

1 Mineralogy, early marine diagenesis, and the chemistry of shallow water carbonate sediments
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17 **ABSTRACT**
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19 Shallow-water carbonate sediments constitute the bulk of sedimentary carbonates in the
20 geologic record and are widely used archives of Earth's chemical and climatic history. One of
21 the main limitations in interpreting the geochemistry of ancient carbonate sediments is the
22 potential for post-depositional diagenetic alteration. In this study, we use paired
23 measurements of calcium (⁴⁴Ca/⁴⁰Ca) and magnesium (²⁶Mg/²⁴Mg) isotope ratios in
24 sedimentary carbonates and associated pore-fluids as a tool to understand the mineralogical
25 and diagenetic history of Neogene shallow-water carbonate sediments from the Bahamas and
26 southwest Australia. We find that the Ca and Mg isotopic composition of bulk carbonate
27 sediments at these sites exhibits systematic stratigraphic variability that is related to both
28 mineralogy and early marine diagenesis. The observed variability in bulk sediment Ca
29 isotopes is best explained by changes in the extent of fluid-dominated early marine diagenesis
30 in both platform and slope sediments. Our results indicate that this process, together with
31 variations in carbonate mineralogy (aragonite, calcite, and dolomite), likely plays a
32 fundamental and underappreciated role in determining the regional and global stratigraphic
33 expressions of geochemical tracers ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, major, minor, and trace elements) in shallow
34 water carbonate sediments in the geologic record.
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1. INTRODUCTION

The chemistry of shallow water marine carbonate sediments has been used to reconstruct the temperature and isotopic composition of seawater as well as the global carbon and oxygen cycles over >3 billion years of Earth history (1, 2). The underlying assumption in these studies is that the chemical composition of the sediment accurately preserves a record of ancient open-ocean seawater (3-5). One of the principal ways in which this assumption is violated is through diagenesis - the chemical changes that occur during the transformation of sediment into rock. Diagenetic alteration of carbonate sediments can occur in association with either meteoric or marine fluids (6-12), is observed at length scales from microns (13) to stratigraphic units (14), and may take the form of recrystallization (no change in mineralogy) or neomorphism (change in mineralogy). In some cases diagenetic alteration is regarded as the dominant source of variability in the geologic record (i.e. $\delta^{18}\text{O}$; (15)) whereas in other cases (i.e. $\delta^{13}\text{C}$) the effects of diagenesis are generally thought to be small though not insignificant (16, 17). The effects of diagenesis, in particular *early marine diagenesis*, on many shallow-water carbonate-bound geochemical proxies (e.g. $\delta^{34}\text{S}$ values of carbonate-associated sulfate (CAS), $\delta^{44}\text{Ca}$, $\delta^{26}\text{Mg}$, $\delta^7\text{Li}$, $\delta^{11}\text{B}$, $\delta^{98/95}\text{Mo}$, $\delta^{238/235}\text{U}$ values, and I/Ca ratios) are either unknown or limited to a handful of studies (18-26). One of the more widely used metrics for characterizing diagenetic alteration in ancient carbonate rocks – the Mn/Sr ratio (27) – can be shown to depend on variables other than early marine diagenesis (mineralogy, bottom-water oxygenation, sedimentation rate, etc.) and at best is only a qualitative indicator.

Recent studies by Blättler et al. (28) and Fantle & Higgins (21) have shown both large variability and co-variation between the stable isotope ratios of magnesium ($^{26}\text{Mg}/^{24}\text{Mg}$) and calcium ($^{44}\text{Ca}/^{40}\text{Ca}$) in authigenic and diagenetic carbonates from the Monterey Formation (Miocene) in offshore southern California and the Marion Plateau off of northeast Australia (Ocean Drilling Program (ODP) Site 1196. In both cases the variability and co-variation are driven primarily by the extent to which diagenesis/authigenesis occurred in fluid-buffered ('open') or sediment-buffered ('closed') conditions. Additional studies on Ca and Mg isotope fractionation in carbonates have shown that it depends on mineralogy – aragonite tends to be depleted in ^{44}Ca and enriched in ^{26}Mg compared to calcite (29) - as well as the rate of mineral precipitation and solution chemistry (30-32). Importantly, the observed variability in the Ca and Mg isotopic composition of bulk carbonate sediments associated with changes in mineralogy and early diagenesis is large compared to other potential sources (i.e. changes in seawater $\delta^{26}\text{Mg}$ and $\delta^{44}\text{Ca}$ values (33-35)), suggesting that these measurements can provide novel insights into both the primary mineralogy and early diagenetic history of carbonate-bound geochemical proxies.

Here we present a large data set (N = 676) of $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$ values in Neogene carbonate sediments and associated pore-fluids from the Bahamas and the Eucla Shelf. The nine studied sites encompass a wide range of depositional, mineralogical, and diagenetic environments and were selected to explore whether these differences are associated with variations in sedimentary carbonate $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$ values. Four of the sites are from cores drilled along a 25-km transect across the western flank of the Great Bahama Bank (GBB; Figure 1) from the platform top and margin to the toe of the slope. Sites along the transect document the effects of Neogene sea-level changes and platform progradation on the supply and diagenetic alteration of aragonitic platform-derived sediments (36). Previous studies have shown that these effects lead to a systematic and globally observed change in the $\delta^{13}\text{C}$

83 values of shallow water carbonate sediments that is decoupled from changes in the global
84 carbon cycle as recorded by deep-sea carbonate sediments (5). Additional studied sites in the
85 Bahamas include four shallow (<100 meter) cores taken from a north-south transect through
86 the interior of the Little Bahama Bank (LBB). Miocene to Pleistocene-age carbonate
87 sediments from these sites have experienced multiple episodes of diagenetic alteration
88 including massive replacement-style dolomitization by seawater (37). Finally, a ninth site,
89 Ocean Drilling Program (ODP) Site 1131, a Quaternary carbonate succession on the
90 uppermost slope adjacent to the Eucla Shelf (Great Australian Bight; (38)), was selected for
91 comparison to the Bahamas. All studied sites are geologically young in that they are
92 composed of carbonate sediments deposited over the last 10 million years. Reconstructions
93 of seawater $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$ values over this time period (23, 34, 35) indicate that changes
94 have been small (<0.2‰). As a result, the observed variability in sediment $\delta^{44}\text{Ca}$ values
95 (>1‰) can be interpreted as largely due to mineralogy, diagenesis, and differences in isotopic
96 fractionation due to precipitation rate (22, 26, 29, 39-49).

97 At all studied sites we observe coherent stratigraphic variability in carbonate Ca and Mg
98 isotopes that can be attributed largely to the effects of mineralogy and diagenesis under both
99 fluid-dominated and rock-dominated conditions. The magnitude of the stratigraphic
100 variability in Ca isotopes is large - >1‰ - and co-varies with bulk sediment geochemistry
101 (Sr/Ca), $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. We interpret this variability as a consequence of changes
102 primary carbonate mineralogy in the extent to which the original carbonate sediment has been
103 neomorphosed and/or recrystallized under fluid-buffered or sediment-buffered conditions.
104 Measured pore-fluid profiles of $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$ values indicate that both fluid-dominated
105 and rock-dominated carbonate diagenesis is ongoing on the western flank of the GBB and
106 provide independent evidence that the rates of early marine diagenesis are sufficient to cause
107 partial to wholesale resetting of the chemistry of shallow-water carbonate sediments on
108 million-year timescales. This work further demonstrates the importance of mineralogy and
109 early diagenesis in shaping the geochemistry of shallow-water carbonate sediments and in
110 particular highlights the utility of using paired measurements of Ca and Mg isotopes as a
111 powerful tool for separating these effects from the environmental signals stored in the
112 carbonate rock record.

113 114 **2. METHODS**

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116 A total of ten sites were selected to explore the effects of both mineralogy and early
117 diagenesis on the $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$ values of shallow marine carbonate sediments in a
118 geological (stratigraphic) context. Eight of the studied sites are from carbonate platform and
119 slope environments in the Bahamas – five sites from a transect across the western flank of the
120 Great Bahama Bank (GBB; (36)) and four sites from a transect across the Little Bahama Bank
121 (LBB; (37)). The tenth site is ODP site 1131, a Pliocene-Pleistocene succession of cool-water
122 carbonates in the Great Australian Bight (Figure 1)

123 124 **2.1 The Bahamas**

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126 *Western flank of the Great Bahama Bank (ODP Sites 1007, 1005, 1003, Clino, and Unda):*
127 The western flank of the Great Bahama Bank (GBB) is a modern example of a low-angle,
128 prograding carbonate platform under the influence of changes in sea-level associated with

129 Neogene glacial cycles (50, 51). The sediment produced on the Bahamas platform is largely
130 composed of aragonite with minor amounts of high-Mg calcite. This bank-top sediment is
131 either deposited on the shelf or exported to the slope where it mixes with variable amounts of
132 carbonate sediment sourced from pelagic environments (14, 36). Studied sites from the
133 Western flank of the GBB form a 25-km transect from water depths of ~ 10 meters in the
134 platform interior (Unda) and margin (Clino), to depths of > 600 meters on the slope (Site
135 1007).

136 Detailed descriptions of the geochemistry, sedimentology and stratigraphy of each site
137 from the GBB transect have been published elsewhere (36, 51) and are only briefly reviewed
138 here. Unda sits at the NE end of the transect and consists of three successions of shallow-
139 water platform and reefal deposits that alternate with intervals of deeper skeletal and peloidal
140 platform margin deposits. Subaerial exposure surfaces and intervals of pervasive
141 dolomitization indicate that the sediments at Unda have seen a wide range of diagenetic
142 conditions. Our samples are restricted to the dolomitized interval between 250 and 350 m.
143 Clino is located at the modern platform margin and is composed of three major lithologic
144 units: an upper succession of shallow-water platform and reefal deposits (20-200 m), a middle
145 interval composed of fine-grained nonskeletal sediment with thin interbeds of coarse-grained
146 skeletal material (200-370 m), and a lower deeper unit consisting of mixtures of fine-grained
147 skeletal and non-skeletal sediment with thin layers of coarser skeletal material (370-680 m).
148 Between 200 and 680 meters, nearly 80% of the sediment in Clino consists of monotonous
149 intervals of skeletal and peloidal sand and silt-sized grains. The remaining 20% of the
150 sediment are intervals of coarse-grained skeletal packstones to grainstones; two of these
151 intervals, marine hardgrounds at 367 and 536 m, represent prolonged periods of erosion and
152 non-deposition on the slope. The mineralogy of carbonate sediments at Clino varies widely
153 with depth (Figure 2); between 34 and 150 m it consists almost entirely of low-Mg calcite,
154 whereas between 150 and 367 m aragonite is abundant (up to 65 wt%). Below 367 m
155 dolomite makes up a common but minor fraction of the sediment with prominent peaks at 367
156 and 536 m. In an effort to isolate the effects of dolomitization on sediment $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$
157 values we measured a series of successive leach experiments (52) on two of the more heavily
158 dolomitized intervals at Clino (366-378 m and 494-646 m). Each sample was leached once or
159 twice, resulting in a total of two or three samples at each depth.

160 Ocean Drilling Program Sites 1005, 1003 and 1007 were drilled on the prograding western
161 margin of the Great Bahama Bank on the middle slope (350 and 480 meters below sea-level;
162 mbsl) and the toe of slope (650 mbsl), respectively (Figure 1). Carbonate sedimentation at
163 these sites consists almost entirely of a mixture of material sourced from the platform top
164 (aragonite) with smaller contributions from pelagic sources (low-Mg calcite). The
165 sedimentology of the sites is similar and units are generally characterized by mudstones and
166 wackestones coarsening upwards to packstones, grainstones, and floatstones. Both sites are
167 characterized by systematic changes in sediment mineralogy (as determined by XRD; (50, 53)
168 and increasing lithification with depth. Aragonite is abundant in the upper 150-200 meters of
169 the sediment column but largely replaced by low-Mg calcite and minor amounts of dolomite
170 (Figure 2) at greater depths. To complement the measurements of bulk sediment $\delta^{44}\text{Ca}$ and
171 $\delta^{26}\text{Mg}$ values we also measured $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$ values in samples of sedimentary pore-
172 fluids from site 1003 and 1007. These measurements can provide constraints on rates of
173 recrystallization/neomorphism/dolomitization and Ca and Mg isotopic fractionation
174 associated with these diagenetic reactions (22, 23, 54, 55).

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Little Bahama Bank (WC1, SC1, GB2, and GB1): The Little Bahama Bank (LBB) is the northernmost carbonate platform of the Bahamian Archipelago and hosts an extensive dolomite body in Neogene sediments at shallow depths (20-100 meters; Figure 2). Previous studies on the petrography and geochemistry of these dolomites (37, 56) indicate that the dolomitization occurred early after sediment deposition by a fluid that was essentially unaltered seawater. Depositional textures of the original (non-dolomitized) carbonate sediments range from wackestones to grainstones deposited in outer-reef to inner-platform environments. Biogenic carbonates commonly observed include corals, foraminifera, echinoderms, red algae, rhodoliths, and molluscs. Dolomitization of the sediment is generally complete and textures range from fabric-preserving to fabric-destructive. Studied samples are all dolomites from four wells drilled along a N-S transect of the LBB.

2.2 Southwest Australia

ODP Site 1131: Ocean Drilling Program Site 1131 is located on the upper slope (332.4 meters water depth) adjacent to the Eucla Shelf, a mid-latitude cool-water carbonate deposit in the western Great Australian Bight (57). The site captures a set of rapidly accumulating (~25 cm/kyr), prograding clinoforms of Quaternary age. Sediments are predominately bioclastic packstones interrupted by occasional units of wackestone, grainstone and floatstone. Biogenic components include bryozoans (esp. 0 to 30 meters), foraminifera, echinoid spines, and nannofossils. In contrast to the Bahamas where surface sediments are dominated by aragonite, the mineralogy of the carbonate sediments at Site 1131 includes up to 60 wt% high-Mg calcite near the surface that declines to ~0 wt% by 70 meters depth (Figure 2). The decline in high-Mg calcite is mirrored by an increase in low-Mg calcite and minor amounts of dolomite. Aragonite is a minor (~10 wt%) constituent throughout the core {Swart, 2000 #5486}.

2.3 Analytical methods

2.3.1 Sample preparation and ion chromatography: Samples for this study were analyzed in three different laboratories (Princeton University N = 646, University of Saskatchewan N = 19, and the University of Cambridge N = 11). At Princeton, samples for Ca and Mg isotope analyses were processed using an automated high-pressure ion chromatography (IC) system (Dionex ICS-5000+) following previously published methods (28, 35, 58, 59). At the University of Saskatchewan, carbonate samples were dissolved in 1.0N HCl to make a stock solution. 50 ug of Ca was aliquoted from the stock solution and mixed with an isotopically enriched ⁴³Ca-⁴²Ca double-tracer to bring the mixed ⁴⁰Ca/⁴²Ca ratio to ~7.0 (60). The sample-tracer mixtures were dried down to ensure spike-sample equilibration, and subsequently passed through traditional gravity-flow columns containing MP50-cation exchange resin to purify Ca from matrix elements. At Cambridge, the samples for Ca isotope analysis were also processed using a similar HPIC system (Dionex ICS-5000+). The samples were combined with a ⁴⁸Ca-⁴²Ca double spike before separation to assess any isotopic fractionation during this process.

