depth for the Clino (top), Unda (middle) and 1007 cores (bottom). The mineralogy and lines for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  come from Melim and others (1995). Carbon and oxygen isotope data for our specific samples are superimposed (data from Hardisty and others, 2017). The filling of the points corresponds to the mineralogical proportions, as indicated in the legend. The vertical gray bar corresponds to the modern seawater  $\delta^7\text{Li}$  value.

samples ranges from  $4.9$  to  $6.5 \mu\text{mol}\cdot\text{mol}^{-1}$ , averaging  $5.7 \pm 0.6 \mu\text{mol}\cdot\text{mol}^{-1}$  ( $1\sigma$ ,  $n=7$ ). These values are similar to the  $\text{Li}/\text{Ca}$  ratios observed in corals (Rollion-Bard and others, 2009). The  $\text{Li}/(\text{Ca}+\text{Mg})$  ratios of altered low-Mg calcite samples is much lower,  $0.3$  to  $3.7 \mu\text{mol}\cdot\text{mol}^{-1}$  except for sample KL12-6 which has similar  $\text{Li}/(\text{Ca}+\text{Mg})$  ratios to unaltered aragonite. The average  $\text{Li}/(\text{Ca}+\text{Mg})$  ratios of the altered material is  $1.6 \pm 1.4 \mu\text{mol}\cdot\text{mol}^{-1}$  ( $1\sigma$ ,  $n=15$ ).

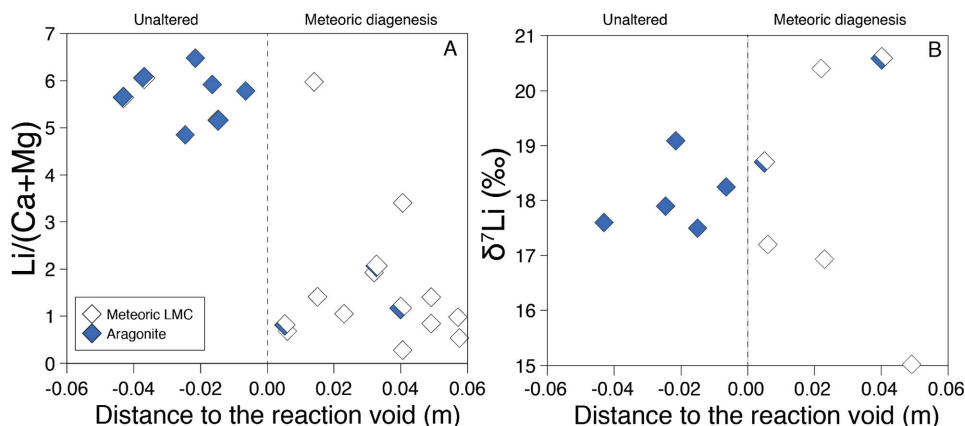


Fig. 6. Meteoric diagenesis alteration profile for (A)  $\text{Li}/(\text{Ca}+\text{Mg})$  (in  $\mu\text{mol.mol}^{-1}$ ) and (B)  $\delta^7\text{Li}$  in Key Largo limestone. The alteration front in these samples (distance = 0 m on the x-axis) represents a shift from aragonite to low-Mg calcite. The filling of the points corresponds to the mineralogical proportions.

## 5.2. Marine Diagenesis Zone

In both the Clino and Unda cores,  $\delta^7\text{Li}$  values increase with depth at the transition between the meteoric and the marine burial diagenetic zone (fig. 5). The  $\delta^7\text{Li}$  values in the marine diagenesis zone of the Clino and Unda cores are  $\sim 30$  to 31 permil ( $+30.2 \pm 1.5\text{‰}$ ,  $1\sigma$ ,  $n=36$ ), identical within uncertainty to the  $\delta^7\text{Li}$  values of modern seawater. Two Clino samples characterized by high proportions of aragonite have low  $\delta^7\text{Li}$  of  $+24.5$  permil. Below 280 m in the Unda core, there is a zone entirely composed by dolomite (massive dolomite) with an average  $\delta^7\text{Li}$  value of  $+30.6 \pm 0.3$  permil ( $1\sigma$ ,  $n=12$ ), also identical to modern seawater. The  $\delta^7\text{Li}$  values in ODP Site 1007 samples range between  $+22.0$  to  $+29.6$  permil, with a progressive increase in  $\delta^7\text{Li}$  value with depth. We observe a positive relationship between the  $\delta^7\text{Li}$  and the weight percent proportion of LMC in 1007 samples (fig. 7B). The  $\text{Li}/(\text{Ca}+\text{Mg})$  in the marine diagenesis zone is generally higher in Unda (from 5–19  $\mu\text{mol.mol}^{-1}$ ) and in 1007 site (6–20  $\mu\text{mol.mol}^{-1}$ ) relative to Clino (5–9  $\mu\text{mol.mol}^{-1}$ ). In Unda, we observe a peak of high  $\text{Li}/(\text{Ca}+\text{Mg})$  ratios that coincides with the peak of dolomite proportion (hardground dolomite sample) at the transition between the meteoric and marine diagenesis zones. For Clino and Unda Pleistocene sediments, the  $\text{Li}/(\text{Ca}+\text{Mg})$  ratio of samples from the marine diagenesis zone in both cores is positively correlated with the proportion of dolomite and inversely correlated with the proportion of low-Mg calcite ( $r^2=0.81$  excluding 1 sample, fig. 7A). In contrast, no clear relationship between  $\text{Li}/(\text{Ca}+\text{Mg})$  and the proportion of LMC is observed for samples from site 1007 (fig. 7A). For Clino and Unda, measured  $\text{Al}/(\text{Ca}+\text{Mg})$  ratios are generally low (0.01–0.50  $\text{mmol.mol}^{-1}$ ) with high values only observed in dolomite rich samples (fig. 5 and Appendix A3). As discussed in the Appendix (A3), samples having  $\text{Al}/(\text{Ca}+\text{Mg})$  ratios ( $> 0.45$   $\text{mmol.mol}^{-1}$ ) are potentially influenced by silicate contamination during digestion of the sediments and are therefore excluded from the rest of the discussion. This cutoff value is half that used in other studies (for example,  $\text{Al}/\text{Ca}$  of 0.80  $\text{mmol.mol}^{-1}$  in Pogge von Standmann and others, 2013; Bastian and others, 2018).

## 6. DISCUSSION

### 6.1. Influence of Marine Burial Diagenesis on $\delta^7\text{Li}$

In this section, we focus first on observations from the marine burial diagenesis zone. The average  $\delta^7\text{Li}$  value of the marine burial samples ( $+30 \pm 1.5\text{‰}$ ) from Clino



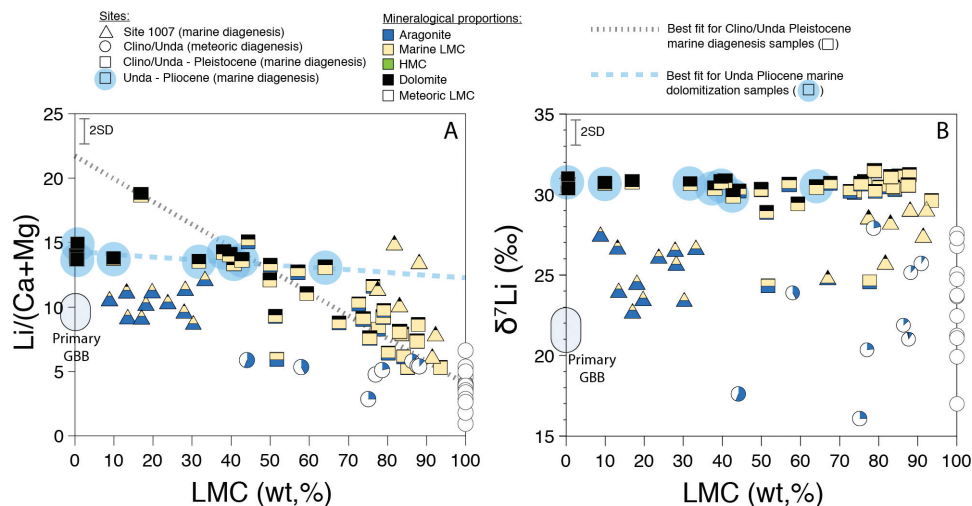


Fig. 7. Mineralogical control on Li isotope composition and Li/(Ca+Mg) values (in  $\mu\text{mol.mol}^{-1}$ ) for the samples from this study. Proportion of Low-Mg calcite (LMC) as a function of (A) the Li/(Ca+Mg) ratio and (B)  $\delta^7\text{Li}$ . The blue dotted line corresponds to the best fit for Pliocene Unda samples from the massive dolomite zone (squares with blue circle), whereas the grey dotted line corresponds to the best fit for Clino and Unda samples from the marine burial zone (squares with no blue circle,  $r^2=0.81$  excluding the Clino sample at 232.96m having high proportion of aragonite). The filling of the points corresponds to mineralogical proportions.

and Unda is identical within uncertainty to the  $\delta^7\text{Li}$  value of modern seawater, but about 8‰ higher than the original  $\delta^7\text{Li}$  value of GBB aragonitic sediments (fig. 5). Thus, marine burial diagenesis imparts a modern seawater-like composition to the Clino and Unda carbonates. However, the same is not true for the periplatform carbonates from the 1007 core, where  $\delta^7\text{Li}$  values vary from +23.3 to +28.6 permil. In addition to different  $\delta^7\text{Li}$  values, Clino/Unda and 1007 sediments define very distinct geochemical trends between  $\delta^7\text{Li}$  values and other geochemical proxies, particularly Li/(Ca+Mg) and Sr/(Ca+Mg) ratios, as well as  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  (fig. 8). The observed variability of  $\delta^7\text{Li}$  values and Li/(Ca+Mg) ratios with respect to depth and the differences between Clino/Unda and Site 1007 result from the combination of two processes: i) diagenetic resetting of primary aragonite signatures during conversion of LMC and dolomite under fluid-buffered vs. sediment buffered conditions and/or ii) changes in the source of the carbonate sediment (pelagic calcite vs. platform aragonite carbonates) with time and distance to the GBB platform (i.e., with more pelagic contribution at the periplatform setting of 1007). Below we discuss the respective influence of these two processes. Overall, we attribute the Clino and Unda Li isotope signatures to diagenetic resetting, and the distinct 1007 patterns to a combination, with at least some influence from variable amounts of primary pelagic calcite.

