Quantifying the effect of diagenetic recrystallization on the Mg isotopic composition of marine carbonates

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Keywords: diagenesis, carbonate recrystallization, geochemical proxy, marine sediments, Mg isotopes, Sr isotopes

Abstract

The Mg and Sr isotopic compositions ($\delta^{26}\text{Mg}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) of pore fluids and bulk carbonates from Ocean Drilling Project Site 1171 (South Tasman Rise; 2148.2 m water depth) are reported, in order to evaluate the potential of diagenesis to alter carbonate-based geochemical proxies in an open marine system. Given the trace amounts of Mg in marine carbonates relative to coexisting pore fluids, diagenesis can alter carbonate $\delta^{26}\text{Mg}$, a promising proxy for seawater $\delta^{26}\text{Mg}$ that may help elucidate long-term changes in the global Mg cycle. Constraints on the effect of diagenetic recrystallization on carbonate $\delta^{26}\text{Mg}$ are therefore critical for accurate proxy interpretations. This study provides context for assessing the fidelity of geochemical proxy-reconstructions using the primary components (i.e., foraminiferal tests and nannofossils) of bulk carbonate sediments.

We find that pore fluid $\delta^{26}\text{Mg}$ values (on the DSM3 scale) at Site 1171 increase systematically with depth (from -0.72‰ to -0.39‰ in the upper ~260 m), while the $\delta^{26}\text{Mg}$ of bulk carbonates decrease systematically with depth (from -2.23‰ to -5.00‰ in the upper ~260 m). This variability is ascribed primarily to carbonate recrystallization, with a small proportion of the variability due to down-hole changes in nannofossil and foraminiferal species composition. The inferred effect of diagenesis on bulk carbonate $\delta^{26}\text{Mg}$ correlates with down-core changes in Mg/Ca, Sr/Ca, Na/Ca, and $^{87}\text{Sr}/^{86}\text{Sr}$. A depositional reactive-transport model is employed to validate the hypothesis that calcite recrystallization in this system can generate sizeable shifts in carbonate $\delta^{26}\text{Mg}$. Model fits to the data suggest a fractionation factor and a partition coefficient that are consistent with previous work, assuming calcite recrystallization rates of $\leq 7\%/ \text{Ma}$ constrained by Sr geochemistry. In addition, either partial dissolution or a distinctly different previous diagenetic regime must be invoked in order to explain aspects of the elemental chemistry and $^{87}\text{Sr}/^{86}\text{Sr}$ of relatively deep sediments from Holes A and C. This study indicates that the dynamics of a given sedimentary system can significantly alter bulk carbonate geochemistry, and presents a framework for considering the potential impact of such alteration on picked archives such as foraminiferal tests and nannofossils. Ultimately, this study contributes to the development of $\delta^{26}\text{Mg}$ as a proxy for seawater $\delta^{26}\text{Mg}$ by quantifying the susceptibility of carbonate $\delta^{26}\text{Mg}$ to diagenetic alteration, particularly in sediments in open marine systems. This study suggests that because of the sensitivity of carbonate $\delta^{26}\text{Mg}$ to diagenetic recrystallization, it can, in certain systems, be used to quantify the impact of diagenesis on carbonate-based geochemical proxies.

1. Introduction

The application of trace elemental and isotopic proxies in marine carbonates has offered unparalleled perspectives on paleoceanographic and paleoclimatic evolution over geologic time scales. Constraints on parameters such as ocean ice volume (Shackleton, 1987; Pekar et al., 2002; Katz et al., 2008; Miller et al., 2008), sea surface and bottom water temperature (Nürnberg et al., 1996; Rosenthal et al., 1997; Lear et al., 2000; Billups and Schrag, 2002; Martin et al., 2002; Billups and Schrag, 2003), dissolved inorganic carbon (DIC) and ocean circulation (Boyle and Keigwin, 1985; Duplessy et al., 1988; Spero et al., 1997; Katz et al., 2010), and seawater pH (Hemming and Hanson, 1992; Hönlisch et al., 2007; Foster, 2008; Hönlisch et al., 2008), as well as on global elemental cycles (Richter et al., 1992; Zhu and Macdougall, 1998; Rocha and DePaolo, 2000; Fantle and DePaolo, 2005; Hodel et al., 2007; Griffith et al., 2008; Higgins and Schrag, 2010; Fantle, 2010; Higgins and Schrag, 2012), have been made using a range of proxies based on major and trace elemental (e.g., Mg/Ca, Ba/Ca, Sr/Ca, B/Ca) and isotopic compositions (e.g., $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $\delta^{44/40}\text{Ca}$, $\delta^{26}\text{Mg}$, $\delta^{11}\text{B}$, $^{87}\text{Sr}/^{86}\text{Sr}$) of marine carbonates.

The accuracy of any geochemical proxy relies not only upon a fundamental understanding of the partitioning behavior of that element and its isotopes during mineral precipitation, but also upon the susceptibility of the primary signal to post-depositional alteration. Diagenetic reactions, which are known to occur over tens of millions of years in marine systems, can significantly impact the fidelity of a range of carbonate-based proxies (e.g., $^{87}\text{Sr}/^{86}\text{Sr}$, Sr/Ca, Mg/Ca, and B/Ca), especially those utilizing trace elements (Richter and DePaolo, 1987; Richter and Liang, 1993; Fantle and DePaolo, 2006; Fantle et al., 2010). As mass spectrometric analyses become more precise, and we seek to interpret small-scale variability in proxy data, decoupling diagenetic effects from the original signal becomes even more relevant.

The Mg isotopic composition ($\delta^{26}\text{Mg}$) of marine carbonates is an emerging proxy for reconstructing secular variations in seawater $\delta^{26}\text{Mg}$ (e.g., Higgins and Schrag, 2012; Pogge von Strandmann et al., 2014), which can elucidate the long-term changes in the global Mg cycle. Such an understanding has broader implications for such topics as the geochemical evolution of the lithosphere and hydrosphere, temporal variability in terrestrial and marine silicate weathering rates, and dolomite formation (Holland, 2005; Tipper et al., 2006a; Tipper et al., 2006b; Shen et al., 2009). Biogenic carbonates have shown promise as proxy archives because the isotopic fractionation of Mg isotopes in foraminiferal calcite appears to exhibit no systematic sensitivity to ambient temperature, solution chemistry (e.g., pH, carbonate saturation, and salinity), and/or growth rate (Chang et al., 2004; Pogge von Strandmann, 2008; Wombacher et al., 2011). This has led to suggestions that $\delta^{26}\text{Mg}$ variability in foraminiferal tests primarily reflects seawater $\delta^{26}\text{Mg}$, with the ultimate proviso that foraminiferal $\delta^{26}\text{Mg}$ is not significantly impacted by diagenesis.

The impact of diagenetic reactions (i.e., dissolution and recrystallization) on marine carbonate $\delta^{26}\text{Mg}$ is not well explored, though such work is feasible. The long residence time of

Mg in seawater (~13 to 20 Ma; Broecker and Peng, 1982) and resulting homogeneity of seawater $\delta^{26}\text{Mg}$ ($-0.84 \pm 0.06 \text{ ‰}$) suggests that diagenesis can be studied over million-year time scales while making well-grounded assumptions regarding initial pore fluid chemistry. Work aimed at quantifying diagenetic effects ($d\delta_s$) is necessarily involved, and requires knowledge of the recrystallization rate (R) of the solid, the isotopic disequilibrium between the solid and co-existing pore fluids ($(\delta_s - \delta_f) - \Delta_{s-f}^{diag}$) and the duration of the reaction (dt ; e.g., Fantle and DePaolo, 2007; Fantle et al., 2010; Fantle, 2015):

$$d\delta_s = -R[(\delta_s - \delta_f) - \Delta_{s-f}^{diag}]dt \quad \text{----(1)}$$

where δ_s and δ_f represent the isotopic compositions of solid and fluid, respectively, and Δ_{s-f}^{diag} represents the isotopic fractionation associated with diagenetic recrystallization.