220 2.3.2 *Dolomite Leachates*: Dolomite in samples of mixed mineralogy were purified using the
221 method outlined by Swart and Melim {Swart, 2000 #1428}. In this method the sample is
222 ground to less than 50 μm in size and treated with buffered acetic acid. After 60 minutes the
223 reaction is quenched and the residual material subjected to X-ray diffraction to assess the
224 effectiveness of the procedure. If the samples still contains non-dolomitic carbonate, the
225 procedure is repeated. In this manner a series of leachates with varying amounts of dolomite
226 is produced.

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228 2.3.3 *Mass spectrometry*: At Princeton dissolved samples were analyzed for $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$
229 values on a Thermo Scientific Neptune Plus MC-ICP-MS (21, 28, 35, 59, 61). Minimum
230 sample sizes are 4-5 μg for Ca and 0.5-1 μg for Mg for a single isotopic analysis (column
231 chromatography and mass spectrometry). Measurements are carried out at low resolution for
232 Mg and medium resolution for Ca to avoid ArHH⁺ interferences. All data are reported in
233 delta notation relative to a known standard for Ca isotopes and measured $\delta^{44/42}\text{Ca}$ values are
234 converted to $\delta^{44/40}\text{Ca}$ values assuming mass-dependent fractionation with a slope of 2.05 (58).
235 Although almost all of the Sr²⁺ is separated from Ca during ion chromatography, we correct
236 for occasional small Sr²⁺ isobaric interferences in the Ca measurements using measurements
237 at $m/z=43.5$ (doubly-charged $^{87}\text{Sr}^{2+}$). All Ca and Mg isotope values are plotted in 3-isotope
238 space ($\delta^{26/24}\text{Mg}$ vs. $\delta^{25/24}\text{Mg}$ and $\delta^{44/42}\text{Ca}$ vs. $\delta^{43/42}\text{Ca}$) to verify that Mg and Ca isotope
239 variability falls along the expected mass-dependent line.

240 Long-term external reproducibility for each isotopic system is determined based on the
241 difference between two known standards taken through the full chemical procedure (column
242 chromatography and mass spectrometry) with each batch of samples. For Ca isotopes we
243 report external reproducibility using the measured value of SRM915b relative to modern
244 seawater, both of which are processed and analyzed alongside a set of 20-30 samples on the
245 same IC run. Our measured $\delta^{44/40}\text{Ca}$ value for SRM915b relative to modern seawater is -1.18
246 $\pm 0.16\%$ (2σ ; $N=125$), indistinguishable from published values determined by both MC-ICP-
247 MS and TIMS (58). All Ca isotope samples are reported relative to modern seawater
248 ($\delta^{44}\text{Ca}_{\text{seawater}} = 0\%$). $\delta^{44}\text{Ca}_{\text{seawater}} = +1.92\%$ on the SRM915a scale and $+0.98\%$ on the bulk
249 silicate Earth (BSE) scale (58). For Mg, the long-term external reproducibility of our
250 measurements is estimated by comparing the Mg standard Cambridge-1 and modern seawater
251 against Dead Sea Metal (DSM-3). Our measured $\delta^{26}\text{Mg}$ values for Cambridge-1 and seawater
252 are $-2.56 \pm 0.09\%$ (2σ , $N=76$) and $-0.83 \pm 0.08\%$ (2σ ; $N=99$), respectively, both
253 indistinguishable from published values (62). Reported errors for each sample depend on the
254 number of times the sample has been separated and analyzed. For a single separation and
255 analysis, we report the long-term external reproducibility of SRM915b or Cambridge-1 ($2\sigma =$
256 $\pm 0.16\%$, and $\pm 0.09\%$, respectively). For multiple separations and analysis ($N > 1$) we also
257 report the standard error of the mean (SE).

258 At the University of Saskatchewan, $\sim 10\text{--}20$ μg of Ca was loaded onto outgassed Ta
259 filaments with phosphoric acid. The measurements were made in a dynamic peak hopping
260 routine. Collector drift was monitored and corrected with standards that were run at the same
261 time as the samples (Holmden and Belanger, 2010; Lehn et al., 2015). The estimated external
262 reproducibility based on repeated measurements of samples and standards using the spike
263 composition and measurement routines documented in Holmden and Belanger (2010) is
264 $\pm 0.06\%$. All Ca isotope analyses are reported on the seawater scale. The $\delta^{44/40}\text{Ca}$ values for
265 SRM 915a and 915b measured over the course of this study is -1.86% and -1.13% .

266 At Cambridge the calcium pore fluid samples were run on a Thermo Scientific Triton Plus
267 MC-TIMS. The separated calcium cuts from the HPIC system were converted to a nitrate
268 form before being evaporated. The sample weights including double spike ranged from 2-4 μg
269 for a single measurement. The samples were re-eluted in 1 μl of 2M Nitric acid and loaded on
270 an outgassed 0.7mm rhenium double filament with 0.5 μl of ultrapure 10% phosphoric acid as
271 an activator. The samples were run for 20 blocks of 10 cycles, after being heated manually to
272 1400°C with a stable beam of 5-10V on ^{40}Ca . Five samples of SRM915b were run within each
273 turret of 21 samples giving an average value of $-1.14 \pm 0.11\%$ (2σ ; $N=10$) relative to modern
274 seawater.

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276 *2.3.4 Major/minor element analyses:* Aliquots of dissolved powders analyzed for Ca and Mg
277 isotopes were also measured for Mg/Ca, Sr/Ca, Mn/Ca and U/Ca ratios on Thermo Finnigan
278 Element-2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The metal to calcium
279 (Me/Ca) ratios of samples were determined using a set of matrix-matched in-house standards
280 spanning the sample range (63). The external reproducibility of the Me/Ca ratios are
281 estimated at $\pm 5-7\%$ (2σ) from replicate measurements of SRM88b, a dolomitic limestone.

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283 *2.3.5 Other geochemical and mineralogical data:* There is a large existing database of pore-
284 fluid chemistry and sediment mineralogy, $\delta^{13}\text{C}$ (‰; PDB scale), $\delta^{18}\text{O}$ (‰; PDB scale), and
285 $^{87}\text{Sr}/^{86}\text{Sr}$ values from previous studies on the sites from the Bahamas (5, 50, 64) and the Eucla
286 Shelf (57). Pore-fluid samples were taken shipboard on 5- to 15- cm-long whole-round
287 sections and a titanium squeezer, modified after the standard ODP stainless steel squeezer of
288 Manheim and Sayles (1974). All interstitial water samples were double-filtered and collected
289 into acid-washed (10% HCl) 50-mL plastic syringes through 0.45 μm and .22 μm Gelman
290 polysulfone disposable filters. For bulk sediment samples, when possible we have measured
291 the same samples as those analyzed in previous studies, though in many cases our samples
292 come from separate, but nearby (within a few meters) sections of the core. For the purpose of
293 plotting pairs of geochemical data (i.e. $\delta^{13}\text{C}$ vs. $\delta^{44}\text{Ca}$) these nearby samples are regarded as a
294 pair (Table S1).

295

296 **3. RESULTS**

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298 Stratigraphic profiles of measured $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$ values, Sr/Ca, Mg/Ca ratios and
299 mineralogy are shown in Figure 2. Measured $\delta^{44}\text{Ca}$, $\delta^{26}\text{Mg}$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ values and Mg/Ca
300 ratios for the subset of Clino samples that underwent gentle acid leaching to isolate dolomite
301 are shown in Figure 3. Measured $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$ values for pore-fluids from Sites 1003 and
302 1007 (Ca only) are shown in Figure 4.

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304 *3.1 Sediment Ca isotopes:* At each studied site we observe stratigraphically coherent
305 variability in bulk sediment $\delta^{44}\text{Ca}$ values, though the magnitude and structure of the
306 variability varies significantly between sites (Figure 2). For example, $\delta^{44}\text{Ca}$ values at Clino
307 vary from -1‰ at 650-675 m, to -0.6‰ at 540-550 m, down to -1.4‰ between 290-320 m
308 then back up to -0.9‰ at 150 m. In contrast, $\delta^{44}\text{Ca}$ values at Site 1131 sit at $-1.10 \pm 0.17\%$
309 (2σ ; $N = 44$) for the entire 550-meter section. Measured $\delta^{44}\text{Ca}$ values from the LBB and
310 Unda are also relatively uniform, though measured $\delta^{44}\text{Ca}$ values are on average $\sim -0.6\%$

311 heavier ($-0.53 \pm 0.18\%$, 2σ ; $N = 27$) than the margin and slope sites ($-1.11 \pm 0.37\%$, 2σ ; $N =$
312 27). The total range in sediment $\delta^{44}\text{Ca}$ values from all studied sites is $>1.2\%$; the highest
313 $\delta^{44}\text{Ca}$ values, up to -0.35% , are found in dolomites from the LBB and Unda and lowest $\delta^{44}\text{Ca}$
314 values, $\sim -1.5\%$, occur in near surface sediments from sites 1003, 1007, and Clino. Minimum
315 $\delta^{44}\text{Ca}$ values are similar to bank-top sediment from the GBB ($\delta^{44}\text{Ca} = -1.36 \pm 0.16\%$, 2σ ; N
316 $= 17$; Table S1) whereas maximum $\delta^{44}\text{Ca}$ values are $\sim 0.8\%$ higher than average pelagic
317 carbonate sediments ($\delta^{44}\text{Ca} = -1.25 \pm 0.30\%$, 2σ ; $N = 179$; (35, 58)) and $\sim 0.6\%$ higher than
318 bulk silicate Earth ($\delta^{44}\text{Ca} = -0.98\%$; (58)).

319 Sediment $\delta^{44}\text{Ca}$ values are strongly correlated with the abundance of aragonite and
320 sediment Sr/Ca ratios in the sites from the Bahamas (Figure 2). Sediments in the upper 100 m
321 from site 1007 and 1003 and between 280-320 m at Clino contain up to 85 wt% aragonite
322 and are characterized by Sr/Ca ratios >6 mmol/mol and $\delta^{44}\text{Ca}$ values between -1.22 and $-$
323 1.56% . The decline in aragonite abundance at Sites 1003, 1007 and Clino is associated with a
324 decline in sediment Sr/Ca ratios and an increase in sediment $\delta^{44}\text{Ca}$ values peaking at ~ 200
325 and ~ 300 m ($\delta^{44}\text{Ca} \sim -0.8\%$) at Sites 1003 and 1007, respectively, and 540-550 m ($\delta^{44}\text{Ca} \sim -$
326 0.6%) at Clino. Bulk sediment $\delta^{44}\text{Ca}$ values at Sites 1003 and 1007 decline and Sr/Ca ratios
327 increase below 200-250 m, however, the shift is not accompanied by a significant increase in
328 aragonite abundance. At all of the sites in the Bahamas, samples with the highest $\delta^{44}\text{Ca}$
329 values (up to -0.35%) and lowest Sr/Ca ratios (down to ~ 0.16 mmol/mol) tend to be partly or
330 fully dolomitized.

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332 *3.2 Pore-fluid Ca isotopes:* Measured $\delta^{44}\text{Ca}$ values of sediment pore-fluids from Sites 1003
333 and 1007 are shown in Figure 4. Both profiles are characterized by large declines in the
334 pore-fluid $\delta^{44}\text{Ca}$ value within the upper 100 m, from the seawater value (0%) to values
335 characteristic of the bulk sediment (-1 to -1.2%). Concentrations of Ca in the pore-fluid do
336 not change appreciably in the upper ~ 100 m of the sediment column at both sites, implying
337 that the associated decline in pore-fluid $\delta^{44}\text{Ca}$ values is due to neomorphism and
338 recrystallization of the carbonate sediments with little net dissolution or precipitation.

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340 *3.3 Sediment Mg isotopes:* Measured $\delta^{26}\text{Mg}$ values of sediments from all studied sites occupy
341 a fairly narrow range ($\delta^{26}\text{Mg} = -2.93 \pm 0.41\%$, 2σ ; $N = 254$). The average $\delta^{26}\text{Mg}$ value for the
342 shallow water sites (Clino, Unda, and LBB) is slightly heavier ($\delta^{26}\text{Mg} = -2.83 \pm 0.29\%$, 2σ ; N
343 $= 103$) than the average $\delta^{26}\text{Mg}$ value ($\delta^{26}\text{Mg} = -3.01 \pm 0.42\%$, 2σ ; $N = 146$) for slope sites
344 (1003, 1007, and 1131) and bank-top sediment ($\delta^{26}\text{Mg} = -3.11 \pm 0.05\%$, 2σ ; $N=5$) but
345 overall there is remarkably little variability considering the samples range from relatively
346 unaltered mixtures of aragonite, high-Mg calcite, and low-Mg calcite to sediments that have
347 undergone pervasive dolomitization. The lack of clear signals in bulk sediment $\delta^{26}\text{Mg}$ values
348 related to changes in aragonite ($\delta^{26}\text{Mg} \sim -1.8\%$; (44, 48) abundance is conspicuous though it
349 is likely due to the very low Mg content of aragonite (2-4 mmol Mg/mol Ca) compared to all
350 other carbonate phases (LMC, HMC and dolomite). The bulk sediment average Mg/Ca ratio
351 (excluding dolomites from Clino, Unda, and LBB) is ~ 50 mmol/mol.

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353 *3.4 Pore-fluid Mg isotopes:* The Mg isotopic composition of pore-fluids from Site 1003
354 (Figure 4) is constant in the upper 62 m of the sediment column (avg. = $-0.78 \pm 0.07\%$, 2σ ; N
355 $= 10$) but increases abruptly thereafter, reaching a maximum value of $+0.12\%$ at 294 m. The

356 increase in pore-fluid $\delta^{26}\text{Mg}$ values is accompanied by a decline in pore-fluid Mg
357 concentrations (Table S1) and an increase in the abundance of dolomite within the sediment
358 column (though it remains a minor component; Figure 2).

359

360 *3.5 Dolomite leach experiments:* Measured Mg/Ca ratios, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $\delta^{44}\text{Ca}$, and $\delta^{26}\text{Mg}$
361 values for 15 leached samples from two depth intervals in Clino (367.10-379.06 m and
362 495.90-648.66 m) are shown in Figure 3A-D. Sequential leaches produce samples with
363 increasing dolomite content as shown by a systematic increase in sediment Mg/Ca ratios,
364 $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ values (Figure 3C, D). In contrast, the average $\delta^{44}\text{Ca}$ value of the 15 samples
365 is similar for all leach steps (-0.91‰, -0.89‰, and -0.98‰, respectively) indicating that
366 sequential leaching and purification of the dolomite fraction is not associated with any
367 systematic change in sediment $\delta^{44}\text{Ca}$ values (Figure 3A). However, the total range in sediment
368 $\delta^{44}\text{Ca}$ values does increase during sequential leaching from 0.5‰ in bulk sediments (-1.10‰
369 to -0.63‰) to 0.8‰ in leached sediments (-1.30‰ to -0.48‰). Average $\delta^{26}\text{Mg}$ values of the
370 bulk and leached sediments (Figure 3B) are indistinguishable from one another (-2.89‰, -
371 2.82‰, and -2.78‰, respectively) and have a similar range of 0.6 to 0.7‰ (-2.4‰ to -3.1‰).