In detail, the bulk Li/(Ca+Mg) of Clino/Unda Pleistocene sediments is controlled by a mineralogical mixture between Li-poor LMC and Li-rich dolomite (fig. 7A). The correlation between Li/(Ca+Mg) and weight percent LMC ( $r^2=0.81$ , fig. 7A) suggests the LMC component in these samples (intercept at 100% LMC of the mineralogical mixing trend of fig. 7A) has a relatively homogeneous composition with a Li/(Ca+Mg) value of  $4 \pm 2 \mu\text{mol.mol}^{-1}$ , a  $\delta^7\text{Li}$  value of 27 to 30 permil a  $\delta^{13}\text{C}$  value of  $\sim 2.2$  permil, and a Sr/(Ca+Mg) ratio  $\sim 2.0 \text{ mmol.mol}^{-1}$  (fig. 8). All these values, particularly the low Li/(Ca+Mg) and the high  $\delta^7\text{Li}$ , are compatible with fluid-buffered

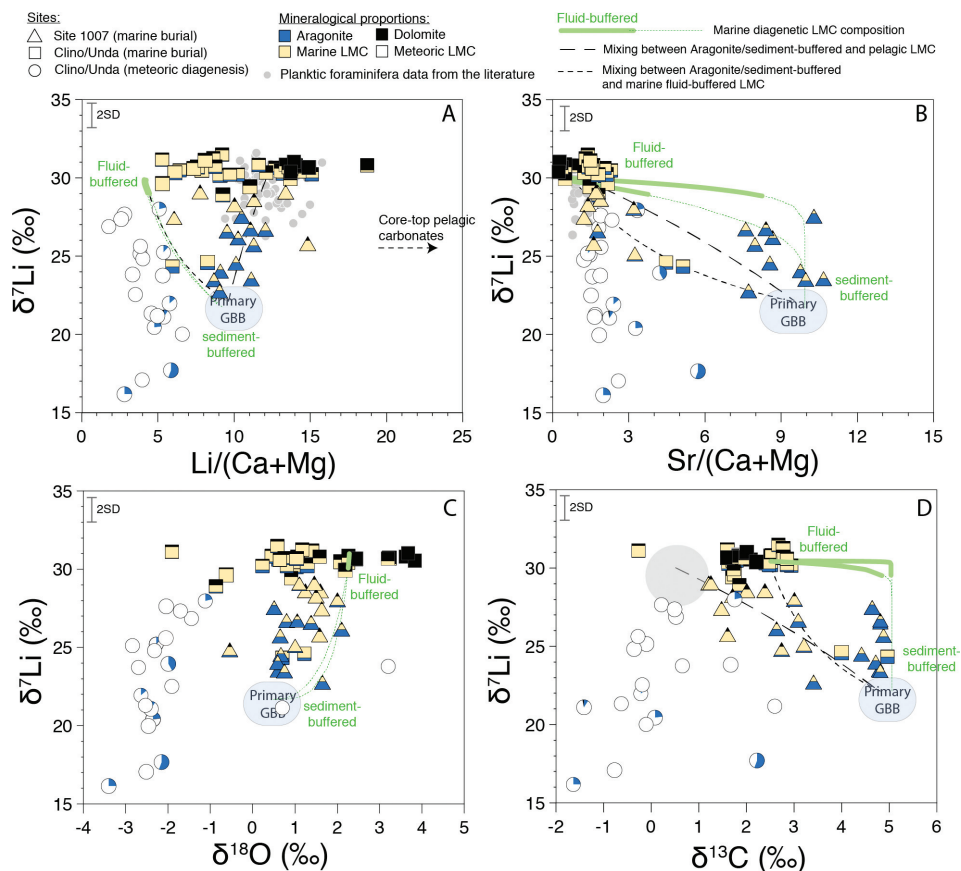


Fig. 8. Diagenetic covariation cross-plots between Li isotope composition and (A) the Li/(Ca+Mg) ratio (in  $\mu\text{mol.mol}^{-1}$ ), (B) the Sr/(Ca+Mg) ratio (in  $\text{mmol.mol}^{-1}$ ), (C)  $\delta^{18}\text{O}$  and (D)  $\delta^{13}\text{C}$  of carbonates. Samples from the Key Largo Limestone are not shown. The thick green lines correspond to the fluid-buffered diagenetic end-member (in regard to Li,  $dEQ^{\text{Li}} > 0.9$ ). The thin green lines in each panel correspond to the whole compositional range of diagenetic end-member values calculated both for low advection rate and high advection rate (see Appendix A1). The black dotted lines are mixing lines between primary GBB and the inferred composition for pelagic carbonates and fluid-buffered marine LMC (in regard to all proxies, i.e.  $dEQ^{\text{C}}$ ,  $EQ^{\text{O}}$ ,  $EQ^{\text{Sr}} > 0.9$ ). Li isotope data for planktic foraminifera are from Hall and others (2005), Hathorne and James (2006) and Misra and Froelich (2012). The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for Site 1007 and inferred range of  $\delta^{13}\text{C}$  for planktic foraminifera are from Swart and Eberli (2005).

diagenesis (with respect to Li, but also Sr, C, and O; see section 2). Inorganic LMC precipitated from seawater should have lower Li/Ca than aragonite due to lower  $K_d^{\text{Li}}$  (section 2), as observed in these samples. Interestingly, these samples have Li isotope ratios  $\sim 30$  to  $31$  permil. Fluid-buffered diagenetic calcite derived from pore waters with a seawater-like  $\delta^7\text{Li}$  value ( $\sim +31$ ‰) should form with  $\delta^7\text{Li} = 27\text{--}30$ ‰ ( $\Delta^7\text{Li}_{\text{LMC-fluid}} \sim -1\text{--}4$ ‰; Marriot and others, 2004b; Pogge von Strandmann and others, 2017). Thus, our observation of diagenetic carbonates at  $\sim 30\text{--}31$ ‰ requires either a fractionation factor at the very lower end of those experimentally determined for LMC, or pore waters that are  $\sim 2$  permil heavier than seawater (due to influence of other processes). In any case, the diagenetic LMC from the burial diagenesis sections of these cores carries a uniform  $\delta^7\text{Li}$ , similar to ambient seawater composition.

The higher Li/(Ca+Mg) ratio for dolomite-rich Clino/Unda samples (up to  $15\text{--}22 \mu\text{mol.mol}^{-1}$ ) suggests that the dolomite precipitated under fluid-buffered

conditions in these cores (Ahm and others, 2018) incorporated a higher proportion of Li than diagenetic LMC. In detail, we note that the intercept at 0 weight percent LMC (or 100 wt% dolomite; fig. 7) is distinct for Pleistocene sediments relative to Pliocene sediments. In other words, the  $\text{Li}/(\text{Ca}+\text{Mg})$  of Pliocene massive dolomites ( $15\pm 2 \mu\text{mol}\cdot\text{mol}^{-1}$ ) is lower than the  $\text{Li}/(\text{Ca}+\text{Mg})$  of the background dolomite in the younger samples ( $\sim 22 \mu\text{mol}\cdot\text{mol}^{-1}$ ). These differences are consistent with a distinct origin of the two different type of dolomites inferred from their different Sr/Ca ratios and  $\delta^{18}\text{O}$  values (Swart and Melim, 2000). However, both dolomites have a seawater-like  $\delta^7\text{Li}$  value similar to that of the fluid-buffered LMC, instead of low  $\delta^7\text{Li}$  as would be predicted (section 2) from the recently reported fractionation factor between inorganic dolomite and fluid that is  $-23\pm 6$  permil at 25 °C (Taylor and others, 2019). Precipitation of dolomite with a  $\delta^7\text{Li}$  value of +31 permil as we observe would, given this fractionation factor, require a fluid with  $\delta^7\text{Li}$  of +54 permil; such enriched  $\delta^7\text{Li}$  has only been measured in a few marine pore fluid samples (Scholz and others, 2010). Independent arguments suggest that the fluid that precipitated the Unda massive dolomite was seawater with “normal composition” (Swart and Melim, 2000; Ahm and others, 2018). In addition, the consistently narrow range of  $\delta^7\text{Li}$  values we observe in dolomites, around +31 permil, match present-day seawater, even though we have sampled a range of dolomites from different depths, cores, and likely mechanisms of precipitation (Swart and Melim, 2000). Altogether, our results point toward a more modest dolomite-fluid Li isotope fractionation factor than extrapolated from high-temperature experiments. At this stage, we cannot completely exclude dolomite precipitating from a seawater derived fluid with very high  $\delta^7\text{Li}$  values and with a very large fractionation factor (Taylor and others, 2019), and more experimental and empirical studies on dolomite will be necessary to ultimately resolve this question.