The key point is that while diagenetic alteration obviously requires a non-zero rate and time, it also requires a relatively strong isotopic contrast between the environment of formation and post-depositional settings. Such contrasts exist when the reacting solid and pore fluid are at chemical or isotopic disequilibrium. In a monomineralic sedimentary column, the difference in the length scales over which disequilibrium exists for given elements is primarily a function of the local residence time of the element of interest in the pore fluid. Additionally, changes in the fractionation factor between solid and fluid, either with depth in the sedimentary column or between the formational and depositional environments, influence the extent of isotopic disequilibrium. Finally, the degree of local chemical disequilibrium between sediments and pore fluids can be influenced by the extent to which a system is locally closed. In a relatively “open system”, in which transport processes are comparable to reactive processes, local disequilibrium can be maintained for long periods of time (e.g., Fantle and Higgins, 2014; Fantle, 2015). In such settings, the extent of diagenetic exchange can be amplified by prolonged disequilibrium between the solids and fluids.

With regard to metal isotopes, little work has been done to date linking the transport regime in a given sedimentary section to the extent of alteration accompanying diagenesis. To this end, the objective of the current study is to constrain diagenetic alteration in a marine sedimentary system influenced by advection (ODP Site 1171, South Tasman Rise). Such a study is meant to constrain an upper limit on the amount of diagenetic alteration expected in marine, carbonate-rich sedimentary systems. The Mg isotopic composition of bulk carbonates and coexisting pore fluids were measured, and these data interpreted using a one-dimensional depositional reactive transport model. Recent Ca and Sr isotope work at Site 1171 has suggested that there is chemically detectable upward advection at Site 1171 (~250 m/Ma), and constrained recrystallization rates to be ~7%/Ma for >1 Ma sediments and ~20 to 40%/Ma for sediments <1 Ma (Fantle, 2015). Fantle (2015) also showed that the $^{87}\text{Sr}/^{86}\text{Sr}$ of bulk carbonates deviated noticeably from the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve (McArthur and Howard, 2004), an effect that is paralleled in bulk carbonate Sr/Ca and Mg/Ca ratios. Altogether, these observations provide us with a rationale for selecting Site 1171 as a study site, and a well-developed geochemical dataset

for aiding interpretation of the Mg isotope data. The focus on bulk sediments offers constraints on the geochemical conditions to which picked proxy archives such as foraminiferal tests and nannofossils are exposed. Such context can be used to estimate errors in proxy interpretation or, in cases where bulk sediments are the preferred archive, to correct for systematic offsets due to diagenesis.

2. Materials and Methods

2.1. Study Location: ODP Site 1171

Site 1171 is located on the South Tasman Rise (48°29.99600'S and 149°06.69010'E) at a water depth of 2148.2 m (Fig. 1a) on a southwesterly dipping slope. The composite stratigraphic section is ~960 m thick. The sediments sampled at the three holes drilled (A, C, and D) range in age from the late Paleocene (~58 Ma) to the Quaternary (Fig. 1b). The Neogene section of the sedimentary column is characterized by high carbonate content (>90% CaCO₃) and low organic carbon content (<1 wt %). The Neogene section is mostly continuous with an exception of a hiatus present in the uppermost Miocene (Fig. 1b). The upper ~275 m of the sedimentary section (Units I, II and III) is composed of foraminifera-bearing nannofossil ooze and chalk (late Oligocene to Pleistocene) with a significant increase in siliciclastic components below ~275 mbsf. Sediments below 275 mbsf (Units IV and V) are dominated by clayey glauconitic siltstone and nannofossil bearing diatomaceous silty claystone with very low carbonate content (<10%).

Sediments near the seafloor have porosities of ~66%. There is a sharp decrease in porosity (to ~53%) at 42 mbsf, followed by relative constancy ($60 \pm 3\%$) to the carbonate-silicate transition (Fig. 1b). Temperature increases downhole from ~4°C near the sediment-water interface to ~18.5 °C at ~575 mbsf (data only available for Hole D; Fig. 1b; Exon et al., 2001a).

The ages of the sediments from Site 1171 are assigned based on previously reported biostratigraphic and magnetostratigraphic data (Supplementary Material, Fig. A1; Exon et al., 2001a; Stickley et al., 2004). Based on the age-depth relationship, the growth curve of the sedimentary column is constructed. Sedimentation rates were ~1.3 cm/ka in the upper part of the section (0 to 5 Ma age) followed by a ~2.0 Ma hiatus at the Miocene/Pliocene boundary (Exon et al., 2001a; Stickley et al., 2004). During the early and middle Miocene, sedimentation rates were low (0.7 to 2.0 cm/ka), increased to 3.8 cm/ka across the mid-late Miocene boundary, and decreased to ~0.5 cm/ka in the late Miocene. Between the Paleocene and middle Eocene, sedimentation rates were significantly higher (ranging from 4.4 to 12.5 cm/ka), with the exception of four brief hiatuses punctuated by short intervals of slow sedimentation (< 1 cm/ka) in the late Oligocene to the middle Eocene.

Pore fluid chemistries from 1171A, 1171C, and 1171D are summarized in Fig. 2. In Holes 1171A and C, the pore fluid Ca concentration shows a slight increase with depth (from 11.3 mM at 11.5 mbsf to 11.8 mM at ~262 mbsf). However, the pore fluid Sr concentration increases sharply from 117 µM at 1.45 mbsf to 419 µM at 49.55 mbsf followed by a gradual

decrease to 391 μM at 117 mbsf. The increase in pore fluid Sr clearly indicates diagenetic exchange of Sr between carbonates and pore fluids during calcite recrystallization. The thin diffusive boundary layer (~ 50 m) suggests significant upward advection of fluid (Fantle, 2015), which is also feasible from a geophysical perspective given the thinness of the carbonate-rich section (Exon et al., 2001a).

In the uppermost carbonates at Site 1171, pore fluid Mg concentrations decrease with depth from 51.3 mM at the sediment-water interface to 40.5 mM at 262.9 mbsf, followed by a rapid decrease in the silicate-rich section to 7.8 mM at ~ 960 mbsf (Hole D). Removal of Mg from the pore fluids by basement alteration (i.e., lower $[\text{Mg}^{2+}]$ at the bottom boundary condition) and silicate diagenesis in the silicate-rich section are plausible explanations for the rapid decrease in Mg in the siliciclastics (Exon et al., 2001a). There is no evidence of authigenic dolomite at 1171, though Robert (2004a; 2004b) detected “minor and sporadic” occurrences of what he concluded were detrital dolomite in the siliclastic section (below ~ 280 mbsf). In the uppermost 270 m, pore fluid SO_4^{2-} concentration decreases in a slow and gradual manner from 26.8 mM (at ~ 1.5 mbsf) to 18.3 mM (at ~ 263 mbsf), as compared to the sharp decrease to near-zero values in the deeper siliciclastics, and increases in alkalinity, pH, and NH_4^+ concentration.

2.2 Sample Preparation

Aliquots of pore fluids were filtered with 0.1 μm PVDF syringe filter membrane and treated with a 1:1 mixture of 25% hydrogen peroxide (H_2O_2) and 6N HNO_3 at 80°C for 40 minutes (3 to 5 times) to digest the organic matter. Digests were then dried down and reserved for chemical purification of Mg.