372

373 4. DISCUSSION

374

375 The process of transforming unlithified metastable carbonate minerals such as aragonite
376 and high-Mg calcite into limestone and dolomite (diagenesis) involves chemical exchange
377 between the solid and the local pore-fluid. The extent to which the chemical composition of
378 the initial sediment is preserved during these transformations depends on four factors: 1) the
379 relative abundance of the element in the fluid and solid phases, 2) the partitioning of that
380 elemental or isotopic system into the primary and diagenetic carbonate phases (i.e. aragonite
381 vs. dolomite), 3) the amount or rate of diagenetic recrystallization or neomorphism and 4) the
382 degree to which the sediment pore-fluid system was 'fluid-buffered' or 'sediment-buffered' for
383 that particular elemental or isotopic system during diagenesis. Here a fluid-buffered (or open)
384 diagenetic system refers to one where the chemical composition of the diagenetic phase
385 largely reflects the chemical composition of the diagenetic fluid whereas in a sediment-
386 buffered (or closed) diagenetic system the chemical composition of the diagenetic phase
387 largely reflects the chemical composition of the primary sediment.

388 With the notable exception of O, the isotopic composition of the major elements in
389 carbonate minerals (Ca, C, and Mg in dolomite only) are thought to be relatively robust to
390 alteration during diagenesis due to the high concentrations of these elements in the sediment
391 compared to most diagenetic fluids, i.e. it is generally assumed that diagenesis occurs under
392 sediment-buffered conditions with respect to these elements. Although the assumption of
393 sediment-buffered conditions appears to be generally valid for major elements in
394 recrystallized carbonate sediments in the deep-sea (22), it has not been shown to be true for
395 shallow-water carbonate sediments.

396 site

397 *4.1 An early diagenetic origin for stratigraphic variability in bulk sediment $\delta^{44}\text{Ca}$, $\delta^{26}\text{Mg}$*
398 *values and major/minor element chemistry:*

399 One of the most compelling aspects of our data is that shallow water (<1000 m) carbonate
400 sediments from the toe-of-the slope to the platform margin along the western flank of the
401 Great Bahama Bank show coherent stratigraphic variability of up to 1‰ in bulk sediment

402 $\delta^{44}\text{Ca}$ values, other major and minor element proxies (e.g. Sr/Ca ratios, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ values)
403 and mineralogy (Figure 2 and 4). Bulk sediments with low $\delta^{44}\text{Ca}$ values typically have high
404 Sr/Ca ratios whereas sediments with high $\delta^{44}\text{Ca}$ values have low Sr/Ca ratios. Low bulk
405 sediment $\delta^{44}\text{Ca}$ values also tend to be associated with high $\delta^{13}\text{C}$ values and low $\delta^{18}\text{O}$ values
406 (Figure 4). The relationship between bulk sediment $\delta^{44}\text{Ca}$ values and mineralogy is more
407 complex – in the upper 200 meters of Sites 1007, 1005, and 1003 the upper 400 meters at
408 Clino there is strong co-variation between bulk sediment mineralogy and $\delta^{44}\text{Ca}$ values with
409 low $\delta^{44}\text{Ca}$ values associated with high wt% aragonite and with heavier $\delta^{44}\text{Ca}$ values
410 associated with calcite and dolomite (Figure 2). However, at both Sites 1003 and 1007, there
411 is also a decline in $\delta^{44}\text{Ca}$ values below 200-400 meters that is not accompanied by any change
412 in bulk sediment mineralogy (i.e. the sediment is overwhelmingly calcite throughout) but is
413 accompanied by an increase in sediment Sr/Ca ratios.

414 There are two processes capable of generating stratigraphic co-variation in bulk sediment
415 geochemistry ($\delta^{44}\text{Ca}$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and Sr/Ca ratios) and mineralogy at the Bahamas sites. The
416 first is mixing of sediment from different carbonate sources. One possibility is differential
417 production and/or transport of aragonite and high-Mg calcite on the platform. Measured
418 $\delta^{44}\text{Ca}$ values for aragonite muds and ooids from Andros Island average -1.36‰ ($N = 14$;
419 Table S1) whereas measured $\delta^{44}\text{Ca}$ values for high-Mg calcite are significantly higher (-0.8‰
420 to -0.9‰ ; Site 1131 and (41)). However, mixing of these two endmembers to explain the
421 variability in bulk sediment $\delta^{44}\text{Ca}$ values is not consistent with the observation that high-Mg
422 calcite makes up only a small portion of the bulk sediment and there is no co-variation
423 between sediment Mg/Ca and $\delta^{44}\text{Ca}$ values in the upper 200-300 meters at Sites 1003 and
424 1007. In addition, high-Mg calcite clearly cannot explain dolomite with a $\delta^{44}\text{Ca}$ values $> -$
425 0.5‰ at Clino, Unda, and the LBB.

426 Mixing of pelagic and platform sources of carbonate sediment is more likely to be an
427 important source of stratigraphic variability in the geochemistry of bulk carbonate sediments,
428 in particular for the more distal sites in this study (Sites 1003 and 1007). Previous work on
429 stratigraphic variations in the $\delta^{13}\text{C}$ values and mineralogy of carbonate sediments on platform
430 slopes in the Bahamas and other carbonate platforms by Swart (5, 14) argued that the $\sim 4\text{‰}$
431 decline in the $\delta^{13}\text{C}$ value of bulk carbonate sediments and loss of aragonite from the surface to
432 ~ 200 meters (Figures 2 and 4) could be explained largely by an increase in contributions from
433 pelagic carbonate sources (with a $\delta^{13}\text{C} \sim 0\text{‰}$). Although we do not know the local $\delta^{44}\text{Ca}$
434 value of pelagic carbonate sources, the average $\delta^{44}\text{Ca}$ value of Cenozoic pelagic carbonates
435 (foraminifera and nannofossils) is $-1.25 \pm 0.15\text{‰}$ (1σ ; $N = 179$; (35, 58)), suggesting that
436 mixing of carbonate sources (e.g. pelagic and platform) may explain some, but not all of the
437 $\sim 0.7\text{‰}$ increase in bulk sediment $\delta^{44}\text{Ca}$ values between the sediment-water interface and 200-
438 300 meters at Sites 1003 and 1007 (Figure 7). This is supported by an analyses of smear
439 slides from the upper ~ 400 meters at Site 1003 which indicate no systematic down-core
440 changes in either relative grain size (sand/silt/clay) or composition
441 (foraminifera/nannofossils/micrite) of the sediment (50). Increasing contributions from
442 pelagic carbonate sources likely plays a more important role in explaining some of the shift to
443 lower $\delta^{44}\text{Ca}$ values in Miocene-aged sediment below 200-400 meters at sites on the slope.

444 The second process capable of generating stratigraphic variability in bulk sediment $\delta^{44}\text{Ca}$
445 values is neomorphism and recrystallization of carbonate sediments occurs under variable
446 (fluid-buffered vs. sediment-buffered) diagenetic conditions. In particular, recrystallization

447 and neomorphism under fluid-buffered conditions in marine sediments is expected to increase
448 the $\delta^{44}\text{Ca}$ value of bulk carbonate sediments because 1) Ca isotope fractionation during calcite
449 precipitation (22, 30, 32) is rate-dependent, approaching a value ($\alpha_{\text{xtal-calcite}}^{44/40}$) of ~ 0.9998 to
450 1.0000 at rates associated with early marine diagenesis in deep-sea sediments and 2) the
451 diagenetic fluid is inferred to be relatively unaltered seawater with a $\delta^{44}\text{Ca}$ value of $\sim 0\text{‰}$. In
452 contrast, recrystallization and neomorphism under sediment-buffered conditions is expected
453 to result in little change in the bulk sediment $\delta^{44}\text{Ca}$ value as the majority of the Ca is inherited
454 from the precursor sediment. One of the advantages of this process is that it neatly explains
455 large enrichments in ^{44}Ca in carbonate sediments – i.e. $\delta^{44}\text{Ca}$ values as high as -0.3‰ – as the
456 consequence of more extensive recrystallization and/or neomorphism under fluid-buffered
457 conditions. In addition, the observation that bulk sediment $\delta^{44}\text{Ca}$ values and other
458 geochemical proxies strongly co-vary with sediment mineralogy (in particular aragonite
459 abundance) does not preclude a diagenetic origin for the co-variation, rather it simply requires
460 that the diagenetic carbonate formed under fluid-buffered conditions. In this way variations in
461 fluid buffered vs. sediment-buffered diagenesis can produce stratigraphic variability in bulk
462 sediment chemistry that is analogous to mixing between two different carbonate sources;
463 however, in this case the two ‘sources’ simply reflect the same primary carbonate sediment
464 recrystallized and/or neomorphosed under different diagenetic conditions (fluid-buffered vs.
465 sediment-buffered).

466 In contrast to the large stratigraphic variability observed in bulk sediment mineralogy and
467 $\delta^{44}\text{Ca}$ values, measured $\delta^{26}\text{Mg}$ values at all sites show little coherent stratigraphic variability
468 and, with few exceptions, fall within a relatively narrow range ($-2.8 \pm 0.5\text{‰}$; Figure 2).
469 Although the offset from seawater ($\sim 2\text{‰}$) is similar to empirical estimates of fractionation
470 factors for Mg-calcite from laboratory experiments at 20-30 °C (65, 66), the lack of variability
471 in bulk sediment $\delta^{26}\text{Mg}$ values is surprising as $\delta^{26}\text{Mg}$ values in bulk carbonate sediments are
472 relatively susceptible to diagenetic alteration – i.e. the low Mg content of the bulk sediment
473 means that diagenesis almost always occurs under fluid-buffered conditions with respect
474 sediment Mg (23). Previous studies have shown that recrystallization of biogenic calcite in
475 deep-sea sediments is associated with greater fractionation of Mg isotopes (i.e. $\alpha_{\text{xtal-calcite}}^{26/24}$
476 ~ 0.9950 ; (23)) and low $\delta^{26}\text{Mg}$ carbonates (down to a $\delta^{26}\text{Mg}$ value of -3.91‰) have been
477 measured in shallow water calcites from the Marion Plateau (21). Although we do not have a
478 definitive explanation for the absence of calcites with $\delta^{26}\text{Mg}$ values $< -3.5\text{‰}$ in the Bahamas
479 or Site 1131 the most straightforward explanation is that this carbonate, if present, is
480 swamped in bulk samples by the Mg in high-Mg calcite (in bank-top sediments) or dolomite
481 (in diagenetically stabilized carbonate sediments). Thus, the lack of stratigraphic variability
482 in bulk sediment Mg isotopes can be attributed to very similar Mg isotope fractionation
483 factors for both high-Mg calcite and dolomite (i.e. $\alpha_{\text{Mg-calcite}}^{26/24} \sim \alpha_{\text{dolomite}}^{26/24}$). This explains why
484 neomorphism of high-Mg calcite and aragonite to dolomite under fluid-buffered conditions
485 leads to very little change in bulk sediment $\delta^{26}\text{Mg}$ values in spite of major changes in
486 mineralogy and bulk sediment chemistry (i.e. $\delta^{44}\text{Ca}$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ values).

487

488 4.2 Fluid-buffered early marine diagenesis and bulk sediment $\delta^{44}\text{Ca}$ values:

489 A surprising result of this study is the extent to which bulk sediment $\delta^{44}\text{Ca}$ values in
490 shallow-water carbonate sediments appear to be affected by fluid-buffered early marine
491 diagenesis. There are at least two processes likely to lead to early diagenetic recrystallization

492 and neomorphism under fluid-buffered conditions for Ca; 1) a reduction in sedimentation rate
493 or depositional hiatus that keeps shallow sediments at or near the seafloor for prolonged
494 periods of time, and 2) fluid flow in shallow sediments driven by various external processes
495 (differences in hydraulic head, compensation for freshwater flow, changes in eustatic sea-
496 level, geothermal heating, density gradients due to evaporation, etc.). Both appear to play a
497 role in determining bulk sediment $\delta^{44}\text{Ca}$ values in the Bahamas. For example, the effects of
498 reduced sedimentation rate can be seen in the elevated $\delta^{44}\text{Ca}$ values (up to -0.6%) in partly
499 dolomitized sediments in Clino below a prominent marine hardground at ~ 536 meters. The
500 hardground coincides with the late Miocene to early Pliocene and is interpreted to have
501 developed from prolonged exposure in response to a decline in sediment supply from the
502 platform (67).

503 The role of fluid flow in maintaining fluid-buffered diagenetic conditions in shallow
504 marine sediments is poorly quantified, though the role of fluid flow in the early marine
505 diagenetic alteration of shallow water carbonate sediments is widely recognized. For
506 example, almost all models (68, 69) of early dolomitization include a source of fluid flow to
507 supply the necessary Mg to turn calcium carbonate into dolomite (a *minimum* of 100 liters of
508 modern seawater is required to transform 1 kg of CaCO_3 into an equivalent number of moles
509 of $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$) but there are only a handful of observations of large-scale active fluid flow
510 in modern shallow-water sedimentary systems. Fortunately, most of these observations come
511 from studies of the Bahamas as part of ODP Leg 166 and the Bahamas Drilling Project (36,
512 51, 70). These studies indicate rates of lateral fluid flow ranging from 5 to 10 cm/yr for
513 sediments on the Bahamas slope (ODP Site 1009) from depth profiles of pore-fluid chemistry
514 ($^{234}\text{U}/^{238}\text{U}$ and $[\text{Cl}^-]$) and temperature. Depth profiles of pore-fluid $[\text{Cl}^-]$ at sites 1003 and
515 1007 are similar to those studied by Henderson et al. (70); constant seawater-like values in the
516 upper 20-30 m followed by a linear increase down to 100 to 200 meters (Table S1).
517 Temperature profiles at Sites 1007 and 1003 are also similar to those observed at other sites
518 on Leg 166 (50) and consistent with significant fluid flow in the upper tens of meters of the
519 sediment column; geotherms in the upper 30-80 meters of the sediment are lower (Site 1007)
520 or non-linear (Site 1003) when compared to geotherms deeper in the sediment column. As a
521 result, though we do not have direct measurements of subsurface fluid flow at Sites 1003 and
522 1007, the pore-fluid chemistry and sediment temperature profiles are consistent with a zone of
523 rapid fluid flow (5-10 cm/yr in the horizontal) in the upper ~ 25 m of the sediment column at
524 both sites. Given the potential for additional sources or focusing of fluid flow on the platform
525 top and margin (e.g. Clino, Unda, and LBB) these rates are likely minimum estimates for
526 these sites. Although the exact mechanism behind the fluid flow observed in shallow
527 sediments from sites on the continental slope in the Bahamas remains uncertain, numerical
528 models indicate that the rates of fluid flow within a carbonate platform on the order of cm/yr
529 can be achieved through multiple means. Examples include geothermal convection, glacial-
530 eustatic variations in sea-level, interactions between seawater and meteoric groundwater, and
531 brine reflux (71-74).

