

Contents lists available at ScienceDirect

# Geochimica et Cosmochimica Acta

journal homepage: www.elsevier.com/locate/gca



# Geochemical fingerprints of early diagenesis in shallow-water marine carbonates: Insights from paired $\delta^{44/40}$ Ca and $\delta^{26}$ Mg values

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#### ARTICLE INFO

# ABSTRACT

Associate editor: Adrian Immenhauser

Keywords: Carbonates Marine diagenesis Meteoric diagenesis Calcium isotopes Magnesium isotopes We present a suite of major element stable isotope ( $\delta^{13}$ C,  $\delta^{18}$ O,  $\delta^{44/40}$ Ca,  $\delta^{26}$ Mg), and selected trace element (Sr/Ca and Mg/Ca) data from Pleistocene sediments from the Great Barrier Reef (IODP Expedition 325), as well as Holocene surface sediments from the Bahamas (Triple Goose Creek, Andros Island) to identify geochemical fingerprints associated with early marine and meteoric diagenesis. Sediments from both sites exhibit co-variation in  $\delta^{13}$ C and  $\delta^{18}$ O values, depletion in trace elements, and distinct geochemical trends in  $\delta^{26}$ Mg and  $\delta^{44/40}$ Ca values that reflect differences between diagenetic alteration in marine and meteoric fluids. While marine diagenesis results in lower Sr/Ca ratios, higher  $\delta^{44/40}$ Ca values, and little effect on bulk sediment  $\delta^{26}$ Mg values, meteoric diagenesis leads to lower Sr/Ca ratios, lower  $\delta^{44/40}$ Ca values, and lower  $\delta^{26}$ Mg values. Using a numerical model of diagenesis, we show how diagenetic alteration by meteoric fluids must occur after an initial period of diagenetic alteration by marine fluids, a two-stepped diagenetic history that complicates the interpretation of geochemical data in meteorically altered marine carbonate sediments. Finally, we discuss how paired metal isotopes may serve as a robust indicator of metoric alteration in ancient shallow-water marine carbonate sediments.

# 1. Introduction

Shallow-water carbonates represent an important archive of paleoclimate, acting as recorders of the history of the global carbon cycle and chemical composition of seawater (e.g. Kump and Arthur, 1999; Veizer et al., 1999; Saltzman and Thomas, 2012). However, the syn- and postdepositional diagenetic alteration of these sediments remains a hurdle in using the preserved chemical and isotopic signatures to reconstruct paleoenvironments (Allan and Matthews, 1982; Banner and Hanson, 1990; Higgins et al., 2018; Gussone et al., 2020). Carbonate sediments deposited and buried in the shallowest marine environments are likely to have some of the most complicated early diagenetic histories due to the potential for alteration by both meteoric and marine fluids (e.g., Melim et al., 1995; Melim et al., 2002; Ahm et al., 2018; Higgins et al., 2018; Swart and Oehlert, 2018).

Meteoric diagenesis, here defined as the near-surface alteration of carbonate minerals within the freshwater phreatic or vadose zones (Allan and Matthews, 1982; James and Choquette, 1984), has been studied in both modern and ancient carbonate depositional environments (e.g. Quinn, 1991; Saller and Moore, 1991; Dyer et al., 2015; Dyer

et al., 2017; Swart and Oehlert, 2018; Jones et al., 2020). This process generally consists of two interdependent steps. First, meteoric fluids, saturated with CO2 but undersaturated with respect to carbonate minerals, lead to the dissolution of more soluble carbonate phases - e.g. aragonite and high-Mg calcite (e.g., McClain et al., 1992). Second, dissolution serves to increase the carbonate saturation of the meteoric fluid, leading to the precipitation of secondary diagenetic minerals, often low-Mg calcite, whose chemical and isotopic composition reflect the evolving meteoric fluid. Traditional geochemical indicators of meteoric diagenesis include loss of trace elements like Sr and Mg (Benson, 1974; Banner and Hanson, 1990), and lowering of bulk carbonate  $\delta^{13}$ C values (due to the incorporation of carbon from soil gas  $CO_2$ ) and  $\delta^{18}O$  values (via distillation and condensation fractionations of oxygen associated with rainfall formation in the atmosphere) (e.g., Allan and Matthews, 1982). In addition to these diagnostic geochemical signatures, meteoric diagenesis may be associated with physical changes that can be identified on both macroscopic (e.g., collapse breccias, karstification) and microscopic (e.g., meniscus cements, dogtooth spar) scales (James and Choquette, 1984; Budd, 1988; Scholle and Ulmer-Scholle, 2003).

https://doi.org/10.1016/j.gca.2024.08.002 Received 22 April 2024; Accepted 2 August 2024

Available online 5 August 2024

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Early marine diagenesis is similar to meteoric diagenesis in that it involves the same interdependent steps of dissolution and reprecipitation, though the rates and processes that drive dissolution and re-precipitation in marine environments may be different (e.g., Bathurst, 1974; Patterson and Walter, 1994; Ahm et al., 2018; Higgins et al., 2018). The other major difference is that early marine diagenesis involves co-eval seawater (with ion concentrations much higher than meteoric fluids), or a seawater-like fluid that has been modified by early diagenetic reactions, mineral precipitation (e.g., dolomitization, evaporite formation, organic carbon respiration) and/or mixing with meteoric fluids (Berner, 1980; Ahm et al., 2018; Higgins et al., 2018). Petrographic indicators of marine diagenesis range from large-scale mineral dissolution and replacement (e.g., aragonite-to-calcite transition or neomorphism, dolomitization) to micron-scale textural (e.g., micrite envelopes, needle and botryoidal cements; Berner, 1980; Beier, 1985; Melim et al., 1995; Gischler et al., 2013)) and geochemical changes (e.g.,  $\mu m$  to mm scale calcite cements with large  $\delta^{\overline{13}}$ C and  $\delta^{\overline{18}}$ O variability: (Xiao et al., 2020)).

Other geochemical indicators of marine diagenesis range from changes in major element composition – e.g., dolomitization – to more subtle signals of chemical and isotopic exchange that depend on the exact chemical and isotopic composition of the seawater or seawaterlike fluid. Recent studies of the major element isotopic composition  $(\delta^{13}C, \delta^{18}O, \delta^{44/40}Ca, and \delta^{26}Mg in dolomite)$  and trace elements (Sr/Ca, Mg/Ca, etc.) in periplatformal marine carbonate sediments have shown that analyzing these geochemical systems together can provide unique semi-quantitative information on mineralogy and early marine diagenesis (Ahm et al., 2018; Higgins et al., 2018; Zhao et al., 2020). For example, Ahm et al., (2018) showed that systematic co-variation between  $\delta^{13}$ C,  $\delta^{18}$ O,  $\delta^{44}$ Ca values and Sr/Ca ratios in periplatformal carbonates from a range of water depths in the Bahamas could be explained largely by early marine diagenesis of platform-derived aragonite under both fluid-buffered and sediment buffered conditions. The recognition that similar geochemical patterns frequently are observed in ancient limestones and dolomites of all ages (e.g., Ahm et al., 2019; Jones et al., 2020; Crockford et al., 2020) indicates that this approach can provide a useful framework for interpreting the depositional and post-depositional environmental (e.g., coeval seawater composition), and histories of alteration that are preserved in the rock record.