Cleaning and selective digestion of bulk carbonates were adopted from the methods of Apitz (1991) and Delaney and Linn (1993). Bulk solids (25 to 50 mg) were gently ground and homogenized with a clean agate mortar and pestle, weighed, and transferred to acid-cleaned pre-weighed polypropylene centrifuge tubes. To each tube was added 10 ml of reducing solution, prepared by dissolving 25 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (hydroxylamine hydrochloride) into 200 ml of concentrated NH_4OH and 300 ml of deionized water, and the resulting solution weighed. Centrifuge tubes were shaken at room temperature for 12 hr in a circular shaker, centrifuged at 4500 rpm for 20 minutes, and the supernatants were removed using acid-cleaned transfer pipettes. The reductive cleaning step was then repeated to make sure that all Fe-Mn oxide coatings were removed.

Subsequently, samples were shaken with 10 ml of 1 N NH_4OH solution for 4 hr at room temperature, centrifuged at 4500 rpm for 20 minutes, and the supernatants were transferred to acid-cleaned teflon vials using clean pipettes. Finally, the carbonate fractions were selectively dissolved in 10 ml of a 0.1 M ammonium acetate-acetic acid buffer (pH ~ 4.7) by shaking for 5 hr, centrifuging at 4500 rpm for 45 minutes, and removing the supernatants. Supernatants were filtered (0.1 μm PVDF syringe filter membrane), weighed, and stored in acid cleaned and pre-weighed teflon vials. An aliquot of each digested sample was analyzed using a Perkin-Elmer

Optima 5300 UV ICP-AES for elemental concentration prior to ion exchange chromatographic purification.

2.3. Ion Chromatographic Purification of Mg and Sr

The ion chromatographic purification of Mg from the digested pore fluids and carbonates was conducted by modifying previously employed techniques (Wombacher et al., 2009; Wombacher et al., 2011) using Bio-Rad's AG-50W-X8 resin and Eichrom's TODGA resin (Horwitz et al., 2005; Pourmand and Dauphas, 2010). Magnesium from pore fluid samples was purified in a single step using Bio-Rad polypropylene columns filled with 1.9 ml of AG-50W-X8 resin. Pore fluid samples containing 18-20 μg of Mg were loaded to the resin columns in 0.4 N HCl acid, Na and K eluted in 50 ml of 0.4 N HCl and 4 ml of 1 N HCl, and Mg eluted in 15 ml of 1 N HCl (Supplementary Material, Fig. A2a).

Bulk carbonate-derived Mg was purified by passing samples with 1-2 μg of Mg through Bio-Rad polypropylene columns containing 1.5 ml TODGA resin to remove Ca; Ca-free cuts were collected in 24 ml of 4 N HNO_3 . The Ca-free elution cuts were dried down, resuspended in 0.1 ml 0.4 N HCl, and loaded onto AG-50W-X8 (1.9 ml resin) columns. Afterwards, the resin columns were washed by 50 ml of 0.4 N HCl to remove Na, K, followed by 12 ml of 0.15 N HF to remove any Al and by 12 ml mixture of 95% acetone and 0.5 N HCl to remove any Fe and Mn. Finally, the Mg cuts were collected in 14 ml of 1 N HCl (Supplementary Material, Fig. A2b and 2c).

Our ion chromatographic procedures successfully separated Mg from both marine pore fluid and carbonate matrices with an average recovery of $99.2 \pm 0.5\%$. The low concentrations of Al, Mn, and Fe in the digested carbonates, in addition to no evidence of a positive correlation between Mg/Ca and Mn/Ca, Al/Ca or Fe/Ca, suggest that the isotopic composition of measured Mg is not measurably impacted by silicate-derived Mg (Table A1). All yield calculations were determined using elemental concentrations measured by ICP-AES. Acid-cleaned containers along with high purity reagents and milli-Q deionized water were used in all procedures to minimize procedural blanks (<10 ng per 1-2 μg of Mg, or $<0.5\%$; $n=6$). The concentrations of Mg in the procedural blanks were calculated using the intensity of the measured $^{24}\text{Mg}^+$ ion beam on the Neptune Plus MC-ICP-MS and a calibration curve developed from a gravimetric single-element (Mg) standard set.

The purification of Sr from the pore fluids and carbonate samples followed previously described method (Fantle and DePaolo, 2006). The ion exchange columns for this separation technique were prepared using acid washed transfer pipettes of 300 – 500 μl column volume, polypropylene frits of 1/16-inch thickness, and Eichrom's Sr Spec resin. The Sr Spec resin was cleaned with 6 N HCl and deionized water. About 500 μl of resin was added to each column, washed 6 times alternately with 1 ml of 4 N HCl and deionized water, and conditioned with 1 ml of 3 N HNO_3 . The filtered pore fluid samples were dried down and resuspended in 3 N HNO_3 and centrifuged. The supernatants were then pipetted off and an aliquot of each supernatant containing 1-2 μg of Sr was loaded on to the column in 0.05 ml of 3 N HNO_3 . After loading the

samples, the columns were rinsed with 3.5 ml of 3 N HNO₃ and Sr was collected in 2.5 ml deionized water (Supplementary Material, Fig. A2d). The procedural blank for the entire column separation was 0.2 to 0.5 ng Sr (i.e., <0.05% of the total Sr in each sample) and the average Sr yield was 98.5 ± 0.5%.

2.4. Mass Spectrometry

Precise and accurate measurements of Mg isotopic composition were performed using a Thermo Scientific Neptune Plus multi-collector ICP-MS in Penn State's Metal Isotope Laboratory (MIL). Our mass spectrometric approach was designed to minimize the impact of polyatomic interferences (¹²C¹⁴N⁺, ¹²C₂⁺, ¹²C₂¹H⁺, ²³Na¹H⁺) and interferences from doubly charged ions (e.g., ⁴⁸Ca²⁺, ⁴⁸Ti²⁺, ⁵⁰Cr²⁺, ⁵⁰V²⁺, ⁵²Cr²⁺, ⁵²Mn²⁺) at masses 24, 25, and 26. In order to minimize the effect of polyatomic interferences containing C, O, H, and N, samples were introduced to the plasma as a dry aerosol using Elemental Scientific's (ESI) Apex IR desolvating nebulizer. The effects of doubly-charged atomic ions are reduced by ion chromatographic purification of Mg.

Purified Mg solutions were diluted to 200 to 250 ppb in 0.3 N HNO₃, which produced a ²⁴Mg⁺ ion beam of ~15 to 20 volts in medium mass resolution (M/ΔM ~7000) on the Neptune Plus. Spectron jet sample cones were used in combination with Thermo H-skimmer cones to enhance sensitivity. Isotope ratios were acquired in one block of 35 ratios with 8.39 s integration time. Instrument operating conditions are described in Supplementary Material (Table A2).

Instrumental mass bias corrected delta values were calculated using a sample-standard bracketing method, with DSM3 as a reference standard; DSM3 is a synthetic standard prepared by dissolving ~10 g of pure Mg metal, produced by Dead Sea Magnesium Ltd., Israel, in 0.3 M nitric acid (Galy et al., 2003). The delta notation used to report Mg isotopic composition is:

$$\delta^x\text{Mg} = \left(\frac{(x_{\text{Mg}/24\text{Mg}})_{\text{sample}}}{(x_{\text{Mg}/24\text{Mg}})_{\text{DSM3}}} - 1 \right) \cdot 1000 \quad \text{----(2)}$$

where x represents either mass 25 or 26. Multiple measurements of in-house laboratory standards (not put through column chemistry) and seawater (purified via the techniques described above) relative to DSM3 resulted in $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values identical to their published values (Table 1). The isotopic composition of each sample is reported as the average $\delta^{26}\text{Mg}$ of 3 to 5 replicates measured over multiple analytical sessions. The reported uncertainty represents two times the standard deviation (SD) of these multi-session replicate analyses (i.e., external reproducibility).