532 Given the high rates of lateral fluid flow in the upper 25 meters of the sediment column at
533 Sites 1003 and 1007 it is surprising that at both sites the $\delta^{44}\text{Ca}$ value of the pore-fluid declines
534 with depth in this interval (Figure 5B). We attribute this decline to a longer path-length (and
535 hence longer residence time) for fluids flowing laterally at greater depths in the sediment
536 column leading to more Ca isotopic exchange between the pore-fluid and sediment due to
537 recrystallization and neomorphism. To explore this hypothesis we constructed a simple

538 model for this process which assumes that the observed $\delta^{44}\text{Ca}$ profiles of the pore-fluid
 539 reflects the local balance between lateral fluid flow (V in cm/yr) and recrystallization and/or
 540 neomorphism:
 541

$$542 \quad \frac{d(\delta^{44}\text{Ca}_{f-out} \cdot M_{f-out}^{Ca})}{dt} = V \cdot (\delta^{44}\text{Ca}_{f-in} \cdot M_{f-in}^{Ca} - \delta^{44}\text{Ca}_{f-out} \cdot M_{f-out}^{Ca}) - \quad (1)$$

$$543 \quad R_p \cdot M_{sed}^{Ca} \cdot (\delta^{44}\text{Ca}_{f-out} + \varepsilon_{xtal}^{44}) + R_d \cdot M_{sed}^{Ca} \cdot \delta^{44}\text{Ca}_{sed}$$

544
 545 where $\delta^{44}\text{Ca}_{f-in/out}$ is the Ca isotopic composition of the incoming/outgoing fluid, $M_{f-in/out}^{Ca}$
 546 is the mass of Ca in the incoming/outgoing fluid (in mol), M_{sed}^{Ca} is the mass of Ca in the
 547 carbonate sediment, $\varepsilon_{xtal}^{44} = (\alpha_{xtal-calcite}^{44/40} - 1) \cdot 10^3$ is the Ca isotopic fractionation factor
 548 associated with recrystallization and neomorphism, $R_{p,d}$ is the rate of mineral dissolution and
 549 precipitation associated with recrystallization and neomorphism (in %/Myr), and $\delta^{44}\text{Ca}_{sed}$ is
 550 the Ca isotopic composition of the bulk sediment. To simplify this equation further we make

551 two additional assumptions: 1) local isotopic steady-state (i.e. $\frac{d(\delta^{44}\text{Ca}_{fluid} \times M_{fluid}^{Ca})}{dt} = 0$) and 2)
 552 the concentration of Ca is equal to that of seawater and does not change along the path of
 553 fluid flow ($M_{f-in}^{Ca} = M_{f-out}^{Ca} = M_{seawater}^{Ca}$ and $R_p = R_d$). The first assumption is reasonable
 554 given the relatively short residence times of fluids in the upper 25 meters (at most 4-8 kyr for
 555 a flow rate of 5-10 cm/yr and a continental slope dip of 3.5°) and the proposed timing of the
 556 current fluid flow regime (Holocene flooding of the platform top at ~ 6 kyr; (75)). The second
 557 assumption is based on observations that the concentration of Ca in the pore-fluid at both sites
 558 1003 and 1007 remains at the seawater value throughout the interval from 0 to >25 m. This
 559 reduces equation (1) to:
 560

$$561 \quad \delta^{44}\text{Ca}_{f-out} = \frac{V \cdot \delta^{44}\text{Ca}_{f-in} \cdot M_{seawater}^{Ca} + R_p \cdot M_{sed}^{Ca} \cdot (\delta^{44}\text{Ca}_{sed} - \varepsilon_{xtal}^{44})}{V \cdot M_{seawater}^{Ca} + R_p \cdot M_{sed}^{Ca}} \quad (2)$$

562
 563 Equation (2) can then be solved iteratively for each box along the path length given rates of
 564 fluid flow (V) and recrystallization/neomorphism (R_p) and given the boundary condition
 565 $\delta^{44}\text{Ca}_{f-in} = \delta^{44}\text{Ca}_{seawater}$ at the sediment-water interface. The path length (i.e. number of
 566 boxes) for each depth in the sediment column is calculated assuming a 3.5° dip of the
 567 continental slope. For rates of lateral fluid flow of 10 cm/yr, fitting the pore-fluid profiles of
 568 $\delta^{44}\text{Ca}$ values at both Sites 1003 and 1007 (Figure 4C) requires rates of recrystallization and/or
 569 neomorphism on the order of 10%/Myr. These rates are on the high end of estimates based on
 570 recrystallization in deep-sea carbonate sediments ($\sim 1\%$ /Myr; (10, 22)) but are consistent with
 571 the million-year timescales estimated for diagenetic alteration and dolomitization of platform
 572 carbonates in the Bahamas using $^{87}\text{Sr}/^{86}\text{Sr}$ isotopes (37, 56).
 573

574 4.3 Sediment-buffered early marine diagenesis and bulk sediment $\delta^{44}\text{Ca}$ values:

575 Perhaps less surprising is the Ca isotope evidence for sediment-buffered recrystallization
 576 and neomorphism from sites on the slope in the Bahamas (Sites 1003 and 1007) and Site 1131
 577 (Australia). We identify bulk carbonate sediments as having undergone sediment-buffered
 578 diagenesis with respect to Ca when they are composed predominately of low-Mg calcite and
 579 dolomite and yet are characterized by $\delta^{44}\text{Ca}$ values that approach or equal surface-sediment

580 $\delta^{44}\text{Ca}$ values and have high Sr/Ca ratios (i.e. 3-7 mmol/mol). Note that in the Bahamas this
581 implies sediment $\delta^{44}\text{Ca}$ values of -1.2 to -1.5‰ for sediment-buffered diagenesis of aragonite,
582 whereas at Site 1131 sediment-buffered diagenesis of high-Mg calcite predicts a $\delta^{44}\text{Ca}$ value
583 closer to -1‰ (Figure 2). At Sites 1003 and 1007, sediment-buffered diagenesis is one
584 potential explanation for the return to lower $\delta^{44}\text{Ca}$ values (and higher Sr/Ca ratios) below 200-
585 300 meters, though increasing contributions from low $\delta^{44}\text{Ca}$ pelagic sources also likely plays
586 a role. At Site 1131 sediment-buffered diagenesis appears to dominate the entire sediment
587 column. In contrast to sites in the Bahamas, pore-fluid Cl^- profiles at Site 1131 increase
588 linearly with depth from the sediment-water interface, consistent with (present-day) diffusion-
589 limited transport and persistent sediment-buffered diagenetic conditions at this site. However,
590 it is important to note that even though diagenetic alteration of these sediments is sediment-
591 buffered with respect to Ca, it is still likely to be fluid-buffered with respect to Mg and many
592 other trace elements.

593

594 *4.4 Using paired Mg and Ca isotopes to fingerprint dolomitization:*

595 The presence of large volumes of dolomitized carbonate sediments in the geologic record
596 has long vexed geologists and geochemists as it is a rare mineral in modern and recent
597 shallow-water environments and difficult to precipitate in the laboratory at low temperatures
598 (68, 69, 76). One of the few things that is agreed upon with regard to massive sedimentary
599 dolomites is that they require a large source of Mg that can be supplied rapidly on million-
600 year timescales. One possibility is diffusion from seawater (28, 77). Another is Mg supplied
601 by fluid flow in sedimentary pore-fluids (71, 73). Although not mutually exclusive, these two
602 modes of Mg supply predict distinct signatures for the $\delta^{26}\text{Mg}$ and $\delta^{44}\text{Ca}$ value of the
603 precipitated dolomite. For example, dolomitizing systems where the supply Mg occurs
604 exclusively by diffusion will tend to result in Rayleigh-type distillation of pore-fluid Mg
605 leading to dolomites with heavy and variable $\delta^{26}\text{Mg}$ values (28). Under these conditions the
606 Ca that ends up in the dolomite will largely consist of Ca from any precursor carbonate
607 sediment plus a smaller amount from the dolomitizing fluid. We term this sediment-buffered
608 or 'closed system' dolomitization as it will be accompanied by little change in the bulk
609 sediment $\delta^{44}\text{Ca}$ value. Alternatively, in systems where Mg is supplied by sedimentary fluid
610 flow, dolomitization is much more likely to occur under fluid-buffered or 'open system'
611 conditions for both sediment Ca and Mg. In this case dolomite $\delta^{26}\text{Mg}$ values will be low and
612 homogeneous, reflecting precipitation from an unaltered dolomitizing fluid with a
613 fractionation factor ($\alpha_{\text{dolomite}}^{26/24}$) of ~ 0.9980 (21, 54). Sediment $\delta^{44}\text{Ca}$ values should similarly
614 reflect fluid-buffered diagenesis and will approach the value predicted for calcite precipitation
615 at these slow rates (i.e. $\alpha_{\text{dolomite}}^{44/40} \sim 0.9998$ to 1.0000 ; (22, 26, 55)). Assuming the fluid is
616 relatively unaltered seawater ($\delta^{44}\text{Ca} = 0\text{‰}$), this would result in dolomites enriched in ^{44}Ca .

617 The magnitude of Mg and Ca isotope fractionation ($\alpha_{\text{dolomite}}^{26/24}$ and $\alpha_{\text{dolomite}}^{44/40}$) associated with
618 dolomite precipitation at low temperatures (5-35 °C) is one of the main sources of uncertainty
619 in using paired measurements of Mg and Ca isotopes to fingerprint the style of dolomitization
620 (sediment-buffered vs. fluid-buffered). For Mg isotopes, previous studies on deep-sea
621 sediment pore-fluid systems actively precipitating authigenic dolomite indicate $\alpha_{\text{dolomite}}^{26/24} \sim$
622 0.9973 - 0.9980 (21, 54). Significantly smaller Mg isotope fractionation factors ($\alpha_{\text{dolomite}}^{26/24} >$
623 0.9999) have been inferred from studies of modern sabka dolomites (25, 78), though sabhka
624 dolomites slightly older in age (Pleistocene) suggest $\alpha_{\text{dolomite}}^{26/24} \sim 0.9987$ to 0.9984 . We suspect

625 that much of this variability is due to later re-setting under fluid-buffered vs. sediment-
626 buffered conditions, though we note that characterizing Mg isotope fractionation in sabka-like
627 dolomitizing systems is significantly more complicated due the presence of multiple Mg-
628 bearing minerals (carbonates, evaporites and clay minerals). Consideration of the pore-fluid
629 $\delta^{26}\text{Mg}$ and Mg/Cl profiles from Site 1003 results in an estimate for $\alpha_{\text{dolomite}}^{26/24}$ of 0.9980
630 assuming the changes can be modeled as Rayleigh fractionation (Figure 4D). Given the
631 greater complexity associated with reconstructing Mg isotope fractionation in heterogeneous
632 deep-sea sediments (54) and a weak temperature dependence ($\sim 1\%$ decline in $\alpha_{\text{dolomite}}^{26/24}$
633 between 0 and 250°C ; (79)), the estimate from 1003 of $\alpha_{\text{dolomite}}^{26/24} \sim 0.9980$ is preferred for
634 dolomitization of shallow-water carbonate sediments. For Ca isotopes the determination of
635 $\alpha^{44/40}$ for dolomite precipitation is more difficult to discern from sediment pore-fluid systems
636 because it occurs in conjunction with the precipitation of diagenetic calcite. Pore-fluid $\delta^{44}\text{Ca}$
637 profiles from Sites 1003 and 1007 both indicate $\alpha_{\text{dolomite}}^{44/40} \sim 0.9998\text{-}1.0000$ for all forms of
638 carbonate diagenesis (recrystallization, neomorphism, and dolomitization; Figure 4A,B). In
639 addition, the dolomite leach experiments showed no resolvable difference in bulk sediment
640 $\delta^{44}\text{Ca}$ values as a function of dolomite content (in spite of an overall range in $\delta^{44}\text{Ca}$ values
641 between samples of $\sim 0.7\%$; Figure 3), suggesting that both the calcite and dolomite
642 endmembers have similar $\delta^{44}\text{Ca}$ values (i.e. $\alpha_{\text{dolomite}}^{44/40} \sim \alpha_{\text{xtal-calcite}}^{44/40}$). Consequently, we
643 tentatively assume that $\alpha_{\text{dolomite}}^{44/40} \sim 0.9998\text{-}1.0000$ for the formation of low-temperature
644 dolomite, in agreement with (80).

645 Both the dolomite leach experiments and bulk samples from Clino, Unda, and the LBB
646 show some co-variation between $\delta^{26}\text{Mg}$ and $\delta^{44}\text{Ca}$ values with higher $\delta^{26}\text{Mg}$ values generally
647 associated with lower $\delta^{44}\text{Ca}$ values (Figure 5 – inset; Figure 6). Overall, however, the
648 measured $\delta^{26}\text{Mg}$ values of the Bahamas dolomites are low (-2.5% to -3%) and have a
649 relatively narrow distribution when compared to the range in $\delta^{26}\text{Mg}$ values observed in
650 authigenic dolomites from the Miocene Monterey Fm. (Figure 5; (28)). Sediment $\delta^{44}\text{Ca}$
651 values span a range of almost 1% , from -1.3 to -0.35% , a range that is similar to that
652 observed in the dolomites from the Monterey Fm. However, the majority of the dolomite
653 samples from the Bahamas have $\delta^{44}\text{Ca}$ values higher than -0.7% , whereas in the Monterey
654 Fm most samples have $\delta^{44}\text{Ca}$ values lower than -0.7% . Given these observations - low and
655 homogeneous $\delta^{26}\text{Mg}$ value and high $\delta^{44}\text{Ca}$ values - the paired Mg and Ca isotope
656 measurements indicate that dolomitization in the Bahamas was largely fluid-buffered. This
657 conclusion agrees with previous studies that have argued based on sediment $\delta^{18}\text{O}$ values and
658 petrography that the fluid responsible for dolomitization at Clino/Unda and the LBB was
659 relatively unaltered seawater (52, 81).

660 But do the dolomites from Clino, Unda, and the LBB represent a fully fluid-buffered
661 endmember? For Mg isotopes, the average value of the Bahamas dolomites is $-2.84 \pm 0.26\%$
662 (2σ ; $N = 41$), similar to platform dolomites measured in a previous study ($\delta^{26}\text{Mg} = -2.68 \pm$
663 0.13% 2σ ; $N = 7$, (21)) and minimum $\delta^{26}\text{Mg}$ values measured in the authigenic dolomites of
664 the Monterey Fm. (Figure 5). This is almost exactly the expected offset given seawater as the
665 dolomitizing fluid with $\delta^{26}\text{Mg}$ value of -0.82% ($\delta^{26}\text{Mg}_{\text{fluid}} = \delta^{26}\text{Mg}_{\text{seawater}}$) and $\alpha_{\text{dolomite}}^{26/24} =$
666 0.9980 . For Ca isotopes the situation is less clear as the dolomite $\delta^{44}\text{Ca}$ values span a $\sim 1\%$
667 range. However, even the most ^{44}Ca -enriched dolomites are $\sim 0.2\%$ lower than the $\delta^{44}\text{Ca}$
668 value expected for $\alpha_{\text{dolomite}}^{44/40} = 0.9998$ to 1.0000 and seawater as the dolomitizing fluid ($\delta^{44}\text{Ca}$
669 $= 0\%$). This result suggests that either $\alpha_{\text{dolomite}}^{44/40} < 0.9998$ for low-temperature dolomite or that

670 dolomitization occurred in conditions that were not fully fluid-buffered for sediment Ca (i.e.
671 $\delta^{44}\text{Ca}_{\text{fluid}} < \delta^{44}\text{Ca}_{\text{seawater}}$). Observations of $\delta^{44}\text{Ca}$ values lower than seawater (0‰) in
672 sedimentary pore-fluids within the zone of active fluid flow at Sites 1003 and 1007 (Figure 4)
673 is consistent with the latter hypothesis.