Here we extend measurements of  $\delta^{13}\text{C},\,\delta^{18}\text{O},\,\delta^{44}\text{Ca},\,\delta^{26}\text{Mg}$  values and trace elements in bulk carbonate sediments to examine early carbonate diagenesis in the peritidal zone. We couple geochemical measurements with a best-fit numerical-model of diagenesis to explore the nature of observed variability, and offer a geochemical fingerprint for meteoric (and marine) diagenesis in shallow-water carbonate sediments. Our sample suite consists of 172 samples from Holocene and Pleistocene shallow water carbonate environments in the Bahamas and the Great Barrier Reef (GBR; IODP 325). The sample suite includes Holocene-aged (<1200 years old; Maloof and Grotzinger, 2012) carbonates deposited in a channelized tidal system (Triple Goose Creek (TGC), Andros Island, Bahamas; (Hardie, 1977; Maloof and Grotzinger, 2012). We also analyzed Pleistocene-aged reef carbonates from the Great Barrier Reef (GBR), Australia, (IODP 325; Gischler et al., 2013; Yokoyama et al., 2011a, 2011b; Yokoyama and Esat, 2011; Webster et al., 2011). Petrographic and geochemical ( $\delta^{13}$ C and  $\delta^{18}$ O) evidence for meteoric diagenesis associated with glacioeustatic sea-level change has been documented for GBR carbonates; the most negative  $\delta^{13}$ C and  $\delta^{18}$ O values are observed in samples characterized by sedimentary fabrics typically associated with meteoric alteration e.g., dogtooth and meniscus cements, caliche (Gischler et al., 2013). Co-variation between  $\delta^{13}$ C and  $\delta^{18}$ O values also is observed in TGC carbonates, although the origin of this co-variation is unknown. In concert, these settings provide modern analogues to constrain diagenetic processes that impact skeletal sediments in shallow-marine settings frequently observed in the ancient rock record (e.g., Lehrmann and Goldhammer, 1999).

#### 2. Methods

#### 2.1. Site description

Samples for this study include 81 samples of surface carbonates from Triple Goose Creek (TGC; approximately 25 00'5.10", -78 10'30.72"; collected March 2014) and 98 samples from shallow drill cores taken form the Great Barrier Reef (GBR) as part of IODP Expedition 325 (Fig. 1). Triple Goose Creek and the Great Barrier Reef both represent examples of modern analogue depositional environments whose diagenetic history should be relatively uncomplicated. TGC is an inter-tidal environment comprised of Holocene-aged sediments that record, at most, the earliest stages of marine diagenetic alteration (syn-depositional neomorphism of aragonite to calcite). GBR provides a clear example of post-depositional meteoric alteration associated with Late Pleistocene sea-level low stands (Webster et al., 2011; Yokoyama and Esat, 2011; Webster et al., 2018).

# 2.1.1. Triple goose creek, Andros Island, Bahamas

We analyzed 81 samples of bulk carbonate sediment for  $\delta^{44}$ Ca,  $\delta^{13}$ C, and  $\delta^{18}$ O values (and 7 for  $\delta^{26}$ Mg values) from Triple Goose Creek (TGC). Sediments commonly found in this region are composed of aragonite mud and varying amounts of Cerithid gastropods and Peneroplis benthic forams (Geyman and Maloof, 2021). A number of subenvironments can be categorized based on elevation, vegetation type, grain size and composition, and exposure indices (a measure of how often an environment is subaerially exposed and inundated with water; Hardie, 1977). Based on exposure index, the TGC region can be grouped into three distinct zones: subtidal environments, which are mostly submerged and only exposed during extreme low-tide events and include both lagoons and more open banktop regions; the inter-tidal zone, which is exposed during low-tide, and is dominated by channel levees; and the supratidal zone, which is only inundated during extreme high-tide or storm events. For a more detailed discussion of subenvironments within these three zones, see Maloof and Grotzinger (2012).

Previous studies from the Bahamas have shown that there is significant source-dependent variability in  $\delta^{18}O$  and  $\delta^{13}C$  values within a single depositional environment. For example, modern bank-top sediment from the Bahamas range from  $\delta^{18}O=+1\%$  to -5% , and  $\delta^{13}C=\sim$ +5% to -5% depending on facies/grain type (Swart et al., 2009; Gevman and Maloof, 2021). This variability likely reflects a combination of vital effects, diurnal carbon cycling, differences in the  $\delta^{13}$ C of source waters, and mixing between these sediment sources (e.g. Geyman and Maloof, 2019; Patterson William and Walter, 1994; Swart and Eberli, 2005). Sampling was conducted along a west to east transect to assess changes in geochemical signatures that might occur along facies and environmental transitions. Surface environments along this transect ranged from open subtidal (e.g., ocean and beach facies), to shoreface, to supratidal (beach crest) to intertidal (beach back slope, marsh) to subtidal (pond) environments. Grain types and microfacies on TGC (and more generally, north-west Andros Island) include carbonate mud, gastropods, bivalves, forams and green algae (including Halimeda and Penicillus) (Geyman and Maloof, 2021). Given the large reported variability in  $\delta^{18}$ O and  $\delta^{13}$ C values for each of these grain types (Geyman and Maloof, 2021), all bivalve, gastropod, foram and algal fractions were removed for this study, with sole focus on the bulk sediment/mud fractions.

# 2.1.2. Great Barrier Reef, Australia

We analyzed 91 samples from six drill cores collected along two transects (Hydrographer's Passage and Noggin Pass) during Integrated Ocean Drilling Program Expedition 325 (Yokoyama et al., 2011a, 2011b; Webster et al., 2011). These sediments represent older Pleistocene reef deposits, and consist of sediments that span the interval between 169 and 10 ka., and are dominated by grain supported textures



**Fig. 1.** Maps showing locations of study sites. A: Triple Goose Creek (TGC), on Andros Island ( $25\ 00'5.10''$ , -78 10'30.72'') represents a modern, shallow-water intertidal environment. Eighty-one samples, representing sub-tidal, inter-tidal and supra-tidal environments were collected in March 2014 and are included in this study. B: Great Barrier Reef (GBR), Australia. Samples from six cores collected along two transects during IODP Expedition 325 (Gischler et al., 2013; Yokoyama et al., 2011a, 2011b; Yokoyama and Esat, 2011; Webster et al., 2011) are included in this study. Cores were collected from water depths ranging 40 to 170 m and represent depositional ages of  $\sim 10$  kya to > 169 kya.

suggesting deposition in high-energy reef or reef slope environments (Webster et al., 2018; Humblet et al., 2019; Yagioka et al., 2019). Microfacies of the cores studied in this work include coralgal boundstones, coralgal-microbialites, skeletal grainstones (including coralline algae, coral, *Halimeda*, foraminifera and molluscs), and packstones (Webster et al., 2011; Gischler et al., 2013). Cores analyzed in this study were collected at water depths between 40 and 170 m, and a subset (specifically, Cores M0057A and portions of M0042A, M0055A and M0056A) were either exposed subaerially or to the freshwater lens during the Last Glacial Maximum (LGM) from approximately 22–19 ka, when regional sea-level was approximately 118 m lower than present day (Yokoyama and Esat, 2011; Gischler et al., 2013; Yokoyama et al., 2018; Humblet et al., 2019).

Petrographic and geochemical analyses indicated the influence of marine or meteoric diagenesis (Gischler et al., 2013). These studies indicate that the youngest samples (27-22 ka) from cores M0032A and M0033A (taken at water depths 91.3 to 91.9 m below modern sea-level, mbsl) exhibit features consistent with marine diagenesis, including micrite envelopes, and needle, botryoidal, and microcrystalline cements in sediment that is mainly aragonite (on average, 70.1%) and highmagnesium calcite (~30%) (Gischler et al., 2013). Cores M0055A and M0056A contain slightly older sediments (>30 ka, taken at water depths of 87.3mbsl and 81.2mbsl) and are characterized by petrographic and geochemical indicators of both marine and meteoric diagenesis, including variable  $\delta^{13}$ C and  $\delta^{18}$ O values, and micrite envelopes and needle and peloidal cements (marine diagenesis), as well as blocky cements indicative of meteoric alteration. Finally, cores M0057A and lower sections of M0042A (>169 ka, taken at water depths between 42.3mbsl and 50.8mbsl), are characterized by pervasive meteoric alteration, as indicated by textural fabrics associated with meteoric alteration, including blocky, dogtooth and meniscus cements (Gischler et al., 2013). These sediments also have low and variable  $\delta^{13}$ C and  $\delta^{18}$ O values, between -8 to +2 ‰, and -4 to +2 ‰, respectively (Fig. 2; Gischler et al, 2013). Details on microfacies and lithologies of the studied cores can be found in Gischler et al. (2013) and Webster et al.