Data quality was assessed by examining both internal and external reproducibility, as well as by multiple measurements of in-house standards (Cambridge-1 and Fang-Zhen Teng's laboratory standard, FZT-Mg) during each analytical session. Typical external standard deviations (2SD) of the $\delta^{26}\text{Mg}$ measurements were ≤ 0.10‰ (Table 2). On an isotope-isotope plot ($\delta^{26}\text{Mg}$ vs. $\delta^{25}\text{Mg}$; Fig. 3c), all mass bias corrected delta values fall along a line with slope

0.515 ± 0.02 , similar to the slopes of the mass dependent fractionation lines (MDFL) for Mg (0.510 and 0.520 as kinetic and equilibrium MDFL, respectively; Young and Galy, 2004).

Measurements of $^{87}\text{Sr}/^{86}\text{Sr}$ were performed on the Neptune Plus in the MIL in low mass resolution mode under wet plasma conditions, yielding a sensitivity of ~ 10 to $12 \text{ V } ^{88}\text{Sr}^+$ at 200 ppb Sr (Balashov et al., 2015; Fantle, 2015). Ion beams were monitored at masses 82, 83, 84, 85, 86, 87, and 88. The instrumental mass bias and Kr interference corrections were performed off-line by calculating the fractionation of $^{82}\text{Kr}/^{83}\text{Kr}$ from its expected value (1.008) using the exponential law:

$$\left(\frac{iX}{jX}\right)_{\text{meas}} = \left(\frac{iX}{jX}\right)_{\text{actual}} * \left(\frac{m_i}{m_j}\right)^p \quad \text{----(3)}$$

where iX and jX represent specific nuclides of the element X and m_i and m_j are the atomic masses of nuclides iX and jX . The p -value derived from the above equation was used to calculate ^{84}Kr and ^{86}Kr ion beam intensities from the measured ion beams at masses 84 and 86, as they are not otherwise resolvable from the ^{84}Sr and ^{86}Sr ion beams on the Neptune. The fractionation-corrected values of ^{84}Kr and ^{86}Kr were then subtracted from the measured intensities of 84 and 86 to calculate $^{84}\text{Sr}^+$ and $^{86}\text{Sr}^+$ intensities. An exponential law was used to correct the Sr isotope ratios using an assumed $^{86}\text{Sr}/^{88}\text{Sr}$ of 0.1194 and the resultant p -value used to calculate a mass bias corrected $^{87}\text{Sr}/^{86}\text{Sr}$.

Typical Kr corrections were less than 0.000010 on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Due to the possibility of an isobaric interference from Rb at mass 87, $^{85}\text{Rb}^+$ was monitored at mass 85 in all runs. All mass 85 intensities were $< 0.00005 \text{ V}$; thus, the $^{87}\text{Rb}^+$ interference at mass 87 was insignificant in all analyses. Replicate measurements of the standard SRM-987 over two years yield an average $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.710223 ± 0.000038 (2SD; NIST certified value: 0.71034 ± 0.00026). Multiple measurements of Sr separated from BCR-1 yield an average $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.705013 ± 0.000002 (2SD), which is comparable to the reported BCR-1 value 0.705020 (Raczek et al., 2003; Balcaen et al., 2005; Jochum et al., 2005; Jochum and Nohl, 2008). In this article, the $^{87}\text{Sr}/^{86}\text{Sr}$ values are linearly detrended in the depth regime in order to facilitate the comparison of relatively small differences in $^{87}\text{Sr}/^{86}\text{Sr}$.

3. Results

3.1. Magnesium isotopic composition ($\delta^{26}\text{Mg}$) of pore fluids and bulk carbonates

Pore fluid and bulk carbonate Mg isotopic compositions ($\delta^{26}\text{Mg}$) from Site 1171, Holes A and C, are summarized in Tables 2 and 3 and Figure 3. The average $\delta^{26}\text{Mg}$ value of the measured pore fluids at Site 1171 ($-0.56 \pm 0.17\text{‰}$) is generally higher than modern seawater ($-0.84 \pm 0.04\text{‰}$). With increasing depth in the sedimentary column, pore fluid $\delta^{26}\text{Mg}$ values exhibit a systematic increase from $-0.72 \pm 0.08\text{‰}$ (1.45 mbsf) to $-0.39 \pm 0.03\text{‰}$ (262.9 mbsf). In Hole A, within the upper 78.0 mbsf, pore fluid $\delta^{26}\text{Mg}$ increases with depth from $-0.72 \pm 0.08\text{‰}$ to $-0.52 \pm 0.06\text{‰}$ followed by a slight decrease to $-0.61 \pm 0.10\text{‰}$ at 117.7 mbsf. In Hole C (below 120 mbsf), pore fluid $\delta^{26}\text{Mg}$ increases gradually with depth ($-0.39 \pm 0.03\text{‰}$ at 262.9 mbsf), except between ~ 177 and ~ 210 mbsf where pore fluid $\delta^{26}\text{Mg}$ shifts slightly towards a lower value ($-0.58 \pm 0.10\text{‰}$ at ~ 205 mbsf).

Compared to the pore fluids, bulk carbonates from Site 1171A exhibit substantial variability in $\delta^{26}\text{Mg}$ over the depth range investigated, generally decreasing from $-2.23 \pm 0.05\text{‰}$ at 0.735 mbsf to $-4.01 \pm 0.05\text{‰}$ at 115.53 mbsf with some small-scale variability. There are two depth intervals over which bulk carbonate $\delta^{26}\text{Mg}$ shifts towards higher values by 0.20 to 0.40‰ relative to the depth above: (i) between 3.73 and 21.145 mbsf, the carbonate $\delta^{26}\text{Mg}$ increases from $-2.72 \pm 0.08\text{‰}$ to $-2.26 \pm 0.09\text{‰}$ and (ii) between 30.635 and 49.635 mbsf the carbonate $\delta^{26}\text{Mg}$ increases from $-3.36 \pm 0.04\text{‰}$ to $-3.16 \pm 0.05\text{‰}$. At Site 1171C, bulk carbonate $\delta^{26}\text{Mg}$ continues to decrease with increasing depth from $-4.78 \pm 0.06\text{‰}$ at 125.16 mbsf to $-5.00 \pm 0.03\text{‰}$ at 258.46 mbsf, though the variability is considerably lower than at Site 1171A.

3.2. Strontium isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}$) of bulk carbonates

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of bulk carbonates from Site 1171A decrease systematically from the modern seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.709174 ± 0.000005) near the sediment-water interface to 0.708834 ± 0.000023 at 115.53 mbsf (Table 4, Fig. 4a-b). Shallower carbonates (0 to 50 mbsf depth) exhibit a monotonic decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ with an increasing offset from the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve, similar to the trend reported by Fantle (2015) for bulk carbonates in this depth range. In this depth interval (0 to 50 mbsf), bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ shifts towards the pore fluid $^{87}\text{Sr}/^{86}\text{Sr}$ (Fantle, 2015). However, between 67 and 115 mbsf, the bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ trend reverses and approaches the seawater curve (McArthur et al., 2001; McArthur and Howarth, 2004; Fig. 4).