Finally, we observe that some LMC-rich samples (that contain low amounts of dolomite and aragonite), particularly from Site 1007, have  $\text{Li}/(\text{Ca}+\text{Mg})$  ratios higher and  $\delta^7\text{Li}$  lower than the inferred fluid-buffered diagenetic end-member (fig. 8). One possibility to explain this signature is that these samples contain pelagic LMC, since modern foraminifera have  $\delta^7\text{Li} \sim 30$  permil and  $\text{Li}/(\text{Ca}+\text{Mg}) \sim 10$  to  $16 \mu\text{mol}\cdot\text{mol}^{-1}$  (see fig. 8A) and bulk top core pelagic carbonates from the Bahamas have  $\delta^7\text{Li} \sim 24$  to  $27$  permil and  $\text{Li}/(\text{Ca}+\text{Mg}) \sim 20$  to  $40 \mu\text{mol}\cdot\text{mol}^{-1}$  (Pogge von Strandmann and others, 2019). A substantial contribution of pelagic material to the 1007 samples is consistent with the conclusions of Swart and Eberli (2005) based on the carbon isotope composition. This interpretation also fits observed mixing trends (fig. 8). An alternative possibility is that the high  $\text{Li}/(\text{Ca}+\text{Mg})$ , low  $\delta^7\text{Li}$  carbonates contain LMC formed during more sediment-buffered diagenetic conditions than Clino and Unda, as has been suggested to explain their Ca isotope composition (Higgins and others, 2018). Transformation of aragonite to LMC under sediment-buffered diagenetic conditions should produce LMC with similar geochemical composition as the original aragonite [ $\delta^7\text{Li} \sim 23\text{‰}$  and  $\text{Li}/(\text{Ca}+\text{Mg}) \sim 8\text{--}12 \mu\text{mol}\cdot\text{mol}^{-1}$ ]. In fact, diagenetic minerals can have compositions that range from pure fluid-buffered to pure sediment-buffered signatures (section 2 and fig. 8). Some LMC-rich samples plot within both the diagenetic trend (green curves) and on the mixing trend (black dotted curve) between fluid- and sediment-buffered marine LMC (fig. 8). However, the presence of aragonite in Plio-Pleistocene Site 1007 samples between 0 and 170 mbsf makes it difficult to quantify more precisely the contribution of primary vs. diagenetically-formed LMC in the top 200m of core 1007, since the aragonite has not yet been completely transformed into low-Mg calcite or dolomite by early diagenetic processes at this site.

Given that we seek to determine the extent to which diagenesis overprints or preserves the primary seawater signal, we use a simple isotope mass-balance attempt to calculate the composition of the LMC component only. We do so by correcting for

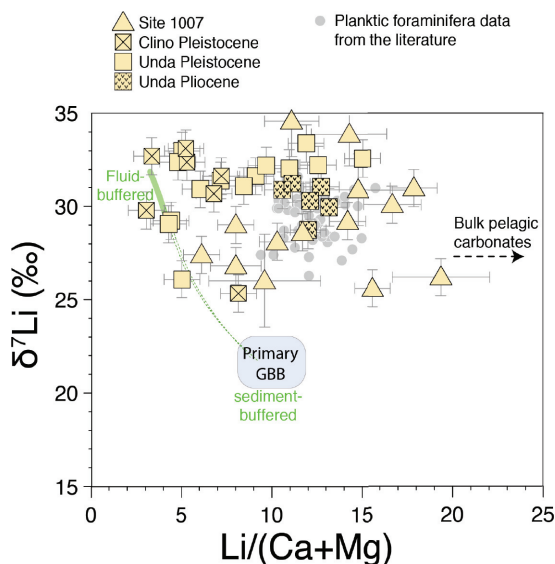


Fig. 9. Calculated geochemical composition ( $\delta^7\text{Li}$  and  $\text{Li}/(\text{Ca}+\text{Mg})$  in  $\mu\text{mol}\cdot\text{mol}^{-1}$ ) of the LMC component for each sample (see supplementary data table, <http://earth.geology.yale.edu/%7eajs/SupplementaryData/2020/Dellinger>). The diagenetic end-members are the same as in figure (8A).

aragonite and dolomite contribution to all samples from the marine diagenetic zone at Site 1007 and Clino-Unda (see Appendix A3 for details and supplementary table for results, <http://earth.geology.yale.edu/%7eajs/SupplementaryData/2020/Dellinger>).

In this manner, we can determine whether the diagenetic LMC records the signature of seawater or not. Results are shown in figure 9, along with the range of expected values for fluid-buffered and sediment-buffered diagenetic LMC formed in marine pore fluids. The  $\delta^7\text{Li}$ - $\text{Li}/(\text{Ca}+\text{Mg})$  variability is well-explained by a 3-component mixture between i) fluid-buffered diagenetic LMC [ $\text{Li}/(\text{Ca}+\text{Mg}) \sim 3\text{--}5 \mu\text{mol}\cdot\text{mol}^{-1}$ ,  $\delta^7\text{Li} \sim 29\text{--}32\text{‰}$ ], ii) sediment-buffered diagenetic LMC [same composition as GBB platform top sediment,  $\text{Li}/(\text{Ca}+\text{Mg}) \sim 9 \mu\text{mol}\cdot\text{mol}^{-1}$ ,  $\delta^7\text{Li} \sim 23\text{‰}$ ] and iii) pelagic LMC [ $\text{Li}/(\text{Ca}+\text{Mg}) \sim 13\text{--}20 \mu\text{mol}\cdot\text{mol}^{-1}$ ,  $\delta^7\text{Li} \sim 31\text{‰}$ ]. Note that some samples have  $\delta^7\text{Li}$  values higher than  $+31\text{‰}$  which might be due to the large uncertainty associated with these isotope mass-balance calculations. For Clino, we observe that all Pleistocene sediments (except one) plot close to the fluid-buffered end-member. For Unda, the Pleistocene samples are between the fluid-buffered and pelagic end-members while the Pliocene sediments plot closer to the pelagic end-member. Finally, for Site 1007, samples plot mostly between diagenetic carbonates with values intermediate between fluid- and sediment-buffered compositions and a pelagic end-member.

In summary, the observed diagenetic transformation of  $\delta^7\text{Li}$  values implies that the Unda and Clino cores were subject to more open-system alteration during marine burial diagenesis than the 1007 samples, supporting interpretations from previous studies (Henderson and others, 1999; Higgins and others, 2018). This difference is probably the result of higher fluid advection rate close to the GBB (Caspard and others, 2004; Higgins and others, 2018). Altogether, the  $\delta^7\text{Li}$  values of the non-meteoritic Bahamian carbonates reflect largely what we would expect: where fluid-rock ratios are high, open-system diagenesis imparts consistent seawater-like  $\delta^7\text{Li}$  values on the buried carbonate (Clino and Unda), but where closed-system diagenesis is rock-

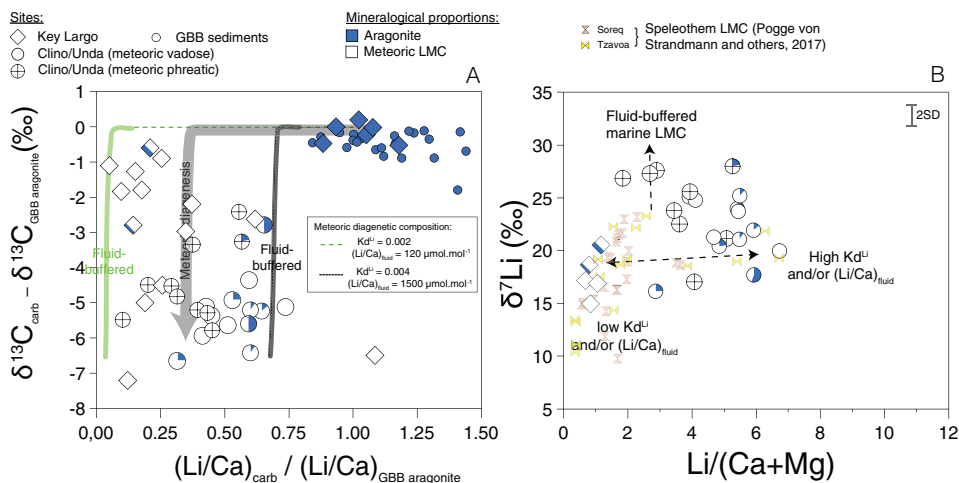


Fig. 10. Effect of meteoric diagenesis on Li/Ca and Li isotopes. (A) Carbon isotopes of Clino, Unda and Key Largo meteoric diagenesis zone corrected for the carbon isotope value of the original aragonite ( $\delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{aragonite}}$ ) as a function of the  $(\text{Li}/\text{Ca})$  ratio of the samples divided by the original  $(\text{Li}/\text{Ca})$  of the aragonite carbonate. Values of  $(\text{Li}/\text{Ca})_{\text{carb}}/(\text{Li}/\text{Ca})_{\text{GBB aragonite}} < 1$  indicates loss of Li during diagenesis. (B)  $\delta^7\text{Li}$  as a function of the  $\text{Li}/(\text{Ca}+\text{Mg})$  (in  $\mu\text{mol}\cdot\text{mol}^{-1}$ ) for meteoric diagenesis samples only. Soreq and Tzavoa travertine samples from Pogge von Strandmann and others (2017) are also represented.

buffered,  $\delta^7\text{Li}$  can be variable, reflecting the different mineralogy-dependent fractionation factors.