674 The presence of dolomite leachates from Clino with $\delta^{44}\text{Ca}$ values as low as -1.3‰ and the
675 mild co-variation between sediment $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$ values (Figure 5 – inset; Figure 6)
676 suggest that dolomitization in the Bahamas can also be sediment-buffered. Mixing of fluid-
677 buffered and sediment-buffered dolomites has been proposed as an explanation for the co-
678 variation in $\delta^{44}\text{Ca}$ and $\delta^{26}\text{Mg}$ values in the Monterey Fm. (Figure 5). In that case the
679 difference between fluid-buffered and sediment-buffered conditions is related to the depth of
680 dolomite precipitation within the shallow sediment column; dolomite precipitated near the
681 sediment-water interface has a fluid-buffered composition whereas dolomite precipitated
682 deeper in the sediment column is sediment-buffered (28). In contrast to the Bahamas,
683 sediment-buffered conditions appear to dominate in the Monterey Fm. as only a handful of the
684 samples have $\delta^{44}\text{Ca}$ values $> -0.7\text{‰}$ and $\delta^{26}\text{Mg}$ values $< -2.6\text{‰}$. This result is perhaps not
685 surprising given the importance of fluid flow in shallow-water carbonate sediments but
686 emphasizes the fundamental role it plays in determining fluid-buffered vs. sediment-buffered
687 conditions during carbonate diagenesis.

688 In summary, paired measurements of Mg and Ca isotopes in marine dolomites can be used
689 to fingerprint whether dolomitization occurred in a diagenetic environment that was fluid-
690 buffered or sediment-buffered with respect to Mg and Ca. Dolomites that are fluid-buffered
691 are predicted to have relatively uniform $\delta^{26}\text{Mg}$ values that are $\sim 2\text{‰}$ lower than seawater and
692 $\delta^{44}\text{Ca}$ values that approach the $\delta^{44}\text{Ca}$ value of seawater (0‰). In contrast dolomites that
693 precipitate under sediment-buffered conditions are predicted to have variable and high $\delta^{26}\text{Mg}$
694 values due to distillation of Mg in the dolomitizing fluid and $\delta^{44}\text{Ca}$ values that are inherited
695 from the precursor carbonate sediment (-1 to -1.5‰). Using this fingerprint, we identify the
696 massive shallow burial dolomites observed in the Bahamas at Clino, Unda, and the LBB as
697 originating in a diagenetic environment that was predominantly (but not exclusively) fluid-
698 buffered with respect to sediment Mg and Ca. This result complements observations Mg and
699 Ca isotopes in authigenic dolomites of the Monterey Fm. a very different dolomite-forming
700 environment that nevertheless has a Mg and Ca isotope fingerprint that can be interpreted
701 using the same diagenetic (fluid-buffered vs. sediment buffered) framework and isotopic
702 fractionation factors ($\alpha_{\text{dolomite}}^{26/24}$ and $\alpha_{\text{dolomite}}^{44/40}$). Applied to ancient dolomites this approach could
703 yield estimates of paleo-seawater $\delta^{26}\text{Mg}$ and $\delta^{44}\text{Ca}$ values (most easily through the
704 identification of the fluid-buffered endmembers) and will aid in the more general
705 characterization of the environmental information stored in the geochemistry of dolomitized
706 carbonate sediments.

707

708 *4.5 Mineralogy, early marine diagenesis, and the geochemistry of shallow-water sedimentary*
709 *carbonates:*

710

711 Marine carbonate sediments serve as both direct (through the burial of the major elements
712 Ca, Mg, and C), and indirect (as archives of information on temperature and seawater
713 chemistry) records of the global carbon cycle over Earth history. Prior to the Mesozoic, it is
714 thought that most carbonate sediments were deposited in shallow-water platform, shelf, and
715 slope environments (3, 82-84). Although these sediments are now mostly composed of calcite

716 and dolomite there is substantial geochemical and petrographic (85) evidence that the primary
717 carbonate minerals deposited included metastable forms such as aragonite and high-Mg
718 calcite. While it is widely recognized that all carbonate sediments undergo diagenesis (11, 12,
719 53, 86-88), the extent to which the bulk and trace element geochemistry of the primary
720 sediment is preserved during the transformation from unlithified sediment into rock is poorly
721 known and widely debated (5, 59, 89-91). The data presented here indicate that paired
722 measurements of Mg and Ca isotopes can be used to identify mineralogical changes
723 (aragonite to calcite/dolomite) and characterize diagenetic environments (fluid-buffered vs.
724 sediment-buffered) in ancient carbonate sediments. When applied to Neogene carbonate
725 sediments from the platform, margin, and slope of the Great and Little Bahama Banks, paired
726 measurements of Mg and Ca isotopes provide clear evidence of the role of both mineralogy
727 and early marine diagenesis in determining the chemical composition and its stratigraphic
728 expression in shallow-water carbonate sediments preserved in the rock record.

729 First, bulk sediment and pore-fluid chemistry from sites throughout the Bahamas indicate
730 that active fluid-buffered carbonate diagenesis occurs in shallow sediments from the platform-
731 top down the slope to at least ~650 m water depth. This fluid-buffered early marine diagenesis
732 appears to be associated with the conversion of aragonite and high-Mg calcite to low-Mg
733 calcite and dolomite and results in extensive chemical exchange between sediment and the
734 diagenetic fluid. In particular, the large increases in bulk sediment $\delta^{44}\text{Ca}$ values we observe
735 (up to 1‰ within Clino) require almost full recrystallization or neomorphism of the carbonate
736 sediment under diagenetic conditions that would lead to the wholesale resetting of bulk
737 sediment chemistry ($\delta^{44}\text{Ca}$, $\delta^{13}\text{C}$, $\delta^{26}\text{Mg}$, $\delta^{18}\text{O}$, Mg/Ca, Sr/Ca, $\delta^{238/235}\text{U}$, $\delta^7\text{Li}$, $\delta^{11}\text{B}$, etc.).
738 Although fluid-buffered carbonate diagenesis is often associated with dolomitization, it can
739 also occur as neomorphism of aragonite to calcite or simply calcite recrystallization (Site
740 1003, 1007 in Figure 2 and dolomite leachates in Figure 3).

741 Second, given that early marine diagenesis can occur under either fluid-buffered or
742 sediment-buffered conditions, temporal changes in the style of diagenesis can produce
743 stratigraphically coherent variability in major and minor element chemistry that can be
744 reproduced regionally and perhaps globally. For example, at Sites 1003 and 1007, the depth
745 profile in bulk sediment $\delta^{44}\text{Ca}$ values indicates a maximum near 200 mbsf with $\delta^{44}\text{Ca}$ values
746 declining both above and below this interval. In addition, the maxima in bulk sediment $\delta^{44}\text{Ca}$
747 occurs >100 m below the zone of present-day active fluid flow. One explanation for these
748 observations is that rates of fluid flow and the extent of fluid-buffered diagenetic alteration
749 have changed systematically with time such that when the sediments near 200 m were initially
750 deposited, rates and/or the depth of fluid flow and the extent of fluid-buffered diagenetic
751 alteration in the upper meters to 10's of meters of the sediment column were at a maximum
752 (and much higher than today). Lower rates of fluid flow both before and after would be
753 associated with increasingly sediment-buffered diagenetic conditions the net result being a
754 pronounced positive excursion in bulk sediment $\delta^{44}\text{Ca}$ values centered around the time of
755 maximum fluid flow (and fluid-buffered diagenesis). Although the drivers of sedimentary
756 fluid flow in the Bahamas remain unknown, glacial-eustatic sea-level changes are often cited
757 as a likely source of sedimentary fluid flow in carbonate platforms (52, 71) and offer a
758 tantalizing link between global processes (changes in Earth's ice volume) and variations in the
759 local early marine diagenesis of carbonate platforms. As the maxima in bulk sediment $\delta^{44}\text{Ca}$
760 values at Sites 1003 and 1007 occurs between 200-300 m in sediments that are mid-Pliocene
761 in age, we speculate that the extent of fluid-buffered diagenesis on the Bahamas platform and

762 slope may be related to the frequency (and not the magnitude) of variations in glacio-eustatic
763 sea-level, though other factors such as changes in sedimentation rate must also play a role.

764

765 *4.5.1 Implications for stratigraphic variations in shallow-water $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values over the*
766 *Neogene:*

767

768 The conclusion that the stratigraphic variability in bulk sediment $\delta^{44}\text{Ca}$ values in the
769 Bahamas is related in large part to the extent of fluid-buffered vs. sediment-buffered
770 diagenetic alteration of platform aragonite has direct implications for the interpretation of the
771 observed stratigraphic variability in bulk sediment $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and other
772 geochemical proxies (e.g. Sr/Ca, Figure 7A). In a previous study, Swart (5) pointed out that
773 carbonate sediments from platform margins around the world (Bahamas, Australia, and
774 Maldives) all show a similar increase in bulk sediment $\delta^{13}\text{C}$ values over the Neogene that are
775 de-coupled from changes in the global carbon cycle. Swart (5) argued that the increases in
776 shallow water carbonate $\delta^{13}\text{C}$ values could be explained as a mixture of a pelagic source with
777 a $\delta^{13}\text{C}$ value of $\sim 0\text{‰}$ and a platform (aragonite) source with a $\delta^{13}\text{C}$ value of $+4\text{--}5\text{‰}$ with
778 increasing contributions from the platform source over the Neogene. Our results do not
779 contradict this hypothesis but suggest that a significant fraction of stratigraphic increase in
780 bulk sediment $\delta^{13}\text{C}$ values could be explained by changes in the extent of diagenetic alteration
781 of aragonite to calcite under fluid-buffered conditions with relatively unmodified seawater
782 ($\delta^{13}\text{C} \sim 0\text{‰}$, $\delta^{18}\text{O} \sim 0\text{‰}$, temperature = 12-16 °C) in the uppermost 10's of meters of the
783 sediment column (e.g. Figure 4). The identification of fluid-buffered diagenesis – in particular
784 spatial and temporal variations in the extent of fluid-buffered vs. sediment-buffered
785 diagenesis - as an alternative mechanism for generating stratigraphic variability in the
786 geochemistry of bulk carbonate sediments is significant because this phenomenon is likely
787 ubiquitous in shallow water carbonate sediments throughout the geologic record.

788 Our interpretation that sediment-buffered diagenesis dominates below 500-800 m at Sites
789 1003 and 1007 and over the entirety of Site 1131 predicts that the $\delta^{13}\text{C}$ values of these
790 sediments should reflect the primary precipitates (aragonite and high-Mg calcite for
791 1003/1007 and 1131, respectively). At Sites 1003 and 1007, the $\delta^{13}\text{C}$ values of these
792 sediment-buffered neomorphosed aragonites are only between $+2$ to $+3\text{‰}$, or $\sim 1\text{--}2\text{‰}$ more
793 negative than the $\delta^{13}\text{C}$ of modern bank-top sediment ((93); Table S1). This could be due in
794 part to greater contributions of pelagic sources to Miocene sedimentation at these sites, but it
795 may also be due to an increase in the $\delta^{13}\text{C}$ value of platform aragonite between the Miocene
796 and the Pliocene. Bulk sediment $\delta^{13}\text{C}$ values at Site 1131 occupy a narrow range from $+1$ to
797 $+2\text{‰}$ but span only the Pliocene and Pleistocene.

798 The approximately linear co-variation observed between bulk sediment $\delta^{13}\text{C}$ and $\delta^{44}\text{Ca}$
799 values in Pliocene and Pleistocene sediments from the Bahamas (Figure 7C) is strikingly
800 similar to the co-variation observed in some ancient carbon isotope excursions (CIE's)
801 preserved in carbonate sediments, where sedimentary successions with extreme (positive and
802 negative) excursions in $\delta^{13}\text{C}$ values exhibit large and stratigraphically coherent variations in
803 bulk sediment $\delta^{44}\text{Ca}$ values (42, 59, 94). In these examples, Hirnantian limestones from the
804 Monitor Range in N. America, Silurian limestones from the Prague Basin (Czech Republic),
805 and Ediacaran limestones and dolomites from the Wonoka formation in Australia,
806 stratigraphic intervals with low $\delta^{44}\text{Ca}$ values are consistent with primary aragonite

807 diagenetically altered to calcite under sediment-buffered conditions. Sediment Sr/Ca ratios
808 are generally elevated but variable when $\delta^{44}\text{Ca}$ values are low, suggesting a mixture of
809 sediment- and fluid-buffered conditions for this trace element.

810 The pairing of extreme $\delta^{13}\text{C}$ values (positive and negative) with independent geochemical
811 indicators of primary aragonite (low $\delta^{44}\text{Ca}$ values and high Sr/Ca ratios) suggest that $\delta^{13}\text{C}$
812 values are both primary (i.e. neomorphosed from aragonite to calcite under sediment-buffered
813 conditions) and likely to be derived from the local DIC reservoir – whether that be on the
814 platform-top environment or in an epicontinental sea. These environment, though in contact
815 with the open ocean, tend to be characterized by shallow water depths (<10 to 100's of m)
816 over large areas (1000's of km^2) and long residence times for surface waters (100's of days;
817 (95, 96)). These factors and others are thought to contribute to platform-top $\delta^{13}\text{C}$ values of
818 dissolved inorganic carbon (DIC) from the modern-day GBB that are up to 2‰ heavier than
819 surface seawater in the open ocean. The $\delta^{13}\text{C}$ values of +4‰ to +5‰ commonly observed on
820 the GBB and other shallow-water platform environments (6, 14) are a consequence of this
821 local enrichment in the $\delta^{13}\text{C}$ of DIC together with mineral-specific effects (aragonite is ~1.5
822 to 2‰ enriched in $\delta^{13}\text{C}$ compared to calcite; (97)). Shallow water environments in the deep
823 geological past are also settings where anomalously high or low $\delta^{13}\text{C}$ values of seawater DIC
824 have been inferred from measurements of $\delta^{13}\text{C}$ in sedimentary organic matter and carbonate
825 sediments. Promising mechanisms for generating local variability in shallow water $\delta^{13}\text{C}$
826 values of DIC include intense photosynthesis and associated hypercalcification(5, 42, 94, 98,
827 99), methanogenesis accompanied by methane escape (100), kinetic isotope effects associated
828 with $\text{CO}_{2(\text{g})}$ hydration coupled to intense local primary production (101, 102), and respiration
829 of terrestrial organic matter (103)). As a result, one possible interpretation of the co-variation
830 between large CIE's and negative excursions in sediment $\delta^{44}\text{Ca}$ values is that they largely
831 reflect changes in the $\delta^{13}\text{C}$ of DIC in shallow-water aragonite-producing environments (and
832 the extent of preservation of that aragonite on platform margins and slopes) and not changes
833 in the $\delta^{13}\text{C}$ of global seawater DIC.

834

835 *4.5.3 Implications for the preservation of minor and trace elements proxies in ancient*
836 *shallow-water carbonate sediments:*

837

838 Early marine diagenesis that is capable of both resetting the chemical and isotopic
839 composition of bulk carbonate sediments on million-year timescales and changing from fluid-
840 buffered to sediment-buffered within a stratigraphic column poses a significant challenge for
841 the application of many minor and trace element proxies to ancient carbonate sediments.
842 Given the relative diagenetic stability of bulk sediment $\delta^{44}\text{Ca}$ and $\delta^{13}\text{C}$ values, the observation
843 that variations in fluid-buffered early marine diagenesis can produce large (~1‰ and 4‰,
844 respectively) changes in bulk sediment $\delta^{44}\text{Ca}$ and $\delta^{13}\text{C}$ values suggests that all minor and
845 trace element proxies in fluid-buffered carbonate sediments will reflect the chemistry of the
846 early diagenetic fluid. However, our results also provide a tool for identifying carbonate
847 sediments lithified under largely sediment-buffered diagenetic conditions where minor and
848 trace elements in the primary carbonate sediment are more likely to be preserved. Although an
849 exhaustive review of carbonate-bound geochemical proxies is also beyond the scope of this
850 study, there are at least three factors that will determine the extent to which these proxies are
851 complicated and/or compromised by variations in mineralogy and fluid-buffered vs. sediment-
852 buffered diagenesis.