3.3. Trace elemental composition of bulk carbonates

The trace elemental compositions of bulk carbonates are summarized in Table 5 and Figure 4c, d, and e. The Sr concentrations of the acetate-digested carbonate fractions from Site 1171A exhibit a systematic decrease with depth from 1487.58 ppm near the sediment-water interface to 1038.76 ppm at 67.275 mbsf, followed by a gradual increase to 1604.25 ppm at 115.53 mbsf. By comparison, Mg concentrations exhibit an increasing trend with depth, from

411.04 ppm at 0.735 mbsf to 683.29 ppm at 49.635 mbsf, followed by a decrease (379.97 ppm at 115.53 mbsf). The trace elemental ratios of bulk carbonates (mmole/mole) display similar trends with depth. The Sr/Ca ratios of the digested carbonates decrease from 1.70 at 0.735 mbsf to 1.19 at 67.135 mbsf, followed by an increase to 1.83 at 115.53 mbsf. The Mg/Ca ratio exhibits a general increase from 1.69 (0.735 mbsf) to 2.81 (49.635 mbsf), followed by a subsequent decrease to 1.56 at 115.53 mbsf. The Na concentration and Na/Ca ratio of bulk carbonates at Site 1171A, on the contrary, continues to decrease with depth from 1059.84 ppm and 4.61 (at 0.735 mbsf) to 370.14 ppm and 1.61 (115.53 mbsf), respectively.

Bulk carbonates from sediments below ~120 mbsf (at Site 1171C) show very little change in Sr concentration between 125.16 and 239.96 mbsf (1355.53 and 1419.33 ppm respectively) and Sr/Ca ratios (1.50 and 1.62, respectively). However, at 258.46 mbsf both values of Sr concentration and Sr/Ca ratio decrease sharply (1092.75 ppm and 1.25, respectively). Similarly, the Mg concentration and Mg/Ca ratio of bulk carbonates remain similar between 125.16 and 239.96 mbsf (440.24 and 404.78 ppm, 1.81 and 1.67 mmole/mole, respectively) although both values increase to 600.16 ppm and 2.47, respectively at 258.46 mbsf. The Na/Ca ratio and Na concentration below 120 mbsf (in Hole C) decrease between 125.16 and 239.96 mbsf (2.20 and 505.23 ppm to 1.170 and 269.66 ppm, respectively). However, at 258.46 mbsf both bulk carbonate Na/Ca ratio and Na concentration increase to 391.87 ppm and 1.70, respectively.

4. Discussion

The current study investigates bulk carbonate diagenesis in a marine sedimentary section (ODP 1171) that was drilled with the purpose of reconstructing past climate (Exon et al., 2001a). Despite the intention that this site would “provide a carbonate sequence unaffected by dissolution” (Exon et al., 2001a), and thus post-depositional alteration, previous work has shown unambiguous evidence of substantial diagenetic alteration in Site 1171 (Fantle, 2015). This alteration, Fantle (2015) suggested, was driven to some extent by pore fluid advection in the system.

While previous work focused on constraining the rate of carbonate recrystallization at Site 1171, the current study focuses on the impact of recrystallization on bulk carbonate $\delta^{26}\text{Mg}$, given the paucity of data to date from marine carbonate sections (Higgins and Schrag, 2012). Marine carbonate $\delta^{26}\text{Mg}$ is a promising tool for reconstructing paleo-seawater $\delta^{26}\text{Mg}$ variability and, by extension, the global Mg cycle, yet our understanding of how diagenesis operates in a range of environments is incomplete. Fantle and Higgins (2014) documented the overprinting of Mg isotopic composition in shallow marine carbonates, and provided a simple model framework for such studies. This project aims to build on this work by quantifying the diagenetic effect in a relatively open pelagic carbonate section (i.e., one influenced by advection).

The current study is motivated by a desire to understand the effect of system conditions on diagenetic effects, with the overall goal of improving proxy-based reconstructions of the past. Accordingly, the ensuing discussion addresses the following topics:

- How does bulk carbonate $\delta^{26}\text{Mg}$ in an open marine system compare to $\delta^{26}\text{Mg}$ in a relatively closed system?
- Are the fractionation factor (α_{s-f}^{diag}) and partition coefficient (K_{Mg}) associated with diagenesis constrained by studies of relatively closed systems applicable to more open systems?
- Could $\delta^{26}\text{Mg}$ be a useful tool for fingerprinting diagenesis?

Such questions are significant, as their answers directly impact such issues as site selection for proxy-based reconstructions, the interpretation of inter-site differences in proxy records, archive selection (i.e., picked tests vs. bulk sediment), and the interpretation of the temporal evolution of carbonate chemistry. More broadly, the answers to these questions inform whether or not $\delta^{26}\text{Mg}$ is a reliable proxy, and under what conditions this may or may not be so.

Ultimately, the current study makes two key observations that motivate the discussion below: (1) pore fluid $\delta^{26}\text{Mg}$ values increase systematically downcore, while (2) bulk carbonate $\delta^{26}\text{Mg}$ values decrease systematically downcore. Generally, both trends are similar to those observed at Site 807, Hole A (Higgins and Schrag, 2012), most notably in the upper ~100-150 m in which there is a rapid decrease in bulk carbonate $\delta^{26}\text{Mg}$ at both sites. At a more detailed level, the pore fluid and bulk carbonate $\delta^{26}\text{Mg}$ trends at Sites 807 and 1171 vary in significant ways (Fig. 3a-b). The primary discrepancy between pore fluid $\delta^{26}\text{Mg}$ at Sites 807 and 1171 is a decrease in the apparent boundary layer thickness (i.e., the length scale over which pore fluid $\delta^{26}\text{Mg}$ reaches a maximum) at Site 1171, relative to Site 807 (Fig. 3a). This difference is similar to that noted in pore fluid Sr concentration at Sites 1171 and 807 (Fantle, 2015; Fantle and DePaolo, 2006; Fig. 2f), which was previously attributed to the influence of upward advection at Site 1171 (Fantle, 2015). The time-integrated influence of advection on diagenetic alteration is also apparent in bulk carbonate $\delta^{26}\text{Mg}$ values, which decrease drastically from about -2.2‰ to -4.0‰ over ~120 meters at 1171 (~2.0‰ decrease in $\delta^{26}\text{Mg}$). At 807A, by comparison, the $\delta^{26}\text{Mg}$ of the <65 μm fraction only decreases by ~1.0‰ over the uppermost 150 meters of the section.

In the following sections, our observations are used to form hypotheses that are subsequently tested using geochemical and paleontological evidence and numerical simulations. In particular, we present geochemical evidence of the alteration of bulk carbonates and suggest that $\delta^{26}\text{Mg}$ is strongly influenced by diagenesis. We then evaluate the alternate hypothesis that the measured bulk carbonate $\delta^{26}\text{Mg}$ reflects the abundance and species composition of the sediment, concluding that these factors do not account for the observed trends. Finally, we apply a simple reactive transport model to demonstrate the consistency of the hypothesis that diagenesis controls bulk carbonate $\delta^{26}\text{Mg}$, considering model-data comparisons that utilize measured pore fluid and bulk solid geochemical data.

4.1. Geochemical evidence of bulk carbonate diagenetic alteration

The interpretation of a distinguishable diagenetic effect on bulk carbonates at Site 1171 is supported by multiple geochemical datasets, including Sr/Ca, Mg/Ca, Na/Ca, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Thus, we use these datasets to guide our interpretation of the Mg isotope data.

The trends in bulk carbonate geochemistry can be broadly classified by the depth regime at 1171A. Above ~67 mbsf, bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ deviates significantly from contemporaneous seawater $^{87}\text{Sr}/^{86}\text{Sr}$ (McArthur and Howard, 2004), approaching pore fluid $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 4a and b). Over the same depth range, bulk carbonate Sr/Ca decrease from ~1.70 to 1.19 while Sr concentrations decrease from ~1488 ppm to ~1039 ppm; Fig. 4c and d). The $^{87}\text{Sr}/^{86}\text{Sr}$ offset from the seawater curve is reasonably correlated with Sr/Ca ($r^2 = 0.753$; Fig. 5a).