## 6.2. Meteoric Diagenesis

**6.2.1. Evidence for diagenetic resetting of carbonate  $\delta^7\text{Li}$  in the meteoric zone.**—The average Li isotope ratio from carbonates in the meteoric alteration zone of Clino and Unda ( $\delta^7\text{Li} = +22.0 \pm 3.8\text{‰}$ ;  $1\sigma$ ,  $n=28$ ) is similar to primary aragonite-dominated carbonate sediment from this region. The same is true for the Key Largo samples. It is thus tempting to interpret these samples as recording primary Li isotope signatures of aragonite (as might be the case for sediment-buffered diagenesis). However, other geochemical proxies ( $\delta^{13}\text{C}$ ,  $\text{Sr}/\text{Ca}$ ,  $\text{Mg}/\text{Ca}$ ) that are less sensitive to meteoric diagenesis than Li (according to calculations from section 2) have fluid-buffered composition and show resetting in these samples (Melim and others, 2001; Gill and others, 2008; Stewart and others, 2015). Moreover, the  $\delta^7\text{Li}$  and  $\text{Li}/(\text{Ca}+\text{Mg})$  from samples in the meteoric zone are negatively correlated with the  $\delta^{13}\text{C}$  (figs. 8D and 10A). Thus, we expect Li to also be reset to the meteoric fluid composition. In addition, the  $\text{Li}/(\text{Ca}+\text{Mg})$  ratio is lower in carbonates from the altered zone than in primary Bahamas carbonates (fig. 8), which is expected from diagenetic transformation of aragonite to calcite (see section 2). Together, these trends indicate LMC precipitation in the presence of meteoric fluids, consistent with conclusions from data on other isotopic systems such as C, O, Sr, U and B that imply high fluid-rock ratios (Melim and others, 1995; Stewart and others, 2015; Swart and Oehlert, 2018; Chen and others, 2018). Therefore, we conclude that meteoric diagenesis in Clino, Unda and Key Largo has altered the primary Li signature, producing variable isotopic compositions controlled by meteoric fluid composition. The resulting carbonates have  $\delta^7\text{Li}$  values that are 3 to 15 permil lower than corresponding seawater and marine fluid-buffered diagenetic LMC, but coincidentally similar on average to primary GBB aragonite.

**6.2.2. Control on the  $\delta^7\text{Li}$  and  $\text{Li}/\text{Ca}$  in the meteoric zone.**—If we accept that the Li system has been reset in the meteoric portions of the Clino and Unda cores, and in the



Key Largo Limestone, then based on mass balance predictions (see section 2), the  $\delta^7\text{Li}$  values and Li/Ca ratios of carbonate in these zones should depend on a combination of (1) the composition of the meteoric fluid itself, which is controlled by soil processes including Li supply from carbonate and minor silicate components (detrital or dust), along with fractionation during Li retention in secondary phases (clay minerals, iron oxides); and (2) the partition coefficient and fractionation factor during formation of the diagenetic carbonates, which may vary to some extent as a function of salinity, temperature, and pH (see section 2). The causes of the 12‰ variability within the meteoric diagenetic zone, in particular the differences between the Clino vadose zone (low  $\delta^7\text{Li}$  values and high Li/Ca ratios), the Clino-Unda phreatic zone (high  $\delta^7\text{Li}$  values and low Li/Ca ratios) and the Key Largo limestone (low  $\delta^7\text{Li}$  values and low Li/Ca ratios), are not known but could be related either to local processes (for example, style of weathering in the overlying soils) or global factors (for example, climatic changes) (fig. 10).

A comparison with speleothem data from Soreq and Tzavoa caves in Israel (Pogge von Strandmann and others, 2017) may hold some clues. In the  $\delta^7\text{Li}$ -Li/Ca space (fig. 10), the Key Largo samples plot in the middle of the trend defined by the majority of Soreq and Tzavoa samples, indicating that their composition can be explained in the same way, that is, by variability in the congruency of meteoric weathering (Pogge von Strandmann and others, 2017)—meaning that climatic variability and other factors that control weathering congruency can impart highly variable  $\delta^7\text{Li}$  (by 10‰ or more) on carbonates that have been exposed to meteoric diagenesis. However, some of the Soreq and Tzavoa samples ( $n=7$ ), along with the Clino samples from the vadose zone, have much higher Li/Ca ratios (3 to 7  $\mu\text{mol}\cdot\text{mol}^{-1}$ ). Such high Li/Ca ratios in carbonates would require calcite precipitation from fluid having much higher Li/Ca ratios (1500–5000  $\mu\text{mol}\cdot\text{mol}^{-1}$ ) than typical Li/Ca ratios of rivers draining limestones and/or a much higher  $K_d^{\text{Li}}$ . We expect that such high Li/Ca is therefore more likely the result of changes in local environment conditions, for example local evaporation of meteoric fluids under drier climatic conditions, increased contribution of silicate phases, mixing with a small proportion of seawater fluids, or effects from local variability in pH and temperature influencing  $K_d^{\text{Li}}$ . Hence, the Clino samples from the vadose zone may have been affected by specific local porewater environments. Finally, we observe that samples from the meteoric phreatic zone in Clino and Unda have in general the highest  $\delta^7\text{Li}$  among meteoric LMC samples. A possible explanation is that phreatic meteoric LMC records the progressive change in the  $\delta^7\text{Li}$  and Li/Ca between LMC formed under meteoric alteration conditions and LMC formed under marine fluid-buffered conditions (fig. 10B). This hypothesis would be in agreement with the proposed explanation for the co-variation of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in this zone (Swart and Oehlert, 2018). Regardless of the specific mechanism explaining differences between the vadose and phreatic zones, it is clear that meteoric diagenesis is imparting highly variable  $\delta^7\text{Li}$  and Li/Ca in altered carbonates and is likely to pose challenges in reconstructing past seawater composition from meteorically altered carbonates, although well-targeted studies may be able to harness this variability to infer information about local weathering and climatic conditions.

#### 7. IMPLICATIONS AND GUIDELINES FOR INTERPRETING THE $\delta^7\text{Li}$ VALUES OF ANCIENT CARBONATES

Our new data and analysis show that diagenetic transformation of aragonite to LMC produces a wide range of Li isotopic compositions and Li/(Ca+Mg) ratios in altered carbonate from the Bahamas. These observations have important implications for reconstructing the past  $\delta^7\text{Li}$  of the ocean using marine carbonates. In figure (11), we summarize the observations about the effects of diagenesis in the Bahamas from this study, and in table 3 we provide general quantitative predictions (that is, for any

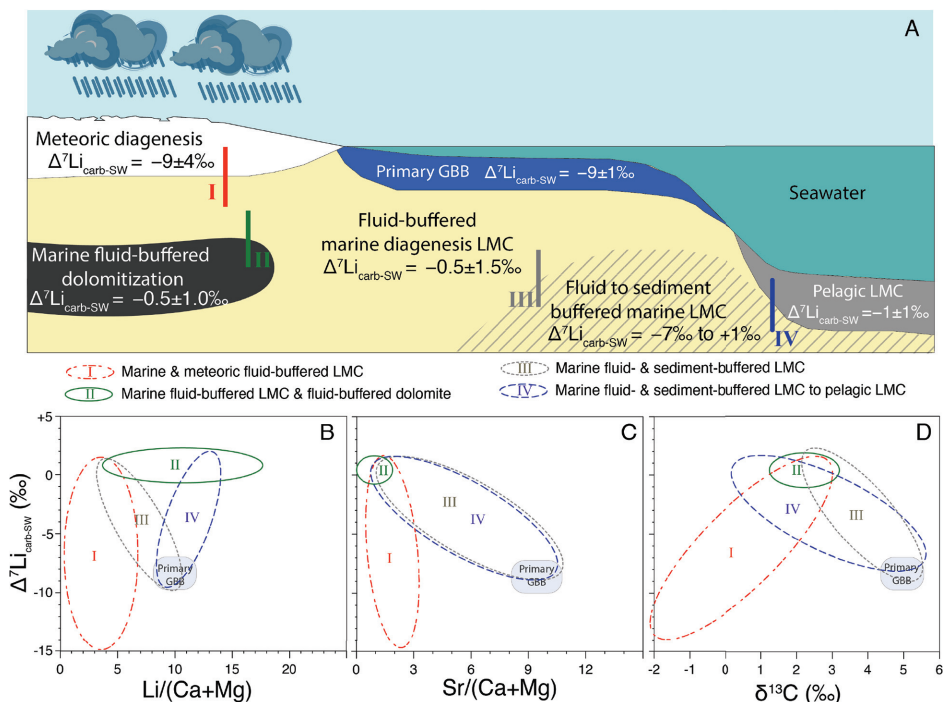


Fig. 11. Summary of the influence of diagenesis on Li isotopes in the Bahamian platform. (A) Range of Li isotope composition ( $\Delta^7\text{Li}_{\text{carb-sw}} = \delta^7\text{Li}_{\text{carb}} - \delta^7\text{Li}_{\text{sw}}$ ) of primary bank top and pelagic carbonates and diagenetic carbonates in the Bahamas. Note that the geographical locations of diagenetic zones is schematic and not representative of the actual location of carbonates in the Bahamas platform. The panels (B), (C) and (D) are cross-plots between  $\Delta^7\text{Li}_{\text{carb-sw}}$  and  $\text{Li}/(\text{Ca}+\text{Mg})$ ,  $\text{Sr}/(\text{Ca}+\text{Mg})$  and  $\delta^{13}\text{C}$ . Are also represented schematic examples of transition and/or mixture of (I) marine and meteoric fluid-buffered LMC (for example, Clino core), (II) marine fluid-buffered LMC and dolomite (for example, Unda core 100-150 m), (III) marine fluid-buffered LMC and sediment-buffered LMC and (IV) marine fluid- to sediment-buffered LMC and pelagic LMC (for example, Site 1007).