# (2011).

# 2.2. Analytical methods

#### 2.2.1. Sample preparation

Approximately 5 mg of bulk carbonate sediment was dissolved in 5 mL of 0.1 M buffered solution of reagent grade anhydrous acetic acid and ammonium hydroxide with a pH of  $\sim$ 5. Dissolved samples were ultra-sonicated for four hours, centrifuged, and decanted into a clean vial. The dissolved sample was then analyzed for major and minor elements (Section 3.1.2) and calcium and magnesium fractions purified for isotopic analyses via an automated ion chromatography system (Thermo Dionex IC-5000<sup>+</sup>; e.g., Blättler and Higgins, 2014; Husson et al., 2015).

# 2.2.2. Major and minor elements

Aliquots of dissolved samples were analyzed for trace element concentrations (e.g., Mg/Ca, Sr/Ca, Mn/Ca, U/Ca) on either a Thermo Finnigan Element-2 inductively coupled plasma mass spectrometer (ICP-MS) or Thermo ICap-Q at Princeton University. Metal to calcium ratios of samples were determined using a set of matrix-matched in-house calibration standards. External reproducibility of these measurements is  $\sim 5$  to 7% from replicate measurements of SRM88b (dolomitic limestone).

# 2.2.3. Isotopic analyses ( $\delta^{44/40}$ Ca, $\delta^{26}$ Mg, $\delta^{13}$ C, and $\delta^{18}$ O)

All  $\delta^{44/\hat{40}}$ Ca and  $\delta^{26}$ Mg isotopic measurements were conducted at Princeton University on a Thermo Scientific Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) equipped with either an ESI Apex-IR inlet (for calcium isotopes; e.g., Blättler et al., 2011) or a cyclonic spray chamber (for magnesium isotopes; e.g., Husson et al., 2015). Measurements were carried out at low resolution for Mg and medium resolution for Ca to avoid ArHH<sup>+</sup> interferences. We refer to previous publications for a detailed outline of the Ca and Mg isotope measurements performed (e.g., Higgins et al., 2018; Blättler et al., 2018; Husson et al., 2015).



Fig. 2. A: Simplified schematic of GBR Noggin Pass and Hydrographer's Passage transects with cores M0057A, M0056A, M0055A, M0042A, M0032A and M0033A showing lithology, coral reef assemblages and bulk sediment  $\delta^{44/40}$ Ca composition. Symbols are color-coded based on  $\delta^{26}$ Mg values. Lowest measured  $\delta^{26}$ Mg values are from Reef 1 assemblages in M0057A, M0056A and M0042A. B: Calcium isotope gradient across the GBR (not to scale) showing lower values for landward cores (M0057A and M0042A) and heavier values for more distal seaward cores. C: Calcium isotope gradient from Great Bahama Bank (Higgins et al., 2018), showing increasing  $\delta^{44/40}$ Ca towards the banktop/margin as a result of marine diagensis.

For calcium, all data are reported in delta notation relative to seawater ( $\delta^{44/40}$ Ca<sub>seawater</sub> = 0 ‰),

$$\delta^{44/40} Ca = \left( {}^{44} Ca / {}^{40} Ca_{sample} / {}^{44} Ca / {}^{40} Ca_{seawater} - 1 
ight) * 1000$$

Due to isobaric inferences with <sup>40</sup>Ar, we are unable to directly measure <sup>40</sup>Ca and instead measure <sup>42</sup>Ca. Measured  $\delta^{44/42}$ Ca values are converted to  $\delta^{44/40}$ Ca assuming mass dependent fractionation with a slope of 2.05 and no excess radiogenic <sup>40</sup>Ca (Fantle and Tipper, 2014). Corrections are made for isobaric Sr<sup>2+</sup> interferences by using measurements at m/z = 43.5, for doubly charged <sup>87</sup>Sr<sup>2+</sup>. Mass dependence is verified using a triple isotope plot ( $\delta^{44/42}$ Ca vs.  $\delta^{44/43}$ Ca) and all measured data fall along a slope of 0.51, similar to the 0.507 slope predicted by the exponential mass-dependent fractionation law. The long-term external reproducibility of  $\delta^{44/40}$ Ca values is estimated through the repeat purification and isotopic analyses of SRM915b (for  $\delta^{44/40}$ Ca values). Our

measured values of  $-1.17\pm0.14$  ‰ (2 $\sigma$ , n=24) for SRM915b agree well with reported values of  $-1.16\pm0.08$ ‰ (Heuser and Eisenhauer, 2008) and  $-1.13\pm0.04$ ‰ (Jacobson et al., 2015). For samples purified and analyzed once, we report the uncertainty as our long-term external reproducibility. When samples are purified and analyzed multiple times, we report the standard error of the mean.

All magnesium isotope data are reported using delta notation relative to the DSM-3 standard,

$$\delta^{26} Mg = \left( \frac{{}^{26} Mg}{{}^{24} Mg_{sample}} / \frac{{}^{26} Mg}{{}^{24} Mg_{DSM-3}} - 1 \right) * 1000$$

The external reproducibility of our method is estimated from replicate measurements of the Cambridge-1 Mg standard, with  $\delta^{26}$ Mg value of  $-2.61\pm0.08~$ ‰ (2 $\sigma$ , n = 17), a synthetic dolomite standard with measured  $\delta^{26}$ Mg of  $-0.55\pm0.07$  (2 $\sigma$ , n = 8), as well as seawater ( $\delta^{26}$ Mg =  $-0.87\pm0.1$ ‰). For Cambridge-1 and seawater, our measured values

are indistinguishable from published value of -2.61~% and -0.83~%, respectively (Ling et al., 2011; Husson et al., 2015). Plotted in triple-isotope space ( $\delta^{25}$ Mg vs.  $\delta^{26}$ Mg), all measured samples fall on a line with a slope of 0.525 (R<sup>2</sup> = 0.998), indistinguishable from the predicted slope of 0.521 (Young and Galy, 2004). Measurements of  $\delta^{13}$ C and  $\delta^{18}$ O values were conducted at Princeton

Measurements of  $\delta^{13}$ C and  $\delta^{19}$ O values were conducted at Princeton University using a Sercon IRMS coupled with a GasBench II sampling device following previously published methods (e.g., Dyer et al., 2015; Husson et al., 2015). Carbonate powders were weighed into individual borosilicate reaction vials and heated to 110 °C to remove water. Five drops of H<sub>3</sub>PO<sub>4</sub> were reacted with the sample at 72.5 °C, and the resultant CO<sub>2</sub> analyte was sent to the IRMS. Measurement precision is  $\pm$ 0.1 ‰ for  $\delta^{13}$ C and  $\pm$  0.25 ‰ for  $\delta^{18}$ O (as determined by repeat measurements of NBS 18, n = 16) and all data are reported in standard delta notation relative to Vienna Pee Dee Belemnite (V-PDB).

#### 2.3. Numerical model of carbonate diagenesis

The role of early diagenetic alteration in determining the chemical and isotopic composition of bulk carbonate sediments was explored using a previously published numerical model of carbonate diagenesis (Ahm et al., 2018). This model has been shown to reproduce geochemical variability in shallow-water carbonate sediments associated with early marine diagenesis and dolomitization. The model consists of n stacked boxes representing a carbonate sedimentary column through which fluid is advected (u, u)cm/yr) along a flow-path, reacting with the surrounding sediment at a prescribed rate (R, 10<sup>3</sup> cm/yr). Additional model assumptions include the chemical and isotopic composition of the primary carbonate mineral, the chemical and isotopic composition of the diagenetic fluid, and any elemental or isotopic fractionation associated with the formation of the secondary (diagenetic) carbonate mineral. The choice of primary mineral end-member(s) represents one of the largest assumptions made for the model simulation and subsequent discussion, especially as geochemical measurements (particularly of carbon and oxygen isotope ratios) at both study sites indicate a large range in natural variability (up to 13 % for  $\delta^{13}$ C and ~ 5 ‰ for  $\delta^{18}$ O; Weber and Woodhead, 1970; Geyman and Maloof, 2021). Ultimately, the choice of starting mineral is based on modern-day mineralogical and measured geochemical composition of carbonate muds in both the Bahamas and the present-day Great Barrier Reef (e.g., Weber and Woodhead, 1970; Gischler et al., 2009; Geyman and Maloof, 2021). Model parameter notations, definitions and values are listed in Table 1.