Both Sr/Ca and Sr concentrations are consistent with the preferential loss of Sr from biogenic carbonates during recrystallization (Manheim and Sayles, 1971), though the extent to which this occurs is considerably higher than that inferred at other carbonate-rich sites (e.g., 807A; Fantle and DePaolo, 2006; 2007). Recently, Fantle (2015) suggested that the more open system dynamics at Site 1171 influenced recrystallization rates and that advection maintained local elemental and isotopic disequilibrium (with respect to Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios) between the bulk solid and coexisting pore fluid. Consequently, the Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in bulk carbonates are undeniably altered at Site 1171.

Over the same depth interval described above (<67 mbsf), bulk carbonate Mg/Ca increases from ~1.69 to ~2.66 while Mg concentrations increase from ~411 to ~646 ppm (Fig. 4e and f), the former correlating quite well with both the offset in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the seawater curve ($r^2 = 0.863$, Fig. 5b) and Sr/Ca ($r^2 = 0.846$; Fig. 5c). The correlations imply that the Mg in the bulk carbonates above 67 mbsf is affected by the same process responsible for the observed decrease in Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$. We suggest that this process is diagenetic recrystallization, which appears to increase the Mg content of the bulk solid. This is qualitatively consistent with a partition coefficient greater than one, which can at least partially explain the decrease in pore fluid Mg concentration with depth. This hypothesis is also consistent with a marked decrease in bulk carbonate Na/Ca over the same depth interval (Fig. 4e), a trend that previous work suggests is a consequence of diagenetic recrystallization (Lorens, 1977; Graham et al., 1982; Delaney et al., 1985).

Given the support for the presence of distinguishable and clear diagenetic effects in bulk carbonates, we interpret the Mg isotope trend at Site 1171 primarily as a diagenetic signal. Such a hypothesis is directly supported by the correlations between $\delta^{26}\text{Mg}$ and the offset of bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ from the seawater curve, Sr/Ca, and Na/Ca (Fig. 5d, e, and f), and is also reasonable from the standpoint of the available leverage to alter bulk carbonate Mg concentrations and Mg isotopic compositions. Not only is there leverage in the temperature-dependent partition coefficient (K_{Mg}) between surface seawater (~25°C) and the sedimentary column (~4°C) to alter Mg geochemically, but the low Mg concentration of carbonates makes it more susceptible to alteration by coexisting pore fluids. From an isotopic perspective, there is likely also reasonable leverage in the fractionation factor ($\alpha_{s-f}^{\text{diag}}$) to alter Mg isotopically,

provided that the initial offset in delta values between pore fluid and bulk carbonate is $\sim 1.5\text{‰}$ while the theoretical equilibrium value is about -5.0‰ (~ -0.9950 ; Rustad et al., 2010).

Finally, it should be noted that the carbonate sediments under investigation are not overtly influenced by dolomite or siliciclastics within the *carbonate-rich* portion of the section. There is neither evidence of dolomite in the section based on previous mineralogical studies (Exon et al., 2001b; Robert, 2004b), nor geochemical evidence (i.e., Mg/Ca) from this study for a dolomite influence. In any case, all bulk carbonates were selectively dissolved using a buffered acetic acid solution (pH 4.7), which will not dissolve dolomite. Finally, dolomite is expected to have an isotopic offset from seawater of -1.8 to -2.6‰ (Higgins and Schrag, 2010; Schauble, 2011; Fantle and Higgins, 2014; Mavromatis et al., 2014; Li et al., 2015). If dolomite formation occurred to an extent that impacts our interpretation, the solid should be shifted to markedly higher $\delta^{26}\text{Mg}$ values than the values observed.

With regard to siliciclastics, similar arguments hold. In the carbonate-rich section under consideration, there are simply not many siliciclastics present. Robert (2004b) suggests no more than 2% clay content at 1171 above ~ 260 mbsf, with 0% clay identified at most depths between 260 and 2.55 mbsf. The influence of siliciclastics below ~ 285 mbsf on the geochemistry of the advecting pore fluid was investigated by varying the Mg concentration and isotopic composition at the lower boundary of the modeled interval (Section 4.3). The sensitivities of the pore fluid and bulk carbonate chemistries to the lower boundary suggest that interaction with siliciclastics at depth does not impact our interpretation of a diagenetic control on bulk carbonate $\delta^{26}\text{Mg}$. Moreover, any contribution of Mg from the clay to the measured Mg of the acetic-digested bulk carbonates should exhibit concomitant increase in Al/Ca, Fe/Ca, and Mn/Ca ratios and positive correlations between Al/Ca, Fe/Ca, Mn/Ca, and Mg/Ca. Because we observe neither increases in trace element concentrations nor any positive correlations between these elemental ratios, we conclude that the effect of siliciclastics on bulk carbonate $\delta^{26}\text{Mg}$ at Site 1171 is negligible.

4.2. Effect of abundance and composition of fossil components on bulk carbonates $\delta^{26}\text{Mg}$

Considering the compelling evidence discussed above, we contend that bulk carbonate $\delta^{26}\text{Mg}$ at Site 1171A is controlled primarily by diagenetic recrystallization. There is, however, an alternate hypothesis that must be considered: that initial variability in bulk carbonate $\delta^{26}\text{Mg}$ is influenced by the abundance and species composition of the bulk sediment. The bulk carbonates at Site 1171 are comprised of both foraminiferal tests and nannoplankton fossils, and Mg isotopic variability has been documented to exist in these components. Therefore, it is feasible that the observed downcore variability in the bulk carbonate $\delta^{26}\text{Mg}$ reflects variability in the relative proportion of biogenic calcareous components.

To evaluate this hypothesis, we conducted a smear slide study of the bulk sediments and compiled previously published observations (Exon et al., 2001a; Stickley et al., 2004; Stant et al., 2004). The data suggest significant variability in nannofossil and foraminiferal abundance and assemblages with depth at Site 1171 (Fig. 6a; Supplementary Material, Fig. A3). In the upper ~ 21 m of the section, nannofossil abundance is $\sim 48\%$, increases to $\sim 80\%$ between 21 and 40

mbsf, and remains high ($\sim 80 \pm 10\%$) below 40 mbsf. Though the different resolutions of the two records make them difficult to compare, the bulk carbonate $\delta^{26}\text{Mg}$ and nannofossil abundance trends are similar at 1171, suggesting lower bulk carbonate $\delta^{26}\text{Mg}$ values associated with higher nannofossil abundances. The downcore variability in nannofossil assemblages and foraminiferal abundance are also noted in Fig. 6a.

Previous work has demonstrated that *Emiliania huxleyi* and *Gephyrocapsa oceanica* measured in culture experiments and natural sediments (Ra et al., 2010a; Ra et al., 2010b; Müller et al., 2011) generally have higher $\delta^{26}\text{Mg}$ values (-1.24‰ to -2.61‰ and -1.11‰ to -2.23‰ , respectively) than planktonic foraminiferal tests (-4.0‰ to -5.0‰). This accounts for the high bulk carbonate $\delta^{26}\text{Mg}$ values at the top of Hole A, in which *Emiliania huxleyi* and *Gephyrocapsa oceanica* dominate. The transition to lower $\delta^{26}\text{Mg}$ values below 21 mbsf, however, cannot be explained by a shift in nannofossil abundance or assemblage (Supplementary Material, Fig. A4).