853 First, as these proxies are by their nature based on minor and trace constituents of
854 sedimentary carbonate minerals they tend to be regarded as susceptible to diagenesis in
855 particular if the abundance of the minor or trace element is high compared to the bulk
856 sediment in early diagenetic fluids. Although this does not guarantee that a proxy will be
857 sensitive to diagenesis due to the potential for offsetting effects associated with partition
858 coefficients and isotopic fractionation factors, it is a key boundary condition in determining
859 proxy behavior during carbonate diagenesis (16, 17). Most trace element proxies should be
860 more sensitive to fluid-buffered diagenetic alteration than major elements like C and Ca. This
861 can be shown for Sr/Ca for depths below 500-800 m at Sites 1003 and 1007; despite bulk
862 sediment $\delta^{44}\text{Ca}$ values that are indistinguishable from surface sediments, Sr/Ca ratios never
863 recover to surface sediment values of ~ 10 mmol/mol. Redox-sensitive trace elements (e.g. U;
864 (19) and I/Ca; (104)) will have the added complication of sensitivity to the oxidation state of
865 the diagenetic fluid. Pore-fluid profiles at Sites 1003 and 1007 (50) as well as fluids in reef
866 and platform interiors (105-107) suggest that reducing conditions prevail even when there is
867 significant fluid flow bringing oxidized bottom-water into the sediment-pore fluid system. As
868 a result, while reducing conditions and preferential addition of U and loss of IO_3^- is expected
869 for carbonate diagenesis under both sediment-buffered and fluid-buffered conditions, our
870 results indicate that it may be particularly severe under fluid-buffered conditions.
871 Observations of elevated $\delta^{44}\text{Ca}$ values and U/Mg+Ca ratios in bulk sediments from the
872 Bahamas are consistent with this prediction (Figure 8A), though we note that the noise of the
873 data suggests that the relationship between major element chemistry and U in the bulk
874 sediment is complex.

875 Second, the isotopic fractionation factors and partition coefficients used in many of the
876 proxies depend on mineralogy. For example, $\delta^7\text{Li}$ values in inorganic aragonite are ~ 8 -10‰
877 depleted compared to calcite precipitated under similar conditions (108). Similarly, the
878 abundance of carbonate-associated sulfate (CAS) in inorganic calcite precipitated from
879 seawater is typically 10,000's of ppm whereas it is substantially lower (1000's of ppm) in
880 inorganic aragonite (109). U partitioning also depends on mineralogy, though in this case U
881 in inorganic aragonite is high (~ 2 ppm) and low in inorganic calcite (< 0.4 ppm; (110)).
882 Although this will not affect the $\delta^{34}\text{S}$ of CAS or $\delta^{238/235}\text{U}$ values directly, it will, through
883 variations in mineralogy and styles of early marine diagenesis (of the kind seen in Site 1003,
884 1007, and Clino), produce stratigraphic variability in CAS or U contents. As minerals with
885 low CAS (aragonite) or U (calcite) will be significantly more susceptible to contamination by
886 later burial diagenesis, authigenic mineral formation, partial dissolution of other phases (111)
887 etc., stratigraphic variability in CAS and U contents may lead to stratigraphic variations in
888 $\delta^{34}\text{S}$ and $\delta^{238/235}\text{U}$ values that are unrelated to global seawater chemistry.

889 Third, to the extent that negative excursions in bulk sediment $\delta^{44}\text{Ca}$ values indicate an
890 increase in the transport and sedimentation of shallow water aragonite (above and beyond
891 changes in fluid-buffered and sediment-buffered diagenesis) we expect that geochemical
892 signals associated with mixing between shallow-water and pelagic environments that may
893 give rise to stratigraphic profiles and co-variation between geochemical proxies that are not
894 related to changes in the global carbon cycle or seawater chemistry. Prior to expansion of
895 pelagic calcification in the Mid-Mesozoic most carbonate sediment is thought to have
896 precipitated in shallow-water platform and marginal marine environments. However, other
897 components of the bulk sediment, in particular sinking organic matter and early diagenetic
898 phases (e.g. pyrite) likely had both shallow-water and pelagic sources with distinct

899 geochemical characteristics (i.e. $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{34}\text{S}_{\text{pyrite}}$ values). Dilution of these pelagic signals
900 by increased delivery of shallow-water carbonate sediment (with bank-top $\delta^{13}\text{C}_{\text{org}}$, $\delta^{13}\text{C}_{\text{carb}}$,
901 $\delta^{34}\text{S}_{\text{CAS}}$, and $\delta^{34}\text{S}_{\text{pyrite}}$ values) may yield co-variation in paired $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ values (112,
902 113) or $\delta^{34}\text{S}_{\text{pyrite}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ values that are also unrelated to changes in the global carbon and
903 sulfur cycles.

904

905 *4.5.4 Mn/Sr ratios as a proxy for diagenetic alteration of major elements*

906

907 The Mn/Sr ratios in carbonate sediments are frequently used as a quantitative indicator of
908 diagenetic alteration with a threshold of ~ 1 -2 typically applied to exclude samples from
909 further consideration (27). The foundation of this diagenetic indicator is that most subsurface
910 (i.e. diagenetic) fluids are low in Sr and high in Mn. As a result, recrystallization,
911 neomorphism, or dolomitization in this fluid will tend to raise the Mn/Sr ratio of the carbonate
912 sediment. Considered in this context, samples from this study do in fact show a positive
913 correlation between Mn/Sr ratio and bulk sediment $\delta^{44}\text{Ca}$ values with higher Mn/Sr ratios
914 associated with heavier $\delta^{44}\text{Ca}$ values (Figure 8B). However, for all the variability in sediment
915 Mn/Sr ratios even the most altered bulk carbonates have Mn/Sr ratios < 1 . In other words, the
916 use of a threshold Mn/Sr ratio of 1 would suggest that diagenetic alteration in the Bahamas
917 sites has been relatively minor in spite of multiple independent lines of evidence that indicate
918 otherwise. Although the correlation between bulk sediment $\delta^{44}\text{Ca}$ values and Mn/Sr ratios
919 (Figure 8B) suggests that this proxy may provide some information on the relative extent of
920 diagenetic alteration, we strongly urge against any use of threshold values of Mn/Sr ratios
921 when trying to determine the potential for diagenetic alteration of major elements (e.g. $\delta^{13}\text{C}$
922 values) in ancient carbonate sediments.

923

924 *4.5.5 Implications for modern $\delta^{44}\text{Ca}_{\text{seawater}}$ mass balance and shelf-basin partitioning of* 925 *global carbonate sediments:*

926

927 Fantle & Tipper (58) compiled a large database of published Ca isotope values taken from
928 the literature and applied a statistical evaluation of the data to deduce average $\delta^{44}\text{Ca}$ values for
929 the major Ca sources and sinks in the Earth's modern exogenic Ca cycle. They concluded
930 from this analysis the $\delta^{44}\text{Ca}$ value of bulk silicate Earth and global rivers is $\sim 0.3\%$ enriched in
931 ^{44}Ca relative to deep-sea carbonate sediments. Rivers are the principle source of Ca to
932 seawater and carbonate sediments are the overwhelming sink. The imbalance of 0.3% could
933 represent non-steady state conditions, however, an equally plausible explanation is that there
934 exists a significantly under-sampled carbonate sink enriched in ^{44}Ca . Results from this study
935 and previous work by Fantle & Higgins (21) and Blättler et al. (28) suggest that this missing
936 sink could be a combination of fluid-buffered diagenetic and authigenic carbonates.
937 Carbonate sediments of these types are underrepresented in the Fantle & Tipper (58)
938 compilation and yet represent potentially globally significant sinks of seawater Ca. The
939 average $\delta^{44}\text{Ca}$ value of samples from platform interiors and margins is -0.90% (Clino, Unda,
940 and LBB; $N = 108$) whereas those from only the platform interior average -0.53% (Unda and
941 LBB; $N = 22$). These $\delta^{44}\text{Ca}$ values are 0.4 - 0.7% enriched in ^{44}Ca relative to the average
942 deep-sea carbonate sink (-1.25%) and 0.1 - 0.4% enriched relative to bulk silicate Earth ($-$
943 0.98% ; (58)). Assuming the modern ocean is near steady-state with respect to Ca isotopes
944 and an average $\delta^{44}\text{Ca}$ value of -0.75% for diagenetically stabilized shallow-water platform

945 carbonates we estimate a ~50/50 partitioning of carbonate burial in shallow-water and deep-
946 sea sediments. This geochemical estimate of present-day shelf to deep partitioning of global
947 carbonate burial is similar to but entirely independent of estimates based on sediment seismic
948 surveys, drill cores, and measurements of modern accumulation rates (114).

949 Our results also provide additional evidence that the $\delta^{44}\text{Ca}$ of seawater on geologic
950 timescales is not governed by changes in the mineralogy of marine carbonate precipitates (the
951 'aragonite seas' and 'calcite seas' of Sandberg (85)). Although sediment-buffered
952 neomorphosed aragonite (low $\delta^{44}\text{Ca}$ values) can be preserved on continental slopes (e.g. Sites
953 1003 and 1007), any Ca isotopic signal of aragonite in the platform margin and interior has
954 been almost completely obliterated; average $\delta^{44}\text{Ca}$ values are heavier than bulk silicate Earth
955 or exactly the opposite of that predicted for an 'aragonite sea' (115). Given the central role of
956 fluid flow in the diagenesis of shallow-water carbonate sediments and its effect on the $\delta^{44}\text{Ca}$
957 of the shallow water carbonate sink we speculate that the $\delta^{44}\text{Ca}$ of seawater may be
958 controlled, in part, by changes in the volume of shallow-water carbonate sediments through
959 time. Lower seawater $\delta^{44}\text{Ca}$ values would be expected during periods of widespread shallow-
960 water carbonate sediments (where fluid-buffered diagenesis dominates) whereas higher
961 seawater $\delta^{44}\text{Ca}$ values would be expected when there is a significant deep-sea carbonate sink
962 (where sediment-buffered diagenesis dominates). In this regard the growth of a large deep-
963 sea carbonate sink since the Mesozoic (at the expense of carbonate sedimentation in shallow-
964 water environments; (84)) should be associated with an increase in the $\delta^{44}\text{Ca}$ of seawater,
965 consistent in sign with observations from fossil corals (35) and minimum $\delta^{44}\text{Ca}$ values of
966 sedimentary CaSO_4 (61).

967

968 *4.5.6 Implications for modern global $\delta^{26}\text{Mg}_{\text{seawater}}$ mass balance and dolomitization:*

969

970 Sedimentary dolomite is believed to play an outsized role in the regulation of seawater
971 Mg/Ca ratios on geologic timescales (69, 116). Mg isotopes offer an excellent opportunity to
972 study this enigmatic process because the formation of dolomite is associated with Mg isotope
973 fractionation (54, 62, 79). This isotopic leverage permits, assuming the modern system is
974 close to steady-state, an estimate of the relative importance of dolomite as a global Mg sink.
975 Using this approach, Tipper et al. (117) arrived at an estimate that at least ~10% of the Mg
976 sink in the modern ocean is associated with the formation of sedimentary dolomite. As
977 discussed in Section 4.4 a critical variable in this estimate is the average Mg isotope
978 fractionation factor associated with the dolomite sink. Our results provide additional support
979 for $\alpha_{\text{dolomite}}^{26/24} = 0.9980$, the value used by Tipper et al. (117). However, this is likely an upper
980 estimate as net fractionation of Mg isotopes will be smaller in sediment-buffered dolomites.
981 For example, the dolomites from the Bahamas average $-2.79 \pm 0.17\text{‰}$ (2σ ; $N = 80$) whereas
982 the authigenic dolomites from the Monterey Fm. average $-2.06 \pm 1.13\text{‰}$ (2σ ; $N = 45$).

983

984 **CONCLUSIONS:**

985

986 Shallow-water carbonate sediments are one of the most extensive and well-studied records
987 of the chemistry and temperature of ancient oceans (1, 2, 118). One of the major limitations
988 in the utilization of this archive is the potential for changes in the chemical composition of the
989 sediments at any time after they were initially precipitated. Using a large data set of Ca and
990 Mg isotope measurements in Neogene shallow-water carbonate sediments and associated

991 pore-fluids from the platform to the slope in the Bahamas we have shown that stratigraphic
992 variability in these isotopic systems is due to variations in both mineralogy and style of
993 diagenetic alteration (fluid-buffered vs. sediment-buffered). This interpretation is rather
994 counterintuitive given that these elements, and Ca in particular, are major components of the
995 carbonate sediment and should be relative robust – almost as robust as C – to diagenetic
996 alteration. However, the large magnitude of the stratigraphic variability in bulk sediment
997 $\delta^{44}\text{Ca}$ values – up to 1‰ – cannot be explained by mixing of sediment from different sources.
998 Rather, the variability in bulk sediment $\delta^{44}\text{Ca}$ values both within and between sites – in
999 particular the presence of bulk sediment $\delta^{44}\text{Ca}$ values that are significantly higher than
1000 modern bank-top sediments – appears to be the consequence of progressive
1001 recrystallization/neomorphism under fluid-buffered diagenetic conditions. This process
1002 implies globally significant mass fluxes of Ca between seawater and shallow marine pore-
1003 fluids, consistent with observations active fluid flow and neomorphism/recrystallization
1004 within the upper 10's of meters of the sediment column from pore-fluid profiles of [Cl],
1005 $[\text{Ca}^{2+}]$, and $\delta^{44}\text{Ca}$ values at some of the Bahamas sites. Modeled rates of
1006 recrystallization/neomorphism using the pore-fluid profiles favor rates that are both higher
1007 than those observed in the deep-sea and capable of re-setting bulk and trace element
1008 chemistry of the sediment on million-year timescales.

1009 In contrast to the large stratigraphic variability observed in sediment $\delta^{44}\text{Ca}$ values,
1010 sediment $\delta^{26}\text{Mg}$ values exhibit much less variability – an apparent consequence of similar Mg
1011 isotope fractionation in high-Mg calcite and dolomite. Paired measurements of $\delta^{26}\text{Mg}$ and
1012 $\delta^{44}\text{Ca}$ values in dolomites exhibit co-variation that is consistent with dolomitization in the
1013 Bahamas occurring under both fluid-buffered and sediment-buffered conditions, with fluid-
1014 buffered conditions predominating. This approach provides a means for distinguishing
1015 between chemical signals in the dolomite from the precursor carbonate vs. those from the
1016 dolomitizing fluid.