ancient carbonate) for how each type of diagenetic processes may affect  $\delta^7\text{Li}$  and other geochemical proxies. We suggest that this framework can serve as a road map for identifying ancient samples recording reliable seawater  $\delta^7\text{Li}$ . We express the  $\delta^7\text{Li}$  of carbonates in terms of the difference between carbonates and corresponding seawater ( $\Delta^7\text{Li}_{\text{carb-sw}} = \delta^7\text{Li}_{\text{carb}} - \delta^7\text{Li}_{\text{sw}}$ ) with a  $\Delta^7\text{Li}_{\text{carb-sw}}$  value of 0‰ indicating that the  $\delta^7\text{Li}$  of carbonates is the same as corresponding  $\delta^7\text{Li}$  of seawater. In the Bahamas, we have identified four types of diagenetic mineral formation pathways:

i) Marine LMC and dolomite formed in fluid-buffered conditions ( $d\text{EQ}^{\text{Li}} > 0.9$ ) have the composition of marine porewaters and yield remarkably consistent  $\delta^7\text{Li}$  that reliably record seawater composition at the time of diagenetic alteration, even following dolomitization ( $\Delta^7\text{Li}_{\text{carb-sw}} \sim -0.5 \pm 1.5\text{‰}$ ). Importantly, these do not record seawater composition at the depositional time of the unit, since the seawater-like signature is acquired during diagenetic transformation rather than primary crystallization. If carbonates have  $\delta^{44}\text{Ca}$ ,  $\delta^{13}\text{C}$  and  $\text{Sr}/(\text{Ca}+\text{Mg})$  values that are not completely sediment-buffered ( $\delta^{13}\text{C} \sim +2\text{‰}$ ,  $\delta^{44}\text{Ca} > -1.5\text{‰}$ ,  $\text{Sr}/\text{Ca} < 2 \text{ mmol.mol}^{-1}$  assuming present-day seawater composition; Ahm and others, 2018) this can be seen as strong evidence for fluid-buffered diagenetic conditions for Li isotopes, and at least based on the results from the Bahamas, we expect such samples to reliably and directly record seawater  $\delta^7\text{Li}$  composition (table 3). In

TABLE 3

Summary of Li isotope and Li/(Ca+Mg) signatures of different diagenetic carbonates and threshold values (assuming present-day seawater composition) for other geochemical proxies for recognizing the influence of diagenesis on Li isotopes

Process	Type of diagenesis	Extent of Diagenesis*	Mineralogy	Mean $\Delta^7\text{Li}_{\text{carb-SW}}$ ( $\pm 1\sigma$ )	Range of $\Delta^7\text{Li}_{\text{carb-SW}}$	Range of Li/(Ca+Mg) ( $\mu\text{mol/mol}$ )	Other geochemical proxies**
Aragonite early diagenesis	Meteoritic	Fluid-buffered	LMC	-9 $\pm$ 4‰	-15 to -3‰	0-6	<ul style="list-style-type: none"> <li>Low <math>\delta^{13}\text{C}</math> (0 to -12‰; <math>\text{dEQ}^{\text{C}} &gt; 0.1</math>)</li> <li>Low B/Ca (<math>&lt; 15 \mu\text{mol/mol}</math>; <math>\text{EQ}^{\text{B}} &gt; 0.9</math>)</li> </ul>
		Fluid-buffered	Dolomite	-0.5 $\pm$ 1.0‰	-1 to +1‰	13-22	<ul style="list-style-type: none"> <li>High <math>\delta^{44/40}\text{Ca}</math> (<math>&gt; -1.5\%</math>; <math>\text{dEQ}^{\text{Ca}} &gt; 0.1</math>)</li> <li>Low Sr/Ca (<math>&lt; 1 \text{ mmol/mol}</math>; <math>\text{EQ}^{\text{Sr}} &gt; 0.9</math>)</li> </ul>
	Marine	Fluid-buffered	LMC	-0.5 $\pm$ 1.5‰	-2 to +1‰	2-6	<ul style="list-style-type: none"> <li>High <math>\delta^{44/40}\text{Ca}</math> (<math>&gt; -1.5\%</math>; <math>\text{dEQ}^{\text{Ca}} &gt; 0.1</math>)</li> <li>Low Sr/Ca (<math>&lt; 2 \text{ mmol/mol}</math>; <math>\text{EQ}^{\text{Sr}} &gt; 0.9</math>)</li> <li><math>\delta^{13}\text{C} \sim +2\%</math></li> </ul>
		Fluid to sediment-buffered	LMC	-	-15 to -1‰	2-20	<ul style="list-style-type: none"> <li>Low <math>\delta^{44/40}\text{Ca}</math> (<math>&lt; -1.5\%</math>; <math>\text{dEQ}^{\text{Ca}} &lt; 0.1</math>)</li> <li>High Sr/Ca (<math>\text{Sr/Ca} &gt; 2</math>; <math>\text{EQ}^{\text{Sr}} &gt; 0.1</math>)</li> </ul>
Mixing with pelagic carbonates	Sediment-buffered	LMC	LMC	-	-15 to -8‰	2-20	<ul style="list-style-type: none"> <li>Preservation of the original <math>\delta^{18}\text{O}</math> (<math>\text{dEQ}^{\text{O}} &lt; 0.1</math>)</li> </ul>
		LMC foraminifera		-1 $\pm$ 1.5‰	-4 to 0‰	12-16	
		LMC bulk		-6.1 $\pm$ 1.3‰	-7 to -4‰	20-40	

\* Extent of diagenesis (fluid and sediment buffered) are defined in regard to Li isotopes.

\*\* References for  $\delta^{13}\text{C}$  of meteoric diagenesis are: Lohmann and others (1988) and Melim and others (1995). For B/Ca of meteoric diagenesis: Stewart and others (2015). For  $\delta^{44/40}\text{Ca}$  and  $\delta^{13}\text{C}$  of marine diagenesis: Higgins and others (2018) and Ahm and others, (2018). For Sr/Ca of marine diagenesis: Banner and Hanson (1990) and Ahm and others (2018). See Banner and Hanson (1990) and equations (3) and (4) for the expression of EQ and dEQ values.

addition, LMC from marine fluid-buffered diagenesis has low  $\text{Li}/(\text{Ca}+\text{Mg})$  ( $2\text{--}6 \mu\text{mol}\cdot\text{mol}^{-1}$ ) relative to most marine carbonates (Dellinger and others, 2018) while dolomite has higher  $\text{Li}/(\text{Ca}+\text{Mg})$  ( $15\text{--}20 \mu\text{mol}\cdot\text{mol}^{-1}$ ).

We note that for periods of time when the rate of change in seawater  $\delta^7\text{Li}$  value was slow (i.e. the Cenozoic record) relative to the timescale of sediment diagenesis after initial carbonate formation (that is, time between carbonate precipitation and diagenesis), marine fluid-buffered diagenesis is likely to preserve the composition of seawater. However, for short events where the marine  $\delta^7\text{Li}$  values likely varied (for example, the Ocean Anoxic Events of the Mesozoic), fluid-buffered diagenetic carbonates may recrystallize from a marine porefluid having distinct  $\delta^7\text{Li}$  value relative to the marine  $\delta^7\text{Li}$  value at the time of the deposition of the original carbonate (before diagenesis), and hence may not preserve the original marine  $\delta^7\text{Li}$  value.

ii) Marine LMC formed in a continuum and/or by a mixture of fluid- to sediment-buffered conditions ( $0.1 < \text{dEQ}^{\text{Li}} < 0.9$ ) records  $\delta^7\text{Li}$  that is not necessarily reset to a seawater value. Thus, these carbonates have a variable and lower isotopic composition relative to seawater ( $\Delta^7\text{Li}_{\text{carb-sw}} \sim -15$  to  $-3\text{‰}$ ). Carbonates formed in these diagenetic conditions would usually have  $\text{Sr}/\text{Ca} > 2 \text{ mmol}\cdot\text{mol}^{-1}$ ,  $\delta^{44}\text{Ca} < -1.5$  permil and higher, more variable  $\text{Li}/(\text{Ca}+\text{Mg})$  (see fig. 11).

iii) Marine burial LMC precipitated in sediment-buffered conditions ( $\text{dEQ}^{\text{Li}} < 0.1$ ) should preserve the original  $\delta^7\text{Li}$  of primary carbonates. If the original sediment was aragonite (as in the Bahamas), then by using the Li isotope fractionation factor between aragonite and seawater, in theory it could be possible to estimate the  $\delta^7\text{Li}$  of corresponding seawater. However, while modern GBB aragonite sediments have a limited range of  $\delta^7\text{Li}$  ( $\Delta^7\text{Li}_{\text{carb-sw}} \sim -9 \pm 1\text{‰}$ ), this is not the case globally, with  $\delta^7\text{Li}$  of modern biogenic aragonite between  $+15$  to  $+24\text{‰}$  ( $\Delta^7\text{Li}_{\text{carb-sw}} \sim -16$  to  $-7\text{‰}$ , Dellinger and others, 2018). Thus, the  $\delta^7\text{Li}$  of ancient LMC formed in sediment-buffered conditions can only be known within  $\pm 5$  permil uncertainty unless the specific origin of the aragonite is known. Evidence for preservation of the  $\delta^{18}\text{O}$  of original aragonite sediments would indicate marine burial diagenesis under completely sediment-buffered conditions (for Li isotopes).

iv) Meteoric LMC formed in fluid-buffered conditions ( $\text{dEQ}^{\text{Li}} > 0.9$ ) may have highly variable Li isotope composition. Meteoric diagenesis, usually characterized by negative  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  excursions (Lohman, 1988; Melim and others, 2001), decreases the  $\text{Li}/(\text{Ca}+\text{Mg})$  ratio to low values ( $0\text{--}6 \mu\text{mol}\cdot\text{mol}^{-1}$ ) and imparts unpredictable Li isotopic signatures ( $\Delta^7\text{Li}_{\text{carb-sw}}$  values  $-15$  to  $-3\text{‰}$ ) unrelated to the original seawater composition. For many carbonates in the geologic record, this type of alteration can be clearly identified using sedimentological and petrographic evidence (see for instance Hood and others, 2018).