As cumulative fluid-to-rock ratios are not well known in many modern or ancient settings, it is more useful to examine the model results as property-property cross-plots (e.g.,  $\delta^{13}$ C vs.  $\delta^{18}$ O values). In this space, each box (1–*n*) is represented by a point that evolves into a trajectory as meteoric alteration proceeds in time (i.e., cumulative fluid-to-sediment ratio increases). Together, the boxes/trajectories carve out an area that encompasses all possible combinations of fluid- and sediment-buffered diagenesis for the single-step meteoric model (Fig. 5). To the extent that our model is an accurate, if simplified, representation of mass balance during meteoric diagenesis, we expect natural sample sets to fall within the modeled area.

#### 3. Results

# 3.1. $\delta^{13}C$ and $\delta^{18}O$ values

Measured  $\delta^{13}C$  values for GBR sediments vary from +4.38 ‰ to -6.87 ‰ (Fig. 3). The most distal (seaward) cores (M0032A and M0033A) are characterized by the highest  $\delta^{13}C$  values, averaging at +2.91  $\pm$  1.27 ‰ (2 $\sigma$ , n = 14). Cores M0042 and M0057A exhibit the lowest  $\delta^{13}C$  values, between -3.4‰ to -6.6‰ (Fig. 3). Core M0056A, presently located at the reef edge, exhibits the largest single-core range in  $\delta^{13}C$  values, from  $\sim$  +3‰ to  $\sim$  -3% at 6 mbsl.

Similar trends are observed in the  $\delta^{18} O$  values of samples from the

#### Table 1

Summary of mo	del notation and	l parameters i	for meteoric a	lteration of	primary
aragonite sedim	ent (Fig. 5).				

Parameter	Definition	Value	References
α <sub>Ca</sub>	Ca isotopic	0.9989	Bradbury and Turchyn
	fractionation factor		(2018)
$\alpha_{Mg}$	Mg isotopic	0.998	Mavromatis et al. (2013);
	fractionation factor		Higgins and Schrag (2010)
$\alpha_{\rm C}$	C isotopic	1.001	Romanek et al. (1992)
	fractionation factor		
α <sub>O</sub>	O isotopic	1.0324	Kim and O'Neil (1997)
	fractionation factor		
K <sub>Sr</sub>	Sr distribution	0.05	Banner and Hanson (1990)
	coefficient		
M <sub>f</sub> (mmol/ Kg)	mass of element in fluid	Ca: 12.4	Langmuir (1997)
	munu	Mg: 5.28	Langmuir (1997)
		C: 4.1	Langmuir (1997)
		Sr: 0.09	Langmuir (1997)
$\delta_f$ (‰)	isotopic composition	$\delta^{44}$ Ca: -0.6	
	or mula	s <sup>26</sup> Ma	
		0 Mg.	
		-3.1 s <sup>13</sup> 0, 10	Clark (2015)
		0 C = 10	Clark (2015)
		(VS. VPDB)	
		$\delta^{10}0:-34$	Clark (2015)
		(vs. VPDB)	
M <sub>s</sub>	mass of element in primary sediment	C: 12%	Based on stoichiometry of aragonite
		Ca: 39%	
		Mg: 2500	
		ppm	
		Sr: 10 000	
		ppm	
δ <sub>s</sub> (‰)	isotopic composition of sediment	$\delta^{44}$ Ca: -1.5	Higgins et al. (2018)
	or securitein	8 <sup>26</sup> Ma	This study
		-30	THIS Study
		δ <sup>13</sup> C· 3.6	Oeblert and Swart (2014)
		0 6.3.0	Courses and Maloof (2021)
		s <sup>18</sup> 0, 1.0	Geyman and Maloof
		0 0:1.0	
			(2021); this study

GBR (Fig. 3). The highest  $\delta^{18}$ O values (between 0 and +1 ‰) are seen in distal cores M0032 and M0033, and the top 5 m of M0056A. The lowest  $\delta^{18}$ O values (<-5‰) occur in cores M0042 and M0057, consistent with petrographic observations of meteoric diagenesis in the vadose zone (dogtooth, caliche, and meniscus textures; Gischler et al., 2013). The greatest range (~6‰) in  $\delta^{18}$ O values is observed in M0056A, and follow the same pattern as  $\delta^{13}$ C values, consistent with petrographic observations of meteoric and marine fluids (e.g., micrite envelopes and microcrystalline cements for marine diagenesis, and blocky and dogtooth cements for meteoric alteration; Gischler et al., 2013).

For sediments collected at TGC, a co-variation between  $\delta^{13}C$  and  $\delta^{18}O$  values is observed, with average measured values of  $+3.05 \pm 1.26$  ‰ and  $+0.27 \pm 0.88$  ‰, respectively ( $2\sigma$ , n = 72). No systematic variability of measured  $\delta^{13}C$  and  $\delta^{18}O$  values is observed as a function of the modern surface environment(s)/tidal zone(s) (Fig. 3).

## 3.2. Sediment trace elements (Sr/Ca and Mg/Ca)

The Sr/Ca ratio of all GBR sediments shows a generally increasing trend with current depth below sea-level (Fig. 3), with values as low as 0.2 mmol/mol in the shallowest core (M0057A), increasing to > 5.5 mmol/mol in the most distal core (M0033A) – although the highest values (between 6.2 and 9.7 mmol/mol) are found in the top 2 m of M0042A. Measured Sr/Ca ratios from TGC sediments show a much narrower range, from 6.6 to 10.4 mmol/mol, with an average of 8.7  $\pm$  1.7 (2 $\sigma$ , n = 70).

Mg/Ca ratios of GBR sediments range from 0.007 to 0.162 mol/mol



**Fig. 3.** Elemental and isotopic data for all measured GBR and TGC sediments. A:  $\delta^{13}$ C vs.  $\delta^{18}$ O; B:  $\delta^{44/40}$ Ca vs. Sr/Ca and C:  $\delta^{26}$ Mg vs. Mg/Ca. Insets for A and B show TGC bulk sediments sorted by surface environment, which does not influence bulk sediment geochemistry. The red line in A represents the range of bulk sediment and mud  $\delta^{13}$ C and is from Geyman and Maloof (2021).

(Fig. 3). Mg/Ca ratios of the TGC sediments average 0.052  $\pm$  0.013 mol/mol, within the range of values observed in samples from the GBR.

## 3.3. Sediment Ca isotopes

Sediment  $\delta^{44/40}\text{Ca}$  values for GBR vary by > 0.8 ‰, from -1.46 to -0.63 ‰. The lowest  $\delta^{44/40}$ Ca values are found in the proximal cores (M0042A and M0057A), all sections with elevated aragonite content (up to 96 wt%; Gischler et al., 2013). The most elevated  $\delta^{44/40}$ Ca values are found in the more distal cores (M0032A, M0033A, M0055A and M0056A; Fig. 2), which have a larger contribution of calcite (both highmagnesium and low-magnesium, see Gischler et al., 2013). The gradient in GBR  $\delta^{44/40}$ Ca is in contrast to the Great Bahama Bank (Fig. 2C; Higgins et al., 2018), where  $\delta^{44/40}$ Ca values increase as water depth decreases due to marine diagenesis.  $\delta^{44/40}\text{Ca}$  values of samples from cores M0032A and M0033A vary from  $-0.7\,\%$  to  $-1.17\,\%$  and are negatively correlated with Sr/Ca ratios (Fig. 3). In contrast,  $\delta^{44/40}$ Ca values in cores M0042A and M0057A range from -1.46 % to -0.76 %, with the majority of values for M0057A around  $-0.98 \pm 0.21$  ‰ (2 $\sigma$ , n = 37).  $\delta^{44/40}$ Ca values for cores from the reef edge (M0055A and M0056A) span the full range observed in this study, with the highest (–0.63 ‰) and lowest (–1.37 ‰)  $\delta^{44/40}$ Ca values observed in core M0055A (Figs. 2 and 3).