1017 The observation that sediment $\delta^{44}\text{Ca}$ values in Neogene shallow-water carbonate
1018 sediments from the platform top, margin, and slope are largely controlled by mineralogy and
1019 the extent of fluid-buffered early marine diagenesis and that temporal variations in fluid-
1020 buffered diagenesis can generate stratigraphically coherent co-variation between many
1021 carbonate-bound geochemical proxies ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, Sr/Ca, etc.) has significant implications for
1022 the interpretation of both the major and trace element chemistry of shallow-water carbonate
1023 sediments in the geologic record. In particular, it suggests that stratigraphic co-variation
1024 between carbonate-bound geochemical proxies need not reflect changes in the global
1025 geochemical cycles of these elements but rather changes in the composition of bank-top
1026 waters and/or the extent of fluid-buffered vs. sediment buffered early marine diagenesis.
1027 Thus, records of secular change and extreme variability in shallow-water carbonate sediments
1028 might be better interpreted as records of the effects of global environmental change and
1029 evolution on shallow-water carbonate-producing environments and not archives of the global
1030 environmental changes themselves.

1031 Our data also provide new constraints on both Ca and Mg isotope mass balance in the
1032 modern ocean. The observation of carbonate sediments enriched in ^{44}Ca in shallow water
1033 environments is contrary to the expectation of variations in the $\delta^{44}\text{Ca}$ of seawater due to
1034 changes in primary sediment mineralogy – i.e. ‘calcite and aragonite’ seas. In addition, a
1035 shallow-water carbonate sink that is characterized by $\delta^{44}\text{Ca}$ values that are higher than bulk
1036 silicate Earth can likely explain the observation that deep-sea carbonate sediments (the other

1037 major sink of Ca from seawater) are $\sim 0.3\%$ lower than bulk silicate Earth. Finally, estimates
1038 of Mg isotope fractionation during dolomitization from both bulk sediments and pore-fluids
1039 indicate that low-temperature dolomite should be $\sim 2\%$ depleted in ^{26}Mg compared to the
1040 precipitating fluid. This result supports the hypothesis that the formation of dolomite has a
1041 significant effect on the $\delta^{26}\text{Mg}$ of seawater but represents a relatively small sink of Mg in the
1042 modern ocean.

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1046 **References Cited**

1047

- 1048 1. Veizer J, *et al.* (1999) Sr-87/Sr-86, delta C-13 and delta O-18 evolution of
1049 Phanerozoic seawater. *Chemical Geology* 161(1-3):59-88.
- 1050 2. Veizer J & Hoefs J (1976) Nature of O18/O16 and C13/C12 secular trends in
1051 sedimentary carbonate rocks. *Geochimica Et Cosmochimica Acta* 40(11):1387-
1052 1395.
- 1053 3. Holmden C, Creaser RA, Muehlenbachs K, Leslie SA, & Bergstrom SM (1998)
1054 Isotopic evidence for geochemical decoupling between ancient epeiric seas and
1055 bordering oceans: Implications for secular curves. *Geology* 26(6):567-570.
- 1056 4. Immenhauser A, Della Porta G, Kenter JAM, & Bahamonde JR (2003) An
1057 alternative model for positive shifts in shallow-marine carbonate delta C-13 and
1058 delta O-18. *Sedimentology* 50(5):953-959.
- 1059 5. Swart PK (2008) Global synchronous changes in the carbon isotopic composition
1060 of carbonate sediments unrelated to changes in the global carbon cycle.
1061 *Proceedings of the National Academy of Sciences of the United States of America*
1062 105(37):13741-13745.
- 1063 6. Swart PK (2015) The geochemistry of carbonate diagenesis: The past, present
1064 and future. *Sedimentology* 62(5):1233-1304.
- 1065 7. Melim LA, Swart PK, & Eberli GP (2004) Mixing-zone diagenesis in the subsurface
1066 of Florida and The Bahamas. *Journal of Sedimentary Research* 74(6):904-913.
- 1067 8. Sass E & Katz A (1982) The origin of platform dolomites - new evidence.
1068 *American Journal of Science* 282(8):1184-1213.
- 1069 9. Budd DA (1997) Cenozoic dolomites of carbonate islands: Their attributes and
1070 origin. *Earth-Science Reviews* 42(1-2):1-47.
- 1071 10. Richter FM & DePaolo DJ (1987) Numerical models for diagenesis and the
1072 Neogene Sr isotopic evolution of seawater from DSDP site 590B. *Earth and*
1073 *Planetary Science Letters* 83(1-4):27-38.
- 1074 11. Ginsburg RN (1957) Early diagenesis and lithification of shallow-water carbonate
1075 sediments in south Florida. *Special Publications Society of Economic*
1076 *Paleontologists and Mineralogists* 5:80-100.
- 1077 12. Berner RA (1966) Chemical diagenesis of some modern carbonate sediments. in
1078 *Am J Sci*, pp 1-13.
- 1079 13. Kozdon R, Kelly DC, Kita NT, Fournelle JH, & Valley JW (2011) Planktonic
1080 foraminiferal oxygen isotope analysis by ion microprobe technique suggests
1081 warm tropical sea surface temperatures during the Early Paleogene.
1082 *Paleoceanography* 26.
- 1083 14. Swart PK & Eberli G (2005) The nature of the delta C-13 of periplatform
1084 sediments: Implications for stratigraphy and the global carbon cycle. *Sedimentary*
1085 *Geology* 175(1-4):115-129.
- 1086 15. Muehlenbachs K & Clayton RN (1976) Oxygen isotope composition of oceanic-
1087 crust and its bearing on seawater. *Journal of Geophysical Research* 81(23):4365-
1088 4369.
- 1089 16. Banner JL & Hanson GN (1990) Calculation of simultaneous isotopic and trace-
1090 element variations during water-rock interaction with applications to carbonate
1091 diagenesis. *Geochimica Et Cosmochimica Acta* 54(11):3123-3137.

- 1092 17. Marshall JD (1992) Climatic and oceanographic isotopic signals from the
1093 carbonate rock record and their preservation. *Geological Magazine* 129(2):143-
1094 160.
- 1095 18. Edgar KM, Anagnostou E, Pearson PN, & Foster GL (2015) Assessing the impact of
1096 diagenesis on delta B-11, delta C-13, delta O-18, Sr/Ca and B/Ca values in fossil
1097 planktic foraminiferal calcite. *Geochimica Et Cosmochimica Acta* 166:189-209.
- 1098 19. Romaniello SJ, Herrmann AD, & Anbar AD (2013) Uranium concentrations and U-
1099 238/U-235 isotope ratios in modern carbonates from the Bahamas: Assessing a
1100 novel paleoredox proxy. *Chemical Geology* 362:305-316.
- 1101 20. Rennie VCF & Turchyn AV (2014) The preservation of delta S-34(SO4) and delta
1102 O-18(SO4) in carbonate-associated sulfate during marine diagenesis: A 25 Myr
1103 test case using marine sediments. *Earth and Planetary Science Letters* 395:13-23.
- 1104 21. Fantle MS & Higgins J (2014) The effects of diagenesis and dolomitization on Ca
1105 and Mg isotopes in marine platform carbonates: Implications for the geochemical
1106 cycles of Ca and Mg. *Geochimica Et Cosmochimica Acta* 142:458-481.
- 1107 22. Fantle MS & DePaolo DJ (2007) Ca isotopes in carbonate sediment and pore fluid
1108 from ODP Site 807A: The Ca²⁺(aq)-calcite equilibrium fractionation factor and
1109 calcite recrystallization rates in Pleistocene sediments. *Geochimica Et*
1110 *Cosmochimica Acta* 71(10):2524-2546.
- 1111 23. Higgins JA & Schrag DP (2012) Records of Neogene seawater chemistry and
1112 diagenesis in deep-sea carbonate sediments and pore fluids. *Earth and Planetary*
1113 *Science Letters* 357:386-396.
- 1114 24. Riechelmann S, *et al.* (2016) Impact of diagenetic alteration on brachiopod shell
1115 magnesium isotope (delta Mg-26) signatures: Experimental versus field data.
1116 *Chemical Geology* 440:191-206.
- 1117 25. Geske A, *et al.* (2015) Magnesium isotope composition of sabkha porewater and
1118 related (Sub-) Recent stoichiometric dolomites, Abu Dhabi (UAE). *Chemical*
1119 *Geology* 393-394:112-124.
- 1120 26. Jacobson AD & Holmden C (2008) delta(44)Ca evolution in a carbonate aquifer
1121 and its bearing on the equilibrium isotope fractionation factor for calcite. *Earth*
1122 *and Planetary Science Letters* 270(3-4):349-353.
- 1123 27. Derry LA, Kaufman AJ, & Jacobsen SB (1992) Sedimentary cycling and
1124 environmental change in the Late Proterozoic - evidence from stable and
1125 radiogenic isotopes. *Geochimica Et Cosmochimica Acta* 56(3):1317-1329.
- 1126 28. Blattler CL, Miller NR, & Higgins JA (2015) Mg and Ca isotope signatures of
1127 authigenic dolomite in siliceous deep-sea sediments. *Earth and Planetary Science*
1128 *Letters* 419:32-42.
- 1129 29. Gussone N, *et al.* (2005) Calcium isotope fractionation in calcite and aragonite.
1130 *Geochimica Et Cosmochimica Acta* 69(18):4485-4494.
- 1131 30. DePaolo DJ (2011) Surface kinetic model for isotopic and trace element
1132 fractionation during precipitation of calcite from aqueous solutions. *Geochimica*
1133 *Et Cosmochimica Acta* 75(4):1039-1056.
- 1134 31. Nielsen LC, De Yoreo JJ, & DePaolo DJ (2013) General model for calcite growth
1135 kinetics in the presence of impurity ions. *Geochimica Et Cosmochimica Acta*
1136 115:100-114.

- 1137 32. Tang J, Dietzel M, Bohm A, Kohler P, & Eisenhauer A (2008) Sr²⁺/Ca²⁺ and
 1138 ⁴⁴Ca/⁴⁰Ca fractioning during inorganic calcite formation: II. Ca isotopes.
 1139 *Geochimica et Cosmochimica Acta* 72:3733-3745.
- 1140 33. Higgins JA & Schrag DP (2015) The Mg isotopic composition of Cenozoic
 1141 seawater- evidence for a link between Mg-clays, seawater Mg/Ca, and climate.
 1142 *Earth and Planetary Science Letters* 416:73-81.
- 1143 34. Griffith EM, Paytan A, Caldeira K, Bullen TD, & Thomas E (2008) A Dynamic
 1144 Marine Calcium Cycle During the Past 28 Million Years. *Science* 322(5908):1671-
 1145 1674.
- 1146 35. Gothmann AM, *et al.* (2016) Calcium isotopes in scleractinian fossil corals since
 1147 the Mesozoic: Implications for vital effects and biomineralization through time.
 1148 *Earth and Planetary Science Letters* 444:205-214.
- 1149 36. Eberli G, *et al.* (1997) Leg 166 - Bahamas Drilling Project. *Initial Reports of the*
 1150 *Ocean Drilling Program*.
- 1151 37. Vahrenkamp VC, Swart PK, & Ruiz J (1991) Episodic dolomitization of Late
 1152 Cenozoic carbonates in the Bahamas - evidence from strontium isotopes. *Journal*
 1153 *of Sedimentary Petrology* 61(6):1002-1014.
- 1154 38. Feary DA, James NP, Hine AC, & Malone MJ (2000) Leg 182 - Great Australian
 1155 Bight: Cenozoic cool-water carbonates. *Initial Reports of the Ocean Drilling*
 1156 *Program*.
- 1157 39. Heuser A, *et al.* (2005) Calcium isotope (delta Ca-44/40) variations of Neogene
 1158 planktonic foraminifera. *Paleoceanography* 20(2):13.
- 1159 40. Tang JW, Dietzel M, Böhm F, Kohler SJ, & Eisenhauer A (2008) Sr(2+)/Ca(2+) and
 1160 (44)Ca/(40)Ca fractionation during inorganic calcite formation: II. Ca isotopes.
 1161 *Geochimica Et Cosmochimica Acta* 72(15):3733-3745.
- 1162 41. Holmden C, Papanastassiou DA, Blanchon P, & Evans S (2012) d44/40Ca variability
 1163 in shallow water carbonates and the impact of submarine groundwater discharge on Ca-
 1164 cycling in marine environments. *Geochimica et Cosmochimica Acta* 83:179-194.
- 1165 42. Holmden C, Panchuk K, & Finney SC (2012) Tightly coupled records of Ca and C
 1166 isotope changes during the Hirnantian glaciation event in an epeiric sea setting.
 1167 *Geochimica Et Cosmochimica Acta* 98:94-106.
- 1168 43. Chang VTC, Williams RJP, Makishima A, Belshawl NS, & O'Nions RK (2004) Mg
 1169 and Ca isotope fractionation during CaCO₃ biomineralisation. *Biochemical and*
 1170 *Biophysical Research Communications* 323(1):79-85.
- 1171 44. Wombacher F, *et al.* (2011) Magnesium stable isotope fractionation in marine
 1172 biogenic calcite and aragonite. *Geochimica Et Cosmochimica Acta* 75(19):5797-
 1173 5818.
- 1174 45. Pogge von Strandmann PAE (2008) Precise magnesium isotope measurements in
 1175 core top planktic and benthic foraminifera. *Geochemistry Geophysics Geosystems*
 1176 9:13.
- 1177 46. Hippler D, Buhl D, Witbaard R, Richter DK, & Immenhauser A (2009) Towards a
 1178 better understanding of magnesium-isotope ratios from marine skeletal
 1179 carbonates. *Geochimica Et Cosmochimica Acta* 73(20):6134-6146.
- 1180 47. Yoshimura T & Tanimizu M (2011) Mg isotope fractionation in biogenic
 1181 carbonates of deep-sea coral, benthic foraminifera, and hermtypic coral. *Anal*
 1182 *Bioanal Chem* 2011(401):2755-2769.