Based on our study of the Bahamas carbonates, we can also make predictions about whether Li isotope excursions measured in platform carbonates correspond to changes in the oceanic  $\delta^7\text{Li}$  or are produced by diagenesis and/or mixing with other types of carbonates (for example, pelagic LMC). For example, a transition from marine to meteoric fluid-buffered diagenetic LMC (I in fig. 11) is characterized by lowering and more variable  $\delta^7\text{Li}$ , positive correlations between  $\delta^7\text{Li}$  and  $\delta^{13}\text{C}$  (and maybe  $\delta^{18}\text{O}$ ), no change or slight decreases of the  $\text{Li}/(\text{Ca}+\text{Mg})$ , and negative correlation between  $\delta^7\text{Li}$  and  $\text{Sr}/(\text{Ca}+\text{Mg})$ . Mixing between marine diagenetic fluid-buffered LMC and pelagic LMC or dolomite (II in fig. 11) is characterized by a homogeneous  $\delta^7\text{Li}$ ,  $\text{Sr}/(\text{Ca}+\text{Mg})$  and  $\delta^{13}\text{C}$  but variable  $\text{Li}/(\text{Ca}+\text{Mg})$ . A transition or mixture between marine fluid-buffered and sediment-buffered diagenetic LMC results in negative correlation between  $\delta^7\text{Li}$  and  $\text{Li}/(\text{Ca}+\text{Mg})$ ,  $\text{Sr}/(\text{Ca}+\text{Mg})$  and  $\delta^{13}\text{C}$  (III in fig. 11). In that case, the correlation between  $\delta^7\text{Li}$  and  $\text{Sr}/(\text{Ca}+\text{Mg})$  is characterized by a significantly less steep slope compared to the transition between fluid-buffered

marine and meteoric LMC (figs. 9 and 11). We also observe that mixing between marine sediment-buffered LMC and pelagic LMC is characterized by a positive correlation between  $\delta^7\text{Li}$  and  $\text{Li}/(\text{Ca}+\text{Mg})$  and negative trends between  $\delta^7\text{Li}$  and  $\text{Sr}/(\text{Ca}+\text{Mg})$  and  $\delta^{13}\text{C}$  (IV in fig. 11).

#### 8. CONCLUSIONS

We have measured the Li isotopic composition and  $\text{Li}/(\text{Ca}+\text{Mg})$  ratio of carbonate samples from an altered coralline Key Largo Limestone from Florida, and from three cores from the Great Bahama Banks. Our results show that meteoric diagenesis of aragonite decreases the  $\text{Li}/(\text{Ca}+\text{Mg})$  ratio of carbonates and changes the  $\delta^7\text{Li}$  value towards values associated with carbonate precipitation from meteoric fluids (+16 to +27‰), consistent with mass balance predictions for open-system meteoric alteration. Thus, meteoric diagenesis imparts large variability and unpredictable isotopic signatures unrelated to the original composition of the carbonates. Considering these results, samples showing signs of meteoric alteration are poor candidates for reconstructing the  $\delta^7\text{Li}$  of past seawater. For many carbonates in the geologic record, such alteration can be clearly identified using sedimentological and petrographic evidence (for example, Hood and others, 2018). In tandem, based on the data from the Bahamas, we suggest that decreases in the  $\text{Li}/(\text{Ca}+\text{Mg})$  ratio associated with decreases in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values are likely to indicate diagenetic disturbance to the Li system.

In contrast, during marine burial diagenesis alteration of aragonite to calcite, data from the Clino and Unda cores suggest that the  $\delta^7\text{Li}$  value of carbonates may be completely reset to the composition of marine porewaters with only small variability (+30.5±1.5‰). This process can yield remarkably consistent Li isotope ratios that could, at least under fluid-buffered conditions, reliably record seawater composition at the time of diagenetic alteration, even following dolomitization. The data from ODP Site 1007, however, add a note of caution: marine burial diagenesis under more closed-system conditions (perhaps typical of periplatform settings) may not similarly reset carbonate  $\delta^7\text{Li}$  values, leaving carbonates with an isotopic composition (+24 to +29‰) that is intermediate between their original mineralogic composition (sediment-buffered diagenesis) and seawater (fluid-buffered diagenesis). Fluid vs. sediment buffered diagenetic conditions in marine pore fluids can be distinguished through the use of related proxies (for example,  $\text{Sr}/\text{Ca}$ , Ca isotopes), which may act as a tool to gauge how we can relate carbonate Li isotope signatures to seawater  $\delta^7\text{Li}$  values in the geologic record. Though many questions remain to be resolved, the results of this study provide some guidelines for interpreting the  $\delta^7\text{Li}$  values in bulk carbonate rocks.

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#### APPENDIX

##### APPENDIX 1: MASS-BALANCE REACTIVE TRANSPORT MODEL

This Appendix presents the equations used to calculate the composition of diagenetic minerals using a simple mass-balance model of carbonate-water interaction, based on the framework developed in previous studies (for example, Banner and Hanson, 1990). This model relies on the difference in composition between the original carbonate and the diagenetic fluids, on the partition coefficient between diagenetic



carbonates and fluids, and on the extent of water-rock interaction (that is, water-rock ratio). Following Ahm and others (2018), we also implement this model within a reactive-transport framework [as developed by Fantle and others (2010) based on diagenesis mass conservation equations of Berner (1980)] to consider the reaction between a downward advecting fluid and limestone. This model allows the evolution of fluid chemistry and diagenetic conditions along the flow path to be taken into account (Ahm and others, 2018). Note also that our reactive transport equations are similar to the model developed by Pogge von Strandmann and others (2014) for Li isotopes. For simplification, we assume constant density of fluid and solid in time and space, constant mass of solid over time (i.e., we assume that all the original limestone is recrystallized), and immobile solid (following Fantle and DePaolo, 2006). Using these assumptions, the change of the Li concentration in limestone ( $[\text{Li}]_{\text{solid}}$ ) over time can be expressed as:

$$\frac{\partial [\text{Li}]_{\text{solid}}}{\partial t} = -R([\text{Li}]_{\text{solid}} - K^{\text{Li}} \times [\text{Li}]_{\text{fluid}}) \quad (\text{A1})$$

and for the fluid, the evolution of the Li concentration with time is described by:

$$\frac{\partial [\text{Li}]_{\text{fluid}}}{\partial t} = D \frac{\partial^2 [\text{Li}]_{\text{fluid}}}{\partial z^2} - v \frac{\partial [\text{Li}]_{\text{fluid}}}{\partial z} + RM([\text{Li}]_{\text{solid}} - K^{\text{Li}} \times [\text{Li}]_{\text{fluid}}) \quad (\text{A2})$$

where  $[\text{Li}]_{\text{solid}}$  and  $[\text{Li}]_{\text{fluid}}$  respectively are the Li concentrations in the limestone and the fluid (in ppm),  $R$  is the reaction rate of the carbonates (in  $\text{g.g}^{-1}.\text{yr}^{-1}$  or  $\%.\text{Myr}^{-1}$ ),  $K^{\text{Li}}$  is the distribution coefficient between precipitating carbonate and fluid (see equation below),  $v$  is the fluid advection rate (in  $\text{m.s}^{-1}$ ),  $M$  is the solid to fluid mass ratio,  $D$  the diffusion coefficient (in  $\text{cm}^2.\text{s}^{-1}$ ) and  $z$  is the vertical spatial dimension of unidirectional flowpath (in m). The Li distribution coefficient between secondary carbonate and fluid ( $K^{\text{Li}}$ ) can be expressed as (Banner and Hanson, 1990):

$$K^{\text{Li}} = \frac{[\text{Li}]_{\text{dCarb}}}{[\text{Li}]_{\text{fluid}}} = Kd^{\text{Li}} \times \frac{[\text{Ca}]_{\text{dCarb}}}{[\text{Ca}]_{\text{fluid}}} \quad (\text{A3})$$

where  $[\text{Li}]_{\text{dCarb}}$  and  $[\text{Ca}]_{\text{dCarb}}$  are respectively the Li and Ca concentrations in diagenetic carbonates and  $Kd^{\text{Li}}$  is the partition coefficient of Li between carbonate and fluid. At steady-state (solid and fluid concentration constant over time), and for a constant solid Li concentration over time ( $[\text{Li}]_{\text{solid}}$  constant), the solution to equation (A2) above can be expressed as (De Paolo, 2006; Fantle and others, 2010; Pogge von Strandmann and others, 2014):

$$[\text{Li}]_{\text{fluid}}(z) = \frac{[\text{Li}]_{\text{prim}}}{K^{\text{Li}}} + \left( [\text{Li}]_{\text{fluid } 0} - \frac{[\text{Li}]_{\text{prim}}}{K^{\text{Li}}} \right) e^{-z/L^{\text{Li}}} \quad (\text{A4})$$