Measured  $\delta^{44/40}Ca$  values of 71 bulk carbonate samples from TGC range from -1.55 ‰ to -1.12 ‰, with an average of  $-1.32\pm0.16$  ‰ (2σ, n = 71) and negatively covary with Sr/Ca ratios (Fig. 3).

#### 3.4. Sediment Mg isotopes

Measured  $\delta^{26}$ Mg values of samples from the GBR span a  $\sim 2 \%$  range, from -5.04 % to -3.08 %, and increase with depth below modern sea-

level (Fig. 2). The lowest  $\delta^{26}Mg$  values are observed in the most proximal core (M0057A) with an average of  $-4.56\pm0.59$  ‰ (2\sigma, n = 34) whereas the most elevated  $\delta^{26}Mg$  values are observed in the distal cores (M0032 and M0033) and vary from -3.1‰ to -3.5‰ (Fig. 2). Cores from the reef edge (M0055A and M0056A) are characterized by  $\delta^{26}Mg$  values intermediate between these two end-members, with measured values between -3.2‰ and -5.1‰ in core M0056A.

Samples (n = 7) from TGC analyzed for Mg isotopes yielded  $\delta^{26}Mg$  values of  $-3.11\pm0.05$ ‰ (2 $\sigma$ ), similar to the highest  $\delta^{26}Mg$  values observed in samples from the GBR (Fig. 3).

#### 3.5. Effects of microfacies on geochemical signatures

Measured isotopic ratios for GBR sediments versus degree of meteoric alteration (quantified by Gischler et al., 2013) and colored by observed microfacies is shown in Fig. 4. No relationship between percentage meteoric cement, isotope ratios ( $\delta^{13}$ C,  $\delta^{18}$ O,  $\delta^{26}$ Mg or  $\delta^{44/40}$ Ca) and microfacies is observed. Generally, the lowest  $\delta^{13}$ C,  $\delta^{18}$ O and  $\delta^{26}$ Mg ratios are observed in sediments with the highest degree of meteoric cement, and no observable relationship with microfacies.

## 4. Discussion

#### 4.1. Modeling diagenesis

The conversion of aragonite to calcite by meteoric fluids is modeled using the initial mineral compositions, diagenetic fractionation factors, and partition coefficients listed in Table 1 (Fig. 5). The choice of primary mineral composition, fractionation factors, and partition coefficients represent the average composition of Bahamian bank-top carbonates



Fig. 4. GBR microfacies for all sediments and measured isotopes: A:  $\delta^{13}$ C; B:  $\delta^{18}$ O; C:  $\delta^{26}$ Mg; and D:  $\delta^{44/40}$ Ca. No relationship between microfacies, reported percentage of meteoric alteration (Gischler et al., 2013) and measured geochemical signatures (this study) is observed.

measured in this study and published values from the literature (Table 1 and references therein). The model results show how the conversion of aragonite to calcite results in different geochemical signatures depending on whether the sediment is near the fluid source (fluid-buffered, i.e., box 1) or at the end of the fluid flow path (sediment-buffered, box *n*). The geochemistry of bulk sediment nearest the fluid source will evolve following a fluid-buffered trajectory where the chemical composition of the diagenetic calcite is set by the meteoric fluid. In contrast, the geochemistry of bulk sediment located further from the fluid-source will follow a more sediment-buffered trajectory where the chemistry of the diagenetic calcite more closely resembles the chemistry of the primary sediment. Because elemental abundances in the fluid and sediment vary for different elements, some proxies will tend to be more fluid-buffered (e.g.  $\delta^{18}$ O,  $\delta^{26}$ Mg values, and Sr/Ca ratios in Fig. 5) while other proxies will tend to be more sediment-buffered (e.g.  $\delta^{13}$ C and to a lesser extent  $\delta^{44/40}$ Ca values in Fig. 5) (Banner and Hanson, 1990; Ahm et al., 2018).

In the model output shown in Fig. 5, the behavior of  $\delta^{13}$ C and  $\delta^{18}$ O values during meteoric alteration is similar to that seen in previous studies (Allan and Matthews, 1982; Banner, 1995; Gischler et al., 2013; Dyer et al., 2017; Swart and Oehlert, 2018, Zhao et al., 2020), where both  $\delta^{13}$ C and  $\delta^{18}$ O values are shifted lower to values that reflect the composition of the meteoric fluid, although the decrease is significantly smaller for  $\delta^{13}$ C values in the sediment-buffered box due to the relatively high carbon content of the sediment compared to the fluid (box *n*; Fig. 5). The  $\delta^{44/40}$ Ca and  $\delta^{26}$ Mg values and Sr/Ca ratios also decline during meteoric alteration, though the reasons for this behavior are different than the decline in bulk sediment  $\delta^{13}$ C and  $\delta^{18}$ O. In the case of  $\delta^{13}$ C and  $\delta^{18}$ O values, the decline is related to the lower  $\delta^{13}$ C and  $\delta^{18}$ O signature of the initial meteoric fluid. In contrast, because there is very little Ca, Mg, or Sr in the initial meteoric fluid, the Ca, Mg, and Sr content

of the evolving meteoric fluid is dominated by contributions from the sediment and the declines observed in Fig. 5 reflect the magnitude of isotopic or elemental fractionation associated with the diagenetic calcite, as well as the extent to which the system is sediment or fluidbuffered. For example, the  $\delta^{44/40}$ Ca of the fluid-buffered end-member in the model is -2.7 ‰, corresponding to the sum of the  $\delta^{44/40}\text{Ca}$  of the initial sediment (-1.6 ‰) and the prescribed fractionation factor for secondary calcite precipitation ( $\alpha = 0.9989$ ; Table 1). This fractionation factor is similar to previously reported fractionation of  $\delta^{44/40}$ Ca during formation of diagenetic and authigenic minerals (see Bradbury and Turchyn, 2018; Blättler et al., 2021). Similarly, the  $\delta^{26}$ Mg value of the fluid-buffered end-member of the model represents the  $\delta^{26}$ Mg of the initial sediment ( $\sim$ -3.0 ‰) and the prescribed fractionation factor for diagenetic mineral formation ( $\alpha = 0.998$ ; Table 1). The similar  $\delta^{26}$ Mg value of the fluid- and sediment- buffered end-member is reflective of the low Mg concentration in meteoric fluids, as the source of Mg incorporated into the diagenetic mineral is via dissolution of the surrounding sediment.

# 4.1.1. Single-step meteoric diagenesis

As is indicated in Fig. 5, while the single-step model for meteoric alteration does a reasonable job fitting some of the data (e.g.,  $\delta^{13}$ C vs.  $\delta^{18}$ O values,  $\delta^{18}$ O vs.  $\delta^{26}$ Mg values) there is significant disagreement between the behavior of bulk sediment  $\delta^{44/40}$ Ca values and modeled trajectories. In particular, for  $\delta^{44/40}$ Ca vs. Sr/Ca ratios, the model predicts that single-step meteoric alteration should, in all cases, result in bulk sediment  $\delta^{44/40}$ Ca values that are similar to or lower than the primary sediment whereas all of the data indicate alteration is associated with lower Sr/Ca ratios bulk sediment  $\delta^{44/40}$ Ca values that are shifted towards the seawater value (0 ‰; Fig. 5).