Utilizing our admittedly limited understanding of coccolithophore $\delta^{26}\text{Mg}$ and the relative amount of Mg in benthic and planktonic foraminifera and nannofossils, we estimate $\delta^{26}\text{Mg}$ values for the initial bulk carbonate with depth using an isotopic mass balance approach:

$$\delta^{26}\text{Mg}_{\text{carb}} = \sum \delta^{26}\text{Mg}_i X_i = \sum \delta^{26}\text{Mg}_i \cdot \frac{\text{mass}_i}{\text{mass}_{\text{carb}}} \cdot \frac{[\text{Mg}]_i}{[\text{Mg}]_{\text{carb}}} \quad \text{----(4)}$$

where the subscripts *carb* and *i* refer to the bulk carbonate and the endmember components, respectively. The term X_i refers the mole fraction of Mg in each component, while $[\text{Mg}]_i$ and $[\text{Mg}]_{\text{carb}}$ represent the concentrations (in units of moles/g CaCO_3) of Mg in the endmember components and bulk carbonate, respectively. The terms mass_i and $\text{mass}_{\text{carb}}$ refer to the masses (g CaCO_3) of the endmember components and bulk carbonate, respectively.

The relative proportions of each endmember are constrained by observations of foraminiferal and nannofossil abundance at Site 1171 (Exon et al., 2001a; Stickley et al., 2004; Stant et al., 2004). The proportions of planktonic and benthic foraminifera in the total foraminiferal fraction are estimated based on previous smear slide observation (Exon et al., 2001a). Accordingly, we assume that planktonic foraminiferal tests comprise $\sim 60\%$ of the total foraminiferal fraction, with a normally distributed variability of $\pm 10\%$ based on the uncertainty in the smear slide counting.

Average endmember $\delta^{26}\text{Mg}$ values are assigned for foraminiferal tests and nannofossils based on published measurements of natural samples, and variability assumed to be normally distributed (Supplementary Material, Table A3, Fig. A5). Average Mg/Ca values for foraminiferal tests and nannofossils are determined based on foraminiferal Mg/Ca data from Site 1171 (Shevenell et al., 2004; Shevenell et al., 2008) and coccolith Mg/Ca data from culture experiments (Stoll et al., 2001; Ra et al., 2010a; Ra et al., 2010b; Müller et al., 2011; Blanco-Ameijeiras et al., 2012; Müller et al., 2014). The uncertainties for all assumed parameters are propagated through the mass balance calculation utilizing a Monte Carlo approach.

The resulting mass balance calculation illustrates that the $\delta^{26}\text{Mg}$ of bulk carbonate should increase with depth (Fig. 6b), the opposite of the measured trend. This suggests that the observed

trend in $\delta^{26}\text{Mg}$ with depth is not explained in any reasonable manner by species composition, and likely reflects an integrated signal of diagenesis.

4.3. Model exploration of bulk carbonate diagenesis

We have proposed that the primary control on bulk carbonate $\delta^{26}\text{Mg}$ at 1171 is diagenetic recrystallization and that variability in species abundance and composition do not explain the observed depth trend. What remains to be evaluated is whether this hypothesis is consistent with pore fluid $\delta^{26}\text{Mg}$ and, if so, what this implies about the potential for recrystallization to alter the $\delta^{26}\text{Mg}$ proxy. Our suggestion is that the diagenetic overprint can be quite substantial in some systems; in these cases, the primary proxy signal must either be deconvolved from the diagenetic signal or $\delta^{26}\text{Mg}$ reenvisioned as an indicator of the extent of diagenesis in marine carbonates.

To address these questions, we utilize a one-dimensional depositional reactive transport model (described in the Appendix), such as has been described previously (Fantle and DePaolo, 2007; Fantle et al., 2010; Fantle, 2015). The primary objective of the modeling was to test the hypothesis that the initial bulk carbonate $\delta^{26}\text{Mg}$ (derived from mass balance) and the measured pore fluid $\delta^{26}\text{Mg}$ values are consistent with diagenetic recrystallization as a controlling process. The modeling was conducted given reasonable estimates for the partition coefficient of Mg in calcite (K_{Mg}), the fractionation factor associated with recrystallization ($\alpha_{s-f}^{\text{diag}}$), the diffusion coefficient (D_{Mg}), and the pore fluid advection velocity (v). Recrystallization rates previously constrained by pore fluid Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ are utilized, though it should be noted that enhanced recrystallization was suggested to occur over the first 1 Ma of deposition (Fantle, 2015). In the discussion that follows, enhanced recrystallization is not considered explicitly, though simulations conducted utilizing fast recrystallization rates in sediments younger than 1 Ma do not alter our conclusions. Sensitivity tests were conducted to help constrain the limits of our interpretations (Supplementary Material Section A1.1; Figs. A6 to A13).

Assuming recrystallization rates $\leq 7\%/ \text{Ma}$ ($R = 0.07e^{-\text{age}/6.6}$), the model generally reproduces the downcore trends in the pore fluid and bulk carbonate $\delta^{26}\text{Mg}$ and Mg concentrations in Hole A, given a partition coefficient (K_{Mg}) between 1.5 and 2.0 and a diagenetic fractionation factor ($\alpha_{s-f}^{\text{diag}}$) between 0.9950 and 0.9955 (Fig. 7). Although the estimate for K_{Mg} is lower than experimentally derived values (Mucci and Morse, 1983; Oomori et al., 1987; Huang and Fairchild, 2001), it is comparable to the range of K_{Mg} values required to model Mg in other marine sedimentary systems (Fantle and DePaolo, 2006; Higgins and Schrag, 2012; Fantle and Higgins, 2014). The $\alpha_{s-f}^{\text{diag}}$ used (0.9950 to 0.9955) is consistent with theoretical constraints on the equilibrium fractionation factor ($\alpha_{s-f}^{\text{diag}} = 0.9950$; Rustad et al., 2010) and the fractionation factor associated with the diagenesis of platform carbonates (Fantle and Higgins, 2014).

The modeling exercise suggests that the characteristic increase in pore fluid $\delta^{26}\text{Mg}$ observed in multiple carbonate-rich sections is a feature that is due to recrystallization. At Site 1171, this increase in pore fluid $\delta^{26}\text{Mg}$ coincides with increases in both bulk carbonate Mg

concentrations (~5 to 10 mmole/kg) and Mg/Ca ratios (~1.3 to 1.5 mmole/mole) and a decrease in $\delta^{26}\text{Mg}$ (0.8‰ to 2.0‰), all of which appear to be diagenetic in origin (Fig. 8). As has been suggested previously (Fantle, 2015), diagenetic recrystallization can therefore significantly modify the long-term trends in carbonate $\delta^{26}\text{Mg}$, as well as the Mg/Ca, over hundreds of meter length scales.

However, the modeling exercise also indicates a clear discrepancy between the model predictions and measured data deeper in the section, with regard to both elemental and isotopic compositions (Mg/Ca, Sr/Ca, and $^{87}\text{Sr}/^{86}\text{Sr}$). There are multiple hypotheses that may explain the discrepancies, including multiple rate regimes, temporally variable lower boundary conditions or pore fluid chemistry, and a more variable initial solid composition than assumed based on the micropaleontology. Below, we briefly explore what we consider to be the most likely scenarios.

We propose two hypotheses to explain the discrepancy between the model and the elemental chemistry, $\delta^{26}\text{Mg}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ of the sediments below ~70 mbsf. The first is that the solid chemistries (deeper than ~70 mbsf) prior to the most recent episode of recrystallization differ from what we assume. If we account for this with respect to the elemental ratios, and take into account how the current reactive regime should alter the bulk carbonates, then the initial solid Sr/Ca would increase with depth, the Mg/Ca would decrease with depth, and the Na/Ca would not require any significant change with depth. With respect to $\delta^{26}\text{Mg}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, the former would not require any change from our assumption, while $^{87}\text{Sr}/^{86}\text{Sr}$ would have to be more radiogenic than contemporaneous seawater.