The Li concentration in the diagenetic carbonate is then:

$$[\text{Li}]_{\text{dCarb}}(z) = [\text{Li}]_{\text{prim}} + (K^{\text{Li}} \times [\text{Li}]_{\text{fluid } 0} - [\text{Li}]_{\text{prim}}) e^{-z/L^{\text{Li}}} \quad (\text{A5})$$

where  $[\text{Li}]_{\text{prim}}$  is the Li concentration in the original limestone. For transformation of aragonite or HM-calcite to LM-calcite,  $[\text{Ca}]_{\text{dCarb}} = [\text{Ca}]_{\text{prim}}$  and the calcium concentration in the fluid are constant, so the Li/Ca ratio can be expressed as:

$$\left( \frac{\text{Li}}{\text{Ca}} \right)_{\text{dCarb}}(z) = \left( \frac{\text{Li}}{\text{Ca}} \right)_{\text{prim}} \left( Kd^{\text{Li}} \times \left( \frac{\text{Li}}{\text{Ca}} \right)_{\text{fluid } 0} - \left( \frac{\text{Li}}{\text{Ca}} \right)_{\text{prim}} \right) e^{-\frac{z}{L^{\text{Li}}}} \quad (\text{A6})$$

The term “ $L^{\text{Li}}$ ” is the lithium reactive length scale, and its value depends upon the advection and diffusion rates of the given element:

$$(L^{\text{Li}})^{-1} = \left( \frac{v^2}{4D^2} + \frac{RMK^{\text{Li}}}{D} \right)^{1/2} - \frac{v}{2D} \quad (\text{A7})$$

For the isotope composition of the fluid, the steady-state expression is:

$$\left(\frac{{}^7\text{Li}}{{}^6\text{Li}}\right)_{\text{fluid}} = \frac{\left(\frac{{}^7\text{Li}}{{}^6\text{Li}}\right)_{\text{prim}}}{\alpha_{\text{prec}}^{\text{Li}}} \times \frac{[\text{Li}]_{\text{prim}}}{K^{\text{Li}} \times [\text{Li}]_{\text{fluid}(z)}} + \left( \left(\frac{{}^7\text{Li}}{{}^6\text{Li}}\right)_{\text{fluid } 0} \times \frac{[\text{Li}]_{\text{fluid } 0}}{[\text{Li}]_{\text{fluid}(z)}} - \frac{\left(\frac{{}^7\text{Li}}{{}^6\text{Li}}\right)_{\text{prim}}}{\alpha_{\text{prec}}^{\text{Li}}} \times \frac{[\text{Li}]_{\text{prim}}}{K^{\text{Li}} \times [\text{Li}]_{\text{fluid}(z)}} \right) e^{-\frac{z}{L}} \quad (\text{A8})$$

with  $({}^7\text{Li}/{}^6\text{Li})_{\text{fluid}}$ ,  $({}^7\text{Li}/{}^6\text{Li})_{\text{fluid } 0}$  and  $({}^7\text{Li}/{}^6\text{Li})_{\text{prim}}$  respectively the Li isotope ratio for the fluid at depth  $z$ , for the initial fluid and for the primary carbonates. For the carbonate, we have:

$$\left(\frac{{}^7\text{Li}}{{}^6\text{Li}}\right)_{\text{dCarb}} = \left(\frac{{}^7\text{Li}}{{}^6\text{Li}}\right)_{\text{prim}} \times \frac{[\text{Li}]_{\text{prim}}}{K^{\text{Li}} \times [\text{Li}]_{\text{fluid}(z)}} + \left( \left(\frac{{}^7\text{Li}}{{}^6\text{Li}}\right)_{\text{fluid } 0} \times \frac{\alpha_{\text{prec}}^{\text{Li}} \times [\text{Li}]_{\text{fluid } 0}}{[\text{Li}]_{\text{fluid}(z)}} - \left(\frac{{}^7\text{Li}}{{}^6\text{Li}}\right)_{\text{prim}} \times \frac{[\text{Li}]_{\text{prim}}}{K^{\text{Li}} \times [\text{Li}]_{\text{fluid}(z)}} \right) e^{-\frac{z}{L}} \quad (\text{A9})$$

with ' $L$ ' being the reactive length scale of the isotope  ${}^6\text{Li}$ :

$$(L')^{-1} = \left( \frac{v^2}{4 \left(\frac{D}{\alpha_{\text{diff}}^{\text{Li}}}\right)^2} + \frac{RMK^{\text{Li}}}{\alpha_{\text{prec}}^{\text{Li}} \left(\frac{D}{\alpha_{\text{diff}}^{\text{Li}}}\right)} \right)^{1/2} - \frac{v}{2 \left(\frac{D}{\alpha_{\text{diff}}^{\text{Li}}}\right)} \quad (\text{A10})$$

The parameters  $\alpha_{\text{prec}}^{\text{Li}}$  and  $\alpha_{\text{diff}}^{\text{Li}}$  are respectively the Li isotope fractionation factors during precipitation of carbonates [ $\Delta^{\text{Li}}_{\text{carb-fluid}} \sim 1000 \times \ln(\alpha_{\text{prec}}^{\text{Li}})$ ] and diffusion in liquid. The depth of the precipitating diagenetic carbonate relative to the reactive length scale exerts a first-order control on the composition of the diagenetic carbonate, in particular influencing whether the carbonate composition is fluid or sediment-buffered (Fantle and others, 2010). According to equation (A4), if the diagenetic carbonate precipitates at a much shallower depth than the reactive length scale ( $z \ll L$ ), then  $[\text{Li}]_{\text{fluid}(z)} = [\text{Li}]_{\text{fluid } 0}$ , and  $[\text{Li}]_{\text{sec}(z)} = K^{\text{Li}} \times [\text{Li}]_{\text{fluid } 0}$ , which means that the composition of the secondary carbonate precipitating at this depth is fluid-buffered. In this case, the Li/Ca ratio of the secondary carbonate minerals is only controlled by the partition coefficient ( $K^{\text{Li}}$ ) and the Li/Ca ratio of the infiltrating fluid ( $[\text{Li}/\text{Ca}]_{\text{fluid } 0}$ , eq. 1). However, if  $z \gg L$ , then  $[\text{Li}]_{\text{fluid}(z)} = (K^{\text{Li}})^{-1} \times [\text{Li}]_{\text{prim}}$  and  $[\text{Li}]_{\text{sec}(z)} = [\text{Li}]_{\text{prim}}$ , so the composition of the secondary carbonate precipitating at the depth  $z$  is sediment-buffered and has the same composition as the primary carbonate minerals. Hence, the Li/Ca ratio of diagenetic carbonates will be unchanged relative to the primary carbonates. In between these two end-members ( $z < L$ ), the composition of the diagenetic carbonate has intermediate values (Ahm and others, 2018) as represented in figures (3C and 3D) and shown in the supplementary data table.

## APPENDIX 2: INFLUENCE OF SILICATE CONTAMINATION DURING CARBONATE LEACHING

### LMC-Rich Samples

Because Li concentrations in carbonates are very low relative to silicates, it is important to determine the extent to which the  $\delta^7\text{Li}$  and  $\text{Li}/(\text{Ca}+\text{Mg})$  values of carbonate leachates are influenced by dissolution of silicates phases during sample preparation (Vigier and others, 2007; Bastian and others, 2018). To assess this effect, some samples were subjected to a series of different leaching steps (between 2 and 5 leaching steps) in order to evaluate the change in  $\text{Li}/(\text{Ca}+\text{Mg})$  and  $\delta^7\text{Li}$  with increasing dissolution of non-carbonate phases. The leaching tests were done on samples from 1007 site (all containing less than 10% dolomite). Two types of leaching tests were done: i) some samples were dissolved twice (two different powder aliquots) with different amounts of acid in order to dissolve about 40 percent and 80 percent of the mass of the sample, ii) another set of samples was sequentially dissolved in 4 steps with the dissolution of about 25 percent each time. In all tests, we used HCl 0.05N. Results are presented in the supplementary data table (<http://earth.geology.yale.edu/%7eajs/SupplementaryData/2020/Dellinger>) and in figure (A1).