**Fig. 5.** Numerical model trajectories for single-step meteoric alteration of bulk sediments from GBR and TGC. A:  $\delta^{13}$ C vs.  $\delta^{18}$ O; B:  $\delta^{44/40}$ Ca vs.  $\delta^{26}$ Mg; C:  $\delta^{44/40}$ Ca vs. Sr/Ca; D:  $\delta^{26}$ Mg vs.  $\delta^{18}$ O; E:  $\delta^{26}$ Mg vs.  $\delta^{13}$ C and F:  $\delta^{26}$ Mg vs. Mg/Ca. Modeled trajectories follow the alteration of primary aragonite to calcite following reaction with meteoric fluids. Grey contour lines represent the degree of alteration of the sediment, ranging from 0% to 100%, and each contour has a fluid-buffered (black-dashed line) and sediment-buffered (red line) endmember. GBR data points are colored by the petrographic incidence of meteoric cements and fabrics (as described by Gischler et al., 2013), where yellow symbols represent samples with low percentage of meteoric cements and blue symbols represents sediments with high percentage of meteoric cement. While the meteoric diagenesis model trajectories approximate behavior of  $\delta^{13}$ C,  $\delta^{18}$ O and  $\delta^{26}$ Mg, a notable misfit between model and data is noted for  $\delta^{44/40}$ Ca (panels B and C).

# 4.1.2. Two step marine-meteoric diagenesis

The misfit between modeled and observed  $\delta^{44/40}$ Ca values can be reconciled by the hypothesis that diagenesis in shallow carbonate environments is a two phase process; a first step of early marine diagenesis that must occur syn- and early post-deposition, followed by a second step of diagenesis with meteoric fluids. In reality, the two steps likely occur simultaneously, in the presence of diagenetic fluid that is a mixture derived from marine and meteoric sources. Here, we have offered a more mechanistic explanation, and modeled diagenesis as a two step process. In this model, the conversion of aragonite to calcite occurs partially or fully during early marine diagenesis (1st step) and this altered bulk sediment then becomes the initial sediment for meteoric diagenesis (2nd step; white stars in Fig. 6). The choice of a single alteration product from early marine diagenesis (1st step) to use as an initial condition for meteoric diagenesis (2nd step) is an oversimplification of the problem as we expect there to be a range of alteration products resulting from early marine diagenesis from pristine to fully recrystallized. We expect this simplification to reduce the quality of fit for single model simulations but not the overall conclusion that two step marine-meteoric alteration is required to explain the observed covariation between geochemical proxies in cores from the GBR, in particular the elevated  $\delta^{44/40}$ Ca values for meteorically altered bulk sediments.

Results of the two step model are shown in Fig. 6 and model variables are listed in Table 2. For bulk sediments from TGC, and most distal cores M0032A and M0033A from GBR (left panel), the observed geochemical co-variation can be explained by just the 1st step – early marine diagenesis with coeval seawater – a result that is consistent with

previously published interpretations of exposure history and stratigraphic, sedimentological and petrographic observations from GBR cores (Gischler et al., 2013) and previous studies on early marine diagenesis in shallow-water marine carbonates using paired  $\delta^{44/40}$ Ca and  $\delta^{26}$ Mg values and trace elements (Higgins et al., 2018). In contrast, samples from the more proximal GBR cores M0055A, M0056A, M0042A, and M0057A require 2 step marine-meteoric alteration to explain the observed geochemical variability in  $\delta^{13}\text{C},\,\delta^{18}\text{O},\,\delta^{26}\text{Mg},\,\delta^{44/}$ <sup>40</sup>Ca values and Sr/Ca ratios (center and right panels in Fig. 6). In particular, the two step model allows us to reconcile the elevated  $\delta^{44/}$ <sup>40</sup>Ca values of the bulk sediments with the theoretical model of meteoric diagenesis presented in Fig. 5. Meteoric diagenesis still tends to shift bulk sediment  $\delta^{44/40}$ Ca values lower (right panel in Fig. 6), but this effect is, in our sample suite, overwhelmed by the  $\delta^{\bar{4}4/40}Ca$  increase associated with early marine diagenesis (1st step). The situation is reversed for bulk sediment  $\delta^{26}\text{Mg}$  values: marine diagenesis produces a subtle shift due to similarities in Mg isotope fractionation between primary and diagenetic carbonate minerals, while meteoric diagenesis leads to a dramatic decline in bulk sediment  $\delta^{26}$ Mg values.

Petrographic support for this 2 step interpretation exists in cores M0055A and M0056A, with evidence for co-occurring marine (as indicated by needle cements and peloidal grains) and meteoric (as indicated by the presence of block cements) diagenesis (Gischler et al., 2013). In cores M0057A and M0042A, petrographic indicators of meteoric diagenesis are abundant (e.g. blocky and dogtooth cements (Gischler et al., 2013)), but indicators of marine diagenesis are absent, an observation we attribute to the potential non-uniqueness of petrographic indicators and/or loss or overprinting of marine diagenetic fabrics during

# subsequent meteoric alteration (e.g., Melim et al., 1995).

#### 4.2. The impact of primary mineralogy on model simulations

The choice of primary mineral composition remains one of the larger assumptions in this study. Our goal in picking a starting composition was to find a set of geochemical values that would satisfy the entirety of the microfacies and mineralogies represented in our sample suite.

To our knowledge, there are no published measurements of Ca and Mg isotopes specific to our GBR study site. Measurements of *Scleractinian* coral  $\delta^{44/40}$ Ca range between -0.83 % to -1.22 % (see Böhm et al., 2006; Chen et al., 2016; Gothmann et al., 2016) and  $\delta^{26}$ Mg between -1.84 % and -2.16 % (Gothmann et al., 2017). Our choice of primary composition reflecting bank-top sediments is a conservative/average estimate of bulk composition, and offers the best-fit model solution. Using the above coralline values for  $\delta^{44/40}$ Ca and  $\delta^{26}$ Mg would require even larger fractionation factors during meteoric alteration to give rise to the observed  $\delta^{44/40}$ Ca and  $\delta^{26}$ Mg signatures for GBR sediment.

# 4.3. Metal (Ca, Mg) isotopes as indicators of meteoric alteration

The mineralogical, petrographic and geochemical changes associated with the alteration of marine carbonate sediments by meteoric fluids have been studied for over 60 years in an attempt to understand the processes that transform carbonate sediment into rock, and the extent to which this process affects the preservation of paleoenvironmental information (e.g., Ginsburg and Lowenstam, 1958; Friedman, 1964). In terms of sediment mineralogy and geochemistry, the earliest studies noted reactions with meteoric fluids resulted in Sr and Mg loss and conversion of metastable high-Mg calcite and aragonite to low-Mg calcite (Francis and Hower, 1961; Friedman, 1964). Subsequently, it was shown that this conversion is often associated with co-variation between  $\delta^{13}$ C and  $\delta^{18}$ O values, with more negative values indicating more extensive neomorophism and/or recrystallization in meteoric fluids (Baertschi, 1951; Allan and Matthews, 1982). Together, paired measurements of  $\delta^{13}$ C and  $\delta^{18}$ O have also been applied widely as a tool to geochemically identify meteoric alteration in shallow water marine carbonate samples to identify subaerial exposure surfaces and characterize the role of eustasy in cyclic shallow-water carbonates sediments (Allan and Matthews, 1982; Christ et al., 2012; Dyer et al., 2015). In



**Fig. 6.** Modeling results (phase space) for shallow water carbonate alteration via 2-step diagenesis for A:  $\delta^{13}$ C vs.  $\delta^{18}$ O, B:  $\delta^{26}$ Mg vs.  $\delta^{18}$ O, C:  $\delta^{44/40}$ Ca vs. Sr/Ca and D:  $\delta^{44/40}$ Ca vs.  $\delta^{26}$ Mg. Primary aragonite first undergoes *syn*-depositional, early-stage marine diagenesis in the presence of co-eval seawater, giving rise to diagenetically stabilized calcite (left column; orange phase space). This secondary calcite then undergoes meteoric diagenesis. The meteoric diagenetic phase space (shown in blue) provides the best-fit explanation for geochemical signatures recorded in the middle (M0055A and M0056A) and right (cores M0057A and M0042A) columns. Dashed contour lines represent percentiles of the degree of alteration of the bulk sediment (between 0% and 100%) and the bold colored line (100% alteration) represents the model-predicted diagenetic end-member. Dashed arrows represent the fluid-buffered (box 1) trajectory while the sediment-buffered (box n) trajectory is represented by the solid black arrow. GBR data points are colored by the petrographic incidence of meteoric cements and fabrics (as in Fig. 4), originally described by Gischler et al. (2013), with samples from cores M0032A and M0033A in the left column, M0055A and M0056A in the middle column and M0057A and M0042A in the right column.