- 1183 48. Wang Z, P., *et al.* (2013) Experimental calibration of Mg isotope fractionation
1184 between aragonite and seawater. *Geochimica et Cosmochimica Acta* 102:113-123.
- 1185 49. Saenger C & Wang ZR (2014) Magnesium isotope fractionation in biogenic and
1186 abiogenic carbonates: implications for paleoenvironmental proxies. *Quaternary*
1187 *Science Reviews* 90:1-21.
- 1188 50. Eberli GP, Swart PK, & Malone MJ (1997) Leg 166. *Proceedings of the Ocean*
1189 *Drilling Program, Initial Reports*, (Ocean Drilling Program, College Station, TX),
1190 Vol 101.
- 1191 51. Ginsburg RN (2001) The Bahamas drilling project: background and acquisition of
1192 the cores and logs. *Special Publication of the SEPM*, ed Ginsburg RN), Vol 70, pp 3-
1193 16.
- 1194 52. Swart PK & Melim LA (2000) The origin of dolomites in tertiary sediments from
1195 the margin of Great Bahama Bank. *Journal of Sedimentary Research* 70(3):738-
1196 748.
- 1197 53. Melim LA, Swart PK, & Maliva RG (2001) Meteoric and marine-burial diagenesis
1198 in the subsurface of the Great Bahama Bank. *Subsurface geology of a prograding*
1199 *carbonate platform margin, Great Bahama Bank: results of the Bahama Drilling*
1200 *Project*, ed Ginsburg RN (Society for Sedimentary Geology), Vol 70, pp 137-163.
- 1201 54. Higgins JA & Schrag DP (2010) Constraining magnesium cycling in marine
1202 sediments using magnesium isotopes. *Geochimica Et Cosmochimica Acta*
1203 74(17):5039-5053.
- 1204 55. Turchyn AV & DePaolo DJ (2011) Calcium isotope evidence for suppression of
1205 carbonate dissolution in carbonate-bearing organic-rich sediments. *Geochimica*
1206 *Et Cosmochimica Acta* 75(22):7081-7098.
- 1207 56. Vahrenkamp VC, Swart PK, & Ruiz J (1988) Constraints and interpretation of
1208 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Cenozoic dolomites. *Geophysical Research Letters* 15(4):385-
1209 388.
- 1210 57. Feary DA, Hine AC, & Malone MJ (2000) Leg 182. *Proceedings of the Ocean Drilling*
1211 *Program, Initial Reports*.
- 1212 58. Fantle MS & Tipper ET (2014) Calcium isotopes in the global biogeochemical Ca
1213 cycle: Implications for development of a Ca isotope proxy. *Earth-Science Reviews*
1214 129:148-177.
- 1215 59. Husson JM, Higgins JA, Maloof AC, & Schoene B (2015) Ca and Mg isotope
1216 constraints on the origin of Earth's deepest $\delta^{13}\text{C}$ excursion. *Geochimica Et*
1217 *Cosmochimica Acta* 160:243-266.
- 1218 60. Holmden C (2005) Measurement of $d^{44}\text{Ca}$ using $a^{43}\text{Ca}$ - ^{42}Ca double-spike TIMS
1219 technique. . *Saskatchewan Industry and Resources Miscellaneous Report*
1220 2005(1):CD-ROM, Paper A-4, 7p.
- 1221 61. Blattler CL & Higgins JA (2014) Calcium isotopes in evaporites record variations
1222 in Phanerozoic seawater SO_4 and Ca. *Geology* 42(8):711-714.
- 1223 62. Young ED & Galy A (2004) The isotope geochemistry and cosmochemistry of
1224 magnesium. *Geochemistry of Non-Traditional Stable Isotopes* 55:197-230.
- 1225 63. Rosenthal Y, Field MP, & Sherrell RM (1999) Precise determination of
1226 element/calcium ratios in calcareous samples using sector field inductively
1227 coupled plasma mass spectrometry. *Analytical Chemistry* 71(15):3248-3253.

- 1228 64. Swart P (2000) The oxygen isotopic composition of interstitial waters: evidence
1229 for fluid flow and recrystallization in the margin of the Great Bahama Bank. *Initial*
1230 *Reports of the Ocean Drilling Program, Scientific Results* 166:91-98.
- 1231 65. Li WQ, Chakraborty S, Beard BL, Romanek CS, & Johnson CM (2012) Magnesium
1232 isotope fractionation during precipitation of inorganic calcite under laboratory
1233 conditions. *Earth and Planetary Science Letters* 333:304-316.
- 1234 66. Saulnier S, Rollion-Bard C, Vigier N, & Chaussidon M (2012) Mg isotope
1235 fractionation during calcite precipitation: An experimental study. *Geochimica Et*
1236 *Cosmochimica Acta* 91:75-91.
- 1237 67. Kenter JAM, Ginsburg RN, & Troelstra SR (2001) Sea-level driven sedimentation
1238 patterns on the slope and margin. *Subsurface Geology of a Prograding Carbonate*
1239 *Platform Margin, Great Bahama Bank: Results of the Bahama Drilling Project*, ed
1240 Ginsburg RN (Society for Sedimentary Geology), Vol 70, pp 61-101.
- 1241 68. Hardie LA (1987) Dolomitization - a critical view of some current views. *Journal*
1242 *of Sedimentary Petrology* 57(1):166-183.
- 1243 69. Holland HD & Zimmerman H (2000) The dolomite problem revisited.
1244 *International Geology Review* 42(6):481-490.
- 1245 70. Henderson GM, Slowey NC, & Haddad GA (1999) Fluid flow through carbonate
1246 platforms: constraints from U-234/U-238 and Cl- in Bahamas pore-waters. *Earth*
1247 *and Planetary Science Letters* 169(1-2):99-111.
- 1248 71. Kaufman J (1994) Numerical models of fluid-flow in carbonate platforms -
1249 implications for dolomitization. *Journal of Sedimentary Research Section a-*
1250 *Sedimentary Petrology and Processes* 64(1):128-139.
- 1251 72. Caspard E, Rudkiewicz JL, Eberli GP, Brosse E, & Renard M (2004) Massive
1252 dolomitization of a Messinian reef in the Great Bahama Bank: a numerical
1253 modelling evaluation of Kohout geothermal convection. *Geofluids* 4(1):40-60.
- 1254 73. Jones GD, Whitaker FF, Smart PL, & Sanford WE (2004) Numerical analysis of
1255 seawater circulation in carbonate platforms: II. The dynamic interaction between
1256 geothermal and brine reflux circulation. *American Journal of Science* 304(3):250-
1257 284.
- 1258 74. Garcia-Fresca B, Lucia FJ, Sharp JM, & Kerans C (2012) Outcrop-constrained
1259 hydrogeological simulations of brine reflux and early dolomitization of the
1260 Permian San Andres Formation. *Aapg Bulletin* 96(9):1757-1781.
- 1261 75. Droxler AW, Schlager W, & Whallon CC (1983) Quaternary aragonite cycles and
1262 oxygen-isotope records in Bahamian carbonate ooze. *Geology* 11(4):235-239.
- 1263 76. Land LS (1998) Failure to precipitate dolomite at 25 degrees C from dilute
1264 solution despite 1000-fold oversaturation after 32 years. *Aquatic Geochemistry*
1265 4(3-4):361-368.
- 1266 77. Compton JS & Siever R (1986) Diffusion and mass balance of Mg during early
1267 dolomite formation, Monterey Formation. *Geochimica et Cosmochimica Acta*
1268 50(1):125-135.
- 1269 78. Geske A, *et al.* (2015) The magnesium isotope (δ Mg-26) signature of
1270 dolomites. *Geochimica Et Cosmochimica Acta* 149:131-151.
- 1271 79. Li WQ, Beard BL, Li CX, Xu HF, & Johnson CM (2015) Experimental calibration of
1272 Mg isotope fractionation between dolomite and aqueous solution and its
1273 geological implications. *Geochimica Et Cosmochimica Acta* 157:164-181.

- 1274 80. Holmden C (2009) Ca isotope study of Ordovician dolomite, limestone, and
1275 anhydrite in the Williston Basin: Implications for subsurface dolomitization and
1276 local Ca cycling. *Chemical Geology* 268(3-4):180-188.
- 1277 81. Vahrenkamp VC, Swart PK, & Ruiz J (1991) Episodic dolomitization of late
1278 Cenozoic carbonates in the Bahamas - evidence from strontium isotopes. *Journal*
1279 *of Sedimentary Petrology* 61(6):1002-1014.
- 1280 82. Ridgwell A (2005) A Mid Mesozoic revolution in the regulation of ocean
1281 chemistry. *Marine Geology* 217(3-4):339-357.
- 1282 83. Boss SK & Wilkinson BH (1991) Planktogenic eustatic control on cratonic oceanic
1283 carbonate accumulation. *Journal of Geology* 99(4):497-513.
- 1284 84. Opdyke BN & Wilkinson BH (1988) Surface area control of shallow cratonic to
1285 deep marine carbonate accumulation. *Paleoceanography* 3(6):685-703.
- 1286 85. Sandberg PA (1983) An oscillating trend in Phanerozoic non-skeletal carbonate
1287 mineralogy. *Nature* 305(5929):19-22.
- 1288 86. Patterson WP & Walter LM (1994) Syndepositional diagenesis of modern
1289 platform carbonates - evidence from isotopic and minor element data. *Geology*
1290 22(2):127-130.
- 1291 87. Walter LM, Bischof SA, Patterson WP, & Lyons TW (1993) Dissolution and
1292 Recrystallization in Modern Shelf Carbonates - Evidence from Pore-Water and
1293 Solid-Phase Chemistry. *Philosophical Transactions of the Royal Society of London*
1294 *Series a-Mathematical Physical and Engineering Sciences* 344(1670):27-36.
- 1295 88. Schrag DP, Depaolo DJ, & Richter FM (1995) Reconstructing past sea-surface
1296 temperatures - correcting for diagenesis of bulk marine carbonate. *Geochimica Et*
1297 *Cosmochimica Acta* 59(11):2265-2278.
- 1298 89. Knauth LP & Kennedy MJ (2009) The late Precambrian greening of the Earth.
1299 *Nature* 460(7256):728-732.
- 1300 90. Schrag DP, Higgins JA, Macdonald FA, & Johnston DT (2013) Authigenic
1301 Carbonate and the History of the Global Carbon Cycle. *Science* 339(6119):540-
1302 543.
- 1303 91. Derry LA (2010) A burial diagenesis origin for the Ediacaran Shuram-Wonoka
1304 carbon isotope anomaly. *Earth and Planetary Science Letters* 294(1-2):152-162.
- 1305 92. Sumner DY & Bowring SA (1996) U-Pb geochronologic constraints on deposition
1306 of the Campbellrand Subgroup, Transvaal Supergroup, South Africa. *Precambrian*
1307 *Research* 79(1-2):25-35.
- 1308 93. Swart PK, Reijmer JJG, & Otto R (2009) A re-evaluation of facies on Great Bahama
1309 Bank II: variations in the delta C-13, delta O-18 and mineralogy of surface
1310 sediments. *Perspectives in Carbonate Geology: a Tribute to the Career of Robert*
1311 *Nathan Ginsburg* 41:47-59.
- 1312 94. Farkas J, Fryda J, & Holmden C (2016) Calcium isotope constraints on the marine
1313 carbon cycle and CaCO₃ deposition during the late Silurian (Ludfordian) positive
1314 delta C-13 excursion. *Earth and Planetary Science Letters* 451:31-40.
- 1315 95. Broecker WS & Takahashi T (1966) Calcium carbonate precipitation on the
1316 Bahama Banks. *Journal of Geophysical Research* 71(6):1575-+.
- 1317 96. Panchuk KM, Holmden C, & Kump LR (2005) Sensitivity of the epeiric sea carbon
1318 isotope record to local-scale carbon cycle processes: Tales from the Mohawkian
1319 Sea. *Palaeogeography Palaeoclimatology Palaeoecology* 228(3-4):320-337.

- 1320 97. Romanek CS, Grossman EL, & Morse JW (1992) Carbon isotopic fractionation in
1321 synthetic aragonite and calcite - effects of temperature and precipitation rate.
1322 *Geochimica Et Cosmochimica Acta* 56(1):419-430.
- 1323 98. Kozłowski W (2015) Eolian dust influx and massive whittings during the
1324 Kozłowski/Lau Event: carbonate hypersaturation as a possible driver of the mid-
1325 Ludfordian Carbon Isotope Excursion. *Bulletin of Geosciences* 90(4):807-840.
- 1326 99. LaPorte DF, *et al.* (2009) Local and global perspectives on carbon and nitrogen
1327 cycling during the Hirnantian glaciation. *Palaeogeography Palaeoclimatology*
1328 *Palaeoecology* 276(1-4):182-195.
- 1329 100. Hayes J & Waldbauer J (2006) The carbon cycle and associated redox processes
1330 through time. *Philosophical Transactions of the Royal Society B: Biological Sciences*
1331 361(1470):931-950.
- 1332 101. Lazar B & Erez J (1992) Carbon geochemistry of marine-derived brines. 1) C13
1333 depletions due to intense photosynthesis. *Geochimica Et Cosmochimica Acta*
1334 56(1):335-345.
- 1335 102. Herczeg AL & Fairbanks RG (1987) Anomalous carbon isotope fractionation
1336 between atmospheric CO₂ and dissolved inorganic carbon induced by intense
1337 photosynthesis. *Geochimica Et Cosmochimica Acta* 51(4):895-899.
- 1338 103. Patterson WP & Walter LM (1994) Depletion of C13 in seawater sigma-CO₂ on
1339 modern carbonate platforms - significance for the carbon isotopic record of
1340 carbonates. *Geology* 22(10):885-888.
- 1341 104. Lu ZL, Jenkyns HC, & Rickaby REM (2010) Iodine to calcium ratios in marine
1342 carbonate as a paleo-redox proxy during oceanic anoxic events. *Geology*
1343 38(12):1107-1110.
- 1344 105. Tribble GW (1993) Organic-matter oxidation and aragonite diagenesis in a coral-
1345 reef. *Journal of Sedimentary Petrology* 63(3):523-527.
- 1346 106. Tribble GW, Sansone FJ, Buddemeier RW, & Li YH (1992) Hydraulic exchange
1347 between a coral-reef and surface sea-water. *Geological Society of America Bulletin*
1348 104(10):1280-1291.
- 1349 107. Falter JL & Sansone FJ (2000) Hydraulic control of pore water geochemistry
1350 within the oxic-suboxic zone of a permeable sediment. *Limnology and*
1351 *Oceanography* 45(3):550-557.
- 1352 108. Marriott CS, Henderson GM, Belshaw NS, & Tudhope AW (2004) Temperature
1353 dependence of d⁷Li, d⁴⁴Ca and Li/Ca during growth of calcium carbonate. *Earth*
1354 *and Planetary Science Letters* 222:615-624.
- 1355 109. Busenberg E & Plummer LN (1985) Kinetic and thermodynamic factors
1356 controlling the distribution of SO₄(²⁻) and Na⁺ in calcites and selected aragonites.
1357 *Geochimica Et Cosmochimica Acta* 49(3):713-725.
- 1358 110. Chen XM, Romaniello SJ, Herrmann AD, Wasylenki LE, & Anbar AD (2016)
1359 Uranium isotope fractionation during coprecipitation with aragonite and calcite.
1360 *Geochimica Et Cosmochimica Acta* 188:189-207.
- 1361 111. Marengo PJ, Corsetti FA, Hammond DE, Kaufman AJ, & Bottjer DJ (2008)
1362 Oxidation of pyrite during extraction of carbonate associated sulfate. *Chemical*
1363 *Geology* 247(1-2):124-132.
- 1364 112. Oehlert AM & Swart PK (2014) Interpreting carbonate and organic carbon
1365 isotope covariance in the sedimentary record. *Nature Communications* 5.

- 1366 113. Oehlert AM, *et al.* (2012) The stable carbon isotopic composition of organic
1367 material in platform derived sediments: implications for reconstructing the
1368 global carbon cycle. *Sedimentology* 59(1):319-335.
- 1369 114. Milliman JD & Droxler AW (1996) Neritic and pelagic carbonate sedimentation in
1370 the marine environment: Ignorance is not bliss. *Geologische Rundschau*
1371 85(3):496-504.
- 1372 115. Farkas J, *et al.* (2007) Calcium isotope record of Phanerozoic oceans: Implications
1373 for chemical evolution of seawater and its causative mechanisms. *Geochimica et*
1374 *Cosmochimica Acta* 71(21):5117-5134.
- 1375 116. Wilkinson BH & Algeo TJ (1989) Sedimentary carbonate record of calcium and
1376 magnesium cycling. *American Journal of Science* 289(10):1158-1194.
- 1377 117. Tipper ET, *et al.* (2006) The magnesium isotope budget of the modern ocean:
1378 Constraints from riverine magnesium isotope ratios. *Earth and Planetary Science*
1379 *Letters* 250(1-2):241-253.
- 1380 118. Kasting JF, *et al.* (2006) Paleoclimates, ocean depth, and the oxygen isotopic
1381 composition of seawater. *Earth and Planetary Science Letters* 252(1-2):82-93.
- 1382