We observe that increasing the amount of carbonate dissolution systematically results in an increase of the  $\text{Al}/(\text{Ca}+\text{Mg})$  and  $\text{Li}/(\text{Ca}+\text{Mg})$ , and there is a positive correlation between  $\text{Li}/(\text{Ca}+\text{Mg})$  and  $\text{Al}/(\text{Ca}+\text{Mg})$  (fig. A1). We attribute this relationship to increasing contribution of silicate minerals during dissolution leading to higher  $\text{Li}/(\text{Ca}+\text{Mg})$  and  $\text{Al}/(\text{Ca}+\text{Mg})$  ratios. This result suggests that  $\text{Li}/(\text{Ca}+\text{Mg})$  is particularly sensitive to silicate contamination during leaching, as expected. The results for Li isotopes are

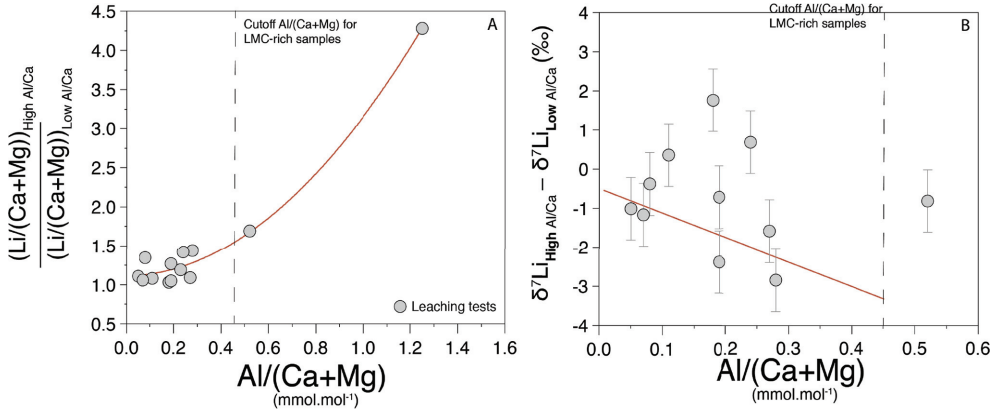


Fig. A1. (A) Li isotope difference between the leached fraction having high Al/(Ca+Mg) and that having low Al/(Ca+Mg) ( $\delta^7\text{Li}_{\text{High Al/Ca}} - \delta^7\text{Li}_{\text{Low Al/Ca}}$ ) as a function of Al/(Ca+Mg). (B)  $(\text{Li}/\text{Ca})_{\text{High Al/Ca}} / (\text{Li}/\text{Ca})_{\text{Low Al/Ca}}$  as a function of Al/(Ca+Mg). By “normalizing” between high and low Al/(Ca+Mg), we just look at the variability in Li/(Ca+Mg) and  $\delta^7\text{Li}$  resulting only from the influence of silicate contamination.

not straightforward as some samples show only small change of  $\delta^7\text{Li}$  as a function of Al/(Ca+Mg) while others have decreasing  $\delta^7\text{Li}$  with Al/(Ca+Mg) and more rarely increase of  $\delta^7\text{Li}$  with Al/(Ca+Mg). Altogether, we observe that at Al/(Ca+Mg) of 0.45 mmol/mol, the  $(\delta^7\text{Li}_{\text{High Al/Ca}} - \delta^7\text{Li}_{\text{Low Al/Ca}})$  is  $-3$  to  $+2\%$  offset compared to the  $\delta^7\text{Li}_{\text{Low Al/Ca}}$  and the  $(\text{Li}/\text{Ca})_{\text{High Al/Ca}} / (\text{Li}/\text{Ca})_{\text{Low Al/Ca}}$  is higher by a factor of 1.5 for each sample (fig. A1). We consider this Al/(Ca+Mg) value of 0.45 mmol/mol as an upper limit (cutoff value) for LMC-rich samples (or dolomite-poor) because higher Al/(Ca+Mg) samples would have an uncertainty too large due to potential silicate contamination. The great majority of the dolomite-poor samples have Al/(Ca+Mg)  $< 0.2$  mmol/mol and only 2 measured samples (both from the 1007 site) have Al/(Ca+Mg)  $> 0.45$  mmol/mol and are excluded from the discussion. Our cutoff Al/(Ca+Mg) value is about two times lower than in other studies on Li isotopes in carbonates; the studies of Pogge von Strandmann (2013, 2017) on past carbonates used a threshold value of 0.8 mmol/mol, whereas Bastian and others (2018) suggest an even higher Al/Ca ratio value for leaching ancient (fossil) carbonate material and foraminifera.

### Dolomite-Rich Samples

There is a positive correlation between Al/(Ca+Mg), %wt dolomite and Mg/(Ca+Mg) in Unda Clino samples from this study (fig. A2). In addition, we observe that the trend defined by Unda samples is very distinct relative to the trend defined by leaching test of LMC-rich samples described above and the trend defined by site 1007 samples. Because Clino-Unda dolomite-rich samples contain no or very few non-carbonate phases we interpret these trends to reflect a higher proportion of Al in dolomite relative to other carbonate phases (fig. A2). Hence the high Al/(Ca+Mg) of dolomite-rich samples is not indicative of silicate contamination and we do not use the cutoff value of 0.45 mmol/mol for these samples.

#### APPENDIX 3: CALCULATION OF THE $\delta^7\text{Li}$ AND Li/Ca RATIO OF THE LMC COMPONENT

In order to quantify the composition of the LMC component in samples from Site 1007 and from the Clino and Unda cores, and to determine its origin, we use a simple mass balance to correct for aragonite and dolomite composition for each sample assuming a mixture between calcite, aragonite and dolomite:

$$\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{LMC}}(z) = \frac{\left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{sample}} - \frac{\text{wt}\%_{\text{arag}}}{(\text{wt}\%_{\text{arag}} + \text{wt}\%_{\text{LMC}} + \text{wt}\%_{\text{dol}})} \times \left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{arag}} - \frac{\text{wt}\%_{\text{dol}}}{(\text{wt}\%_{\text{arag}} + \text{wt}\%_{\text{LMC}} + \text{wt}\%_{\text{dol}})} \times \left(\frac{\text{Li}}{\text{Ca}}\right)_{\text{dol}}}{\frac{\text{wt}\%_{\text{LMC}}}{(\text{wt}\%_{\text{arag}} + \text{wt}\%_{\text{LMC}} + \text{wt}\%_{\text{dol}})}}$$

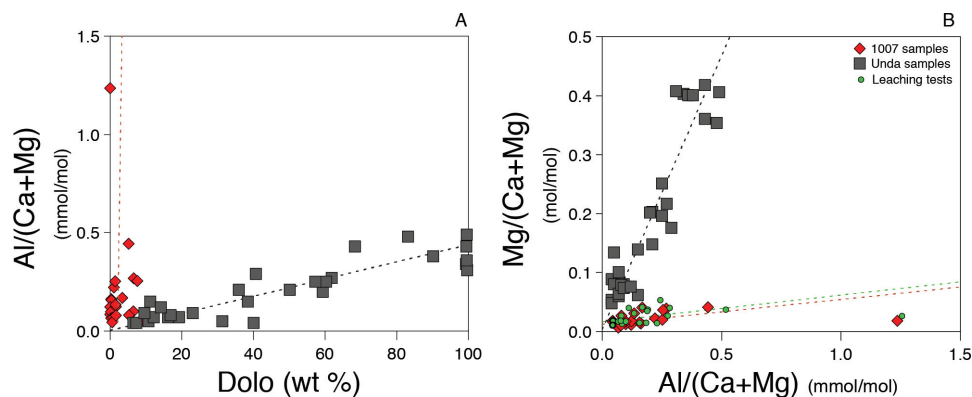


Fig. A2. (A) Al/(Ca+Mg) as a function of the proportion of dolomite for 1007 samples and Unda. (B) Mg/(Ca+Mg) as a function of Al/(Ca+Mg). The dolomite trend is represented by Unda. The silicate contamination trend by the leaching tests of LMC-rich samples is shown based on data.

and

$$\delta^7Li_{LMC}(z) =$$

$$\frac{\delta^7Li_{sample} \times \left(\frac{Li}{Ca}\right)_{sample} - \frac{wt\%_{arag}}{(wt\%_{arag} + wt\%_{LMC} + wt\%_{dol})} \times \delta^7Li_{arag} \times \left(\frac{Li}{Ca}\right)_{arag} - \frac{wt\%_{dol}}{(wt\%_{arag} + wt\%_{LMC} + wt\%_{dol})} \times \delta^7Li_{dol} \times \left(\frac{Li}{Ca}\right)_{dol}}{\frac{wt\%_{LMC}}{(wt\%_{arag} + wt\%_{LMC} + wt\%_{dol})} \times \left(\frac{Li}{Ca}\right)_{LMC}}$$

We assume a constant Li/Ca of  $9.2 \pm 1.2 \mu\text{mol}\cdot\text{mol}^{-1}$  and a  $\delta^7\text{Li}$  of  $22 \pm 1\text{‰}$  for the aragonite component, a value of Li/Ca of  $32 \pm 3 \mu\text{mol}\cdot\text{mol}^{-1}$  and  $\delta^7\text{Li}$  of  $31 \pm 1\text{‰}$  for dolomite for Clino and Unda Pleistocene sediments (see section 7), and values of  $23 \pm 1 \mu\text{mol}\cdot\text{mol}^{-1}$  and  $\delta^7\text{Li}$  of  $31 \pm 1\text{‰}$  for dolomite for Unda Pliocene sediments. The Li/Ca and  $\delta^7\text{Li}$  of the LMC of each sample can be calculated from the equations above. For three 1007 samples (71.1 mbsf, 78.4 mbsf, 152.3 mbsf) and four Unda samples (between 281.99 and 286.82 mbsf) the calculated uncertainty ( $\pm 6\text{‰}$  to  $\pm 12\text{‰}$  for  $\delta^7\text{Li}$ ) was too high due to low proportion of LMC ( $<15\%$ ) and therefore these samples are excluded from figure 8 and from the interpretation. All the data are in the supplementary data table (<http://earth.geology.yale.edu/%7Ecajs/SupplementaryData/2020/Dellinger>).

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