#### Table 2

Model parameters and best-fit conditions for two-step alteration including (1) early-stage marine diagenesis and alteration of primary aragonite to low-Mg calcite (e.g., Triple Goose Creek) in the presence of modern seawater (using parameters from Ahm et al. (2018)) and (2) meteoric diagenesis, as observed in GBR sediments (in particular, cores M0042A and M0057A) and shown in Fig. 6.

Parameter	[1]	[2]	
$\alpha_{Ca}$	1.000	0.998	
$\alpha_{Mg}$	0.998	0.998	
α <sub>C</sub>	1.001	1.001	
αο	1.0330	1.0289	
K <sub>Sr</sub>	0.05	0.05	
Primary Mineralogy	Aragonite	Calcite	
Diagenetic Mineralogy	Calcite	Calcite	
M <sub>f</sub> (mmol/Kg)	Ca: 10.6	Ca: 12.4	
	Mg: 52.8	Mg: 5.28	
	C: 2.9	C: 4.1	
	Sr: 0.09	Sr: 0.09	
$\delta_f$ (‰)	$\delta^{44}$ Ca: 0	$\delta^{44}$ Ca: -0.4	
	$\delta^{26}$ Mg: -0.79	$\delta^{26}$ Mg: -3.3	
	$\delta^{13}$ C: -2	$\delta^{13}$ C: -10	
	$\delta^{18}$ O: -30.5	$\delta^{18}$ O: -34	
M <sub>s</sub>	Ca: 39%	Ca: 38.6%	
	C: 12%	C: 12%	
	Mg: 2500 ppm	Mg: 10 000 ppm	
	Sr: 10 000 ppm	Sr: 4000 ppm	
$\delta_s$ (‰l)	$\delta^{44}$ Ca: -1.6	$\delta^{44}$ Ca: -0.7	
	$\delta^{26}$ Mg: -3.0	$\delta^{26}$ Mg: -3.4	
	δ <sup>13</sup> C: 3.6	$\delta^{13}$ C: 2.0	
	δ <sup>18</sup> O: 1.0	δ <sup>18</sup> O: 0	

addition, co-variation between  $\delta^{13}$ C and  $\delta^{18}$ O values in carbonate sediments that may have undergone meteoric alteration has been used to argue for (Knauth and Kennedy, 2009; Dyer et al., 2015) and against (Jones et al., 2015) an early origin of the terrestrial biosphere.

However, co-variation between  $\delta^{13}$ C and  $\delta^{18}$ O isotopes and/or low  $\delta^{18}$ O values and trace element contents are not unique geochemical indicators of meteoric diagenesis for several reasons. First, low  $\delta^{18}$ O values can also result from recrystallization and neomorphism at elevated temperatures during burial and lithification (van der Kooij et al., 2009). This process can produce co-variation between  $\delta^{13}$ C and  $\delta^{18}$ O values if there is a change in the fraction of carbonate sediment that escapes neomorphism and recrystallization near the sediment–water interface (Ahm et al., 2021). Second, sediments may be altered by meteoric diagenesis but do not show the characteristic depletions in  $\delta^{13}$ C and  $\delta^{18}$ O due to differences in the isotopic composition of the meteoric fluid (rainfall or ground water) and organic matter (Wright, 1990; Christ et al., 2012). Finally, co-variation between  $\delta^{13}$ C and  $\delta^{18}$ O values can also arise from syn-depositional sedimentary source mixing (Swart and Eberli, 2005).

Our results for calcium ( $\delta^{44/40}$ Ca) and magnesium  $\delta^{26}$ Mg) isotopes indicate that these systems constitute a complimentary set of geochemical indicators of meteoric diagenesis in bulk carbonate sediments. The utility of using these two isotope systems is best illustrated in bulk sediment  $\delta^{26}$ Mg values, which show strong co-variation with both  $\delta^{18}$ O values and  $\delta^{13}$ C values (Figs. 5 and 6). The extremely low  $\delta^{26}$ Mg values of meteorically altered bulk carbonate sediments is the product of three factors. The first is the  $\delta^{26}$ Mg value of the precursor carbonate minerals which is the source of most of the Mg in the meteoric fluid. With regards to both modern examples presented here from the Bahamas and GBR, the initial  $\delta^{26}$ Mg value of the sediments of  $\sim -3\%$  is significantly lower than modern seawater ( $\delta^{26}Mg = -0.82$  %). This ~ 2.2 ‰ offset likely reflects fractionation associated with high-Mg calcite as the Mg budget of bulk sediment from both of these sites is dominated by this mineral (Higgins et al., 2018) and this value is similar to laboratory and theoretical estimates of Mg isotope fractionation in high-Mg calcite (Li et al., 2012; Saulnier et al., 2012; Mavromatis et al., 2013). The second factor is that the precipitation of diagenetic carbonate minerals in meteoric fluids is associated with significant fractionation of Mg isotopes. Laboratory and empirical studies of Mg isotope fractionation in inorganic carbonates indicates that Mg isotope fractionation factors for calcite are on the order of 0.99 to 0.991 and increase as precipitation rate decreases (Mavromatis et al., 2013; Higgins and Schrag, 2015). Our preferred model fits to the data utilize Mg isotope fractionation factor of 0.998, consistent with studies from the laboratory and deep-sea environments. Third, despite the large fractionation factor associated with low-Mg calcite precipitation, meteoric diagenesis is characterized by a large supply of  $Mg^{2+}$  from dissolution of the primary high-Mg calcite, leading to consistently low  $\delta^{26}$ Mg values with little to no distillation of the pore-fluid. This behavior will be similar for other carbonate mineralogies as well, where the partition coefficient for Mg is higher in the primary mineral relative to the diagenetic phase. These conditions permit the expression of Mg isotopic fractionation associated with the formation of diagenetic calcite without resulting in the isotopic distillation of the fluid. The high supply of Mg<sup>2+</sup> from high-Mg calcite dissolution is indicated both in our data and the results of numerical modeling (Figs. 5 and 6).

Both theory and our data (Fig. 6) indicate that the effect of meteoric diagenesis on bulk carbonate  $\delta^{44/40}$ Ca values is similar to, but more subtle than,  $\delta^{26}$ Mg values. There are two likely reasons for this. First, unlike  $\delta^{26}$ Mg values, fractionation of  $\delta^{44/40}$ Ca values declines with precipitation rate, suggesting that the precipitation rates associated with meteoric diagenesis may lead to a smaller fractionation of Ca isotopes (compared to Mg isotopes) in the diagenetic calcite and a more muted response of bulk  $\delta^{44/40}$ Ca values to meteoric diagenesis (Tang et al., 2008; Mills et al., 2021). Small fractionation of calcium isotopes during remineralization has been described previously (Bradbury and Turchyn, 2018; Blättler et al., 2021), with magnitudes similar to those described above. Second, early marine diagenesis that occurs prior to meteoric diagenesis results in bulk  $\delta^{44/40}\text{Ca}$  values that tend to be elevated relative to the primary carbonate mineral. Notably, these  $\delta^{44/40}$ Ca sediment values control the composition of the meteoric fluid, as most of the dissolved calcium is sourced from the surrounding bulk carbonate (See section 5.4; Fig. 6).

The geochemical fingerprint of meteoric diagenesis in metal isotopes  $(\delta^{26}Mg \text{ and } \delta^{44/40}Ca \text{ values})$  with trace elements (Sr/Ca and Mg/Ca ratios) has major advantages over more traditional isotopic indicators (e.g.,  $\delta^{13}$ C and  $\delta^{18}$ O values) for identifying and characterizing meteoric diagenesis in ancient shallow marine carbonate sediments (Table 3). First, unlike both  $\delta^{13}$ C and  $\delta^{18}$ O values, the behavior of Mg and Ca isotopes during meteoric diagenesis is independent of the initial fluid composition because the initial Ca and Mg content of meteoric fluids is trivial and there are no exogenous sources (other than the rock itself) in sediment system. As a result, as the isotopic effect of meteoric diagenesis for metal isotopes is driven by internal recycling and fractionation during the formation of diagenetic carbonate minerals making  $\delta^{26}$ Mg and  $\delta^{44/40}$ Ca isotopes a potentially more robust geochemical indicator of meteoric diagenesis. This may be of particular importance in Precambrian sediments that predate the growth of the terrestrial biosphere (the source of the <sup>13</sup>C depleted dissolved inorganic carbon (DIC) in meteoric fluids) and in cases where low  $\delta^{18}$ O values can be ambiguously interpreted as either meteoric alteration, elevated temperatures associated with burial diagenesis, or a secular change in the  $\delta^{18}$ O of seawater.

#### 4.4. Two stepped marine-meteoric diagenesis

One of the important results from this study is the recognition that marine carbonate sediments at the studied sites appear to have undergone significant early marine diagenesis prior to meteoric diagenesis. This is most easily identified with  $\delta^{44/40}$ Ca values as marine and meteoric diagenesis shift bulk sediment  $\delta^{44/40}$ Ca values in different directions (marine = increase  $\delta^{44/40}$ Ca; meteoric = decrease  $\delta^{44/40}$ Ca). The strong imprint of early marine diagenesis is indicated by the fact that, with few exceptions, measured  $\delta^{44/40}$ Ca values in even the most meteorically altered samples are similar to or higher than the  $\delta^{44/40}$ Ca values of the

#### Table 3

Comparison of physical and geochemical features of modern shallow-water carbonates and two main styles of alteration (marine and meteoric diagenesis), as defined by  $\delta^{13}$ C and  $\delta^{18}$ O (Allan and Matthews, 1982; Ahm et al., 2018; Higgins et al., 2018; Swart and Oehlert, 2018; Geyman and Maloof, 2021 and this paper),  $\delta^{44/40}$ Ca,  $\delta^{26}$ Mg and trace elements (Sr/Ca and Mg/Ca) (Ahm et al., 2018; Higgins et al., 2018 and this paper). Petrographic fabrics may be used as independent indicators of diagenetic style, some of these textures are listed (e.g. Budd, 1988; Scholle and Ulmer-Scholle, 2003; Gischler et al., 2013). In the interest of simplicity, meteoric diagenesis here includes both vadose and phreatic zone alteration.

	(Relationship between) $\delta^{13}C$ and $\delta^{18}O$ values	δ <sup>44</sup> Ca	$\delta^{26}Mg$	Trace element concentrations (Sr/Ca, Mg/ Ca)	Petrographic indicators
Primary carbonate (modern, shallow- water carbonate)	Variable, generally positively correlated. Isotopic values and relationships show a dependence on facies.	Varies from $\sim -1.5 \%$ (aragonite) to $-1\%$ (calcite).	Approximately –2.8 ‰.	High (~10 mmol/mol, aragonite) to moderate (calcite) Sr/Ca ratios, depending on mineralogy.	Lacking evidence of dissolution or cements; aragonite is dominant mineralogy
Marine diagenesis	$\delta^{13}$ C and $\delta^{18}$ O values generally heavy/positive, reflecting mixture of original sediment composition, and recrystallization/neomorphism by seawater.	Sediment buffered retains low $\delta^{44}$ Ca (from primary composition) while fluid buffered has high $\delta^{44}$ Ca, approaching modern seawater.	Slight lowering of $\delta^{26}$ Mg from primary composition. If dolomitized, sediment buffered $\delta^{26}$ Mg is high and variable while fluid buffered $\delta^{26}$ Mg is low.	$Sr/Ca$ ratios lowered $\leq 1$ mmol/mol. Mg/Ca ratios lowered during aragonite to calcite neomorphism, increased during dolomitization.	Cementation, dolomitization, micrite envelope, needle cement. Evidence for dissolution and reprecipitation.
Meteoric diagenesis	$\delta^{13}$ C negative and variable, while $\delta^{18}$ O negative but homogenous. Slight positive correlation might be present in phreatic zone.	$\delta^{44}$ Ca relatively homogenous due to low Ca concentration in meteoric fluids	$\delta^{26}$ Mg negative (~-5‰) and variable. Small difference between sediment and fluid buffered end- members.	Both Sr/Ca and Mg/Ca ratios decrease with progressing alteration	Evidence for dissolution and reprecipitation. Dogtooth cement, blocky cement, meniscus cement, caliche

primary carbonate sediment. Other diagenetic indicators (e.g., Sr/Ca,  $\delta^{13}$ C, and  $\delta^{18}$ O values) behave similarly in most marine and meteoric diagenetic settings and thus cannot be used to distinguish these two styles of diagenesis. The recognition of a two-stepped marine-meteoric diagenetic history is important for two reasons. First, it highlights the extent to which syn-depositional early marine diagenesis appears to be both a rapid and ubiquitous process in most shallow-water environments where carbonate sediments are deposited. Second, a two-step process further complicates the interpretation of carbonate-bound geochemical proxies, in particular those that might be expected to behave differently in marine and meteoric diagenetic environments.

#### 5. Conclusions

We have presented a geochemical and numerical framework for fingerprinting meteoric alteration in carbonate sediments. The model simulates diagenesis by tracking the elemental and isotopic composition of Ca, Mg, C, O and Sr/Ca and Mg/Ca ratios in bulk sediment. We ground truth our modeled trajectories against geochemical measurements of modern carbonates from Andros Island (Bahamas) and Pleistocene reef assemblages from the Great Barrier Reef. We explain observed trends in the data (particularly  $\delta^{44/40}$ Ca and  $\delta^{26}$ Mg values) as indicative of 2-step alteration: syn-depositional early marine diagenesis followed by alteration by meteoric fluids. Our results underscore the importance of a multi-proxy approach to identifying meteoric diagenesis in ancient shallow-marine carbonate sediments.

# CRediT authorship contribution statement

Alliya A. Akhtar: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization. Anne-Sofie Cruger Ahm: Writing – review & editing, Supervision, Software, Methodology, Investigation, Formal analysis, Conceptualization. John A. Higgins: Writing – review & editing, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data Availability

All data associated with this paper are available through EarthChem at https://doi.org/10.60520/IEDA/113214.

#### Acknowledgements

We thank Adrien Immenhauser for editorial handling and Dr. David Jones for his constructive reviews. An earlier version of this manuscript greatly benefited from reviews by two anonymous reviewers and discussions with Adam Maloof and Matt Nadaeu. We would like to thank Liz Lundstrom, Nic Slater, Sam Gwizd and Disha Okhai for laboratory assistance. Preston Kemeny, Charlotte Conner, Blake Dyer, Jenn Kasbohm, Akshay Mehra and members of the GEO370/570 class (Spring 2014) provided invaluable assistance in the field. This work was supported by a grant from the Simons Foundation (SCOL 611878 to ASCA) and the Carlsberg Foundation to ASCA. AAA acknowledges support from the Scott Vertebrate Paleontology Fund (Princeton University).

#### Appendix A. Supplementary material

Supplementary material to this article can be found online at htt ps://doi.org/10.1016/j.gca.2024.08.002.

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