Such an explanation is surely feasible, but is difficult to evaluate. It is logical to posit that the change in the initial bulk carbonate chemistry was a geochemical consequence of a previous diagenetic regime, and does not reflect temporal variations in seawater chemical. In other words, there were at least two diagenetic regimes at Site 1171, which geochemically altered the bulk carbonates in different ways. Because this previous regime is likely unique to Site 1171, it is difficult to compare Site 1171 to existing nearby sites in order to seek support for this hypothesis. If this hypothesis *is* valid, it would require the pore fluid during the previous diagenetic regime to have substantially higher Sr/Ca, and lower Mg/Ca, relative to modern seawater, as well as a higher $^{87}\text{Sr}/^{86}\text{Sr}$. In theory, such a fluid could be sourced from the siliciclastics below the carbonate section.

Alternatively, it is possible that carbonates at Site 1171 are chemically impacted by both recrystallization and partial (net) dissolution. In this scenario, carbonates below ~70 mbsf would have been initially recrystallized and altered in a manner similar to the models presented herein. Subsequently, an episode of partial dissolution overprinted the geochemical signal of diagenetic recrystallization in the lowermost sediments. Such a scenario assumes that partial dissolution preferentially acts on higher solubility carbonate(s), in this case relatively high Mg and high Na. In order to be consistent with the data, the carbonates impacted by dissolution would also have to be relatively high $\delta^{26}\text{Mg}$, low Sr, and high $^{87}\text{Sr}/^{86}\text{Sr}$. This suggests at least two sedimentary components were impacted: a pristine endmember (assumed to be high Mg/Ca and high Na/Ca) and a diagenetic endmember (assumed to be low Sr/Ca and high $^{87}\text{Sr}/^{86}\text{Sr}$). The latter must have

had $^{87}\text{Sr}/^{86}\text{Sr}$ higher than contemporaneous seawater, perhaps due to the dissolution of clastic terrigenous sediment at depth.

The partial dissolution hypothesis is supported by observations of net dissolution in Pliocene and Miocene sediments at Site 1171 (Exon et al., 2001b). It is inferentially supported by the chemical similarity of Hole C carbonates to those at the bottom of Hole A: the deeper sediments at Hole C and the overlying sediments at Hole A have similar Sr/Ca, Mg/Ca, and Na/Ca ratios and Mg isotopic compositions. This similarity supports the presumption that partial dissolution was driven from below and that carbonates in Hole C were likewise affected by this process. The siliclastics generally have much lower carbonate contents than the overlying sediments, which could be at least in part a result of dissolution. In all fairness, however, the chemical similarity of the Hole C carbonates could also be considered supportive of the sequential diagenetic regimes hypothesis.

Ultimately, it is simply not possible to distinguish unambiguously between the partial dissolution hypothesis and the sequential diagenetic regimes hypothesis. If the partial dissolution hypothesis is valid, however, then the immediate implication is that $\delta^{26}\text{Mg}$ is not significantly altered by partial dissolution, at least not at the scale of our observations. It would then follow logically that Mg/Ca and $\delta^{26}\text{Mg}$ may be decoupled by different diagenetic processes in the sedimentary column, which is a critical observation when interpreting the two proxies together.

Finally, it is impossible to explain bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ without invoking a temporal change in the Sr geochemistry of the advecting fluid (i.e., the fluid composition at the lower boundary). In order to explain bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ in a recrystallizing diagenetic regime, this fluid must have had a lower $^{87}\text{Sr}/^{86}\text{Sr}$ at the lower boundary at some point in the past, compared to the current lower boundary ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.70865$). Because of the trade-off between $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentration of the fluid, it is difficult to constrain the Sr geochemistry of this fluid uniquely. Assuming a Sr concentration $< 1000 \mu\text{mol/kg}$, the lower boundary $^{87}\text{Sr}/^{86}\text{Sr}$ must be < 0.708 . If the fluid generated at the lower boundary has a Sr concentration $> 1000 \mu\text{mol/kg}$, then the bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ data can be explained by a lower boundary that has a $^{87}\text{Sr}/^{86}\text{Sr}$ between 0.706 and 0.708 between 3.5 and 2.5 Ma (Supplemental Material, Fig. A13), followed by an increase to the current value of 0.70865. If the $^{87}\text{Sr}/^{86}\text{Sr}$ at the lower boundary was ~ 0.710 prior to the decrease at 3.5 Ma, then this would explain bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ in Hole A in its entirety without having to call upon partial dissolution of an isotopically heterogeneous, recrystallized endmember (as mentioned above).

The analysis presented above is important to undertake, because it suggests that the geochemical snapshot of pore fluid chemistry that is taken at the time of sampling may not in all cases be appropriate for all times. Sedimentary systems are long-lived and dynamic, and these dynamics may be imparted on the geochemistry of carbonates. Because carbonate chemistry offers an invaluable window into the past, we must understand and quantify diagenetic effects in a range of different environments to elucidate the past.

4.4. Implications for the application of geochemical proxies in picked archives

The current study focuses on the measurement of bulk sediment in order to quantify the diagenetic effect on $\delta^{26}\text{Mg}$. Bulk sediment is a heterogeneous mixture of various biogenic carbonate components, which likely have different reactivities that are a function of surface area, small-scale porosity and microstructure, mineralogy, chemical composition, and/or morphology. When we select individual components, such as foraminiferal tests, from bulk sediments in order to reconstruct the past, we sub-sample this heterogeneous assemblage out of necessity. In some cases, the motivation for such sub-sampling is to avoid diagenetic effects and in other cases it is dictated by limitations of specific analytical procedures.

Our study suggests that preferential sampling of a heterogeneous substrate may generate spurious $\delta^{26}\text{Mg}$ proxy records. It is plausible to assume that all components react to a certain extent in the sedimentary column, and that this extent cannot be determined with certainty for any given component. It then stands to reason that the selection of a given material as a proxy archive that is predicated on species, for instance, and not integrated reaction represents a random sampling of the heterogeneous substrate. This proposition does not consider the possibility that species identity (or some other equally useful identifier) allows geochemists to select components that are inherently less altered. While this may be a valid scenario, evidence in support of this contention is not abundantly clear. Accordingly, we presume random sampling simply to make a general point regarding the potential impact of the sub-sampling of a heterogeneous proxy archive on proxy-based reconstructions.

To illustrate this concept, and its implications for Mg isotope-based reconstructions, a Monte Carlo simulation is presented in which a population of particles at each depth interval is assigned a range of $\delta^{26}\text{Mg}$ values, dictated by the difference between our calculated and measured $\delta^{26}\text{Mg}$ curves (Fig. 6b). The distribution is assumed to be a gamma distribution (Fig. 9a), uniquely determined for each depth, the mean of which is identical to the measured bulk sediment. From 5000 datums in this distribution, four “datasets” are randomly selected, downsampled in the depth regime ($n=25$) to reflect a realistic dataset, and plotted as a function of depth (Fig. 9b).

The results suggest that a random sampling of a heterogeneous substrate, as described above, has the potential to generate Mg isotope records that are not representative of either the initial or final states. Instead, the sub-sampled datums fall between the two records. Interestingly, the randomly sub-sampled trends can appear, in some cases, to have structure that could be interpreted as real temporal variability. In other words, the random sampling does not always exhibit itself as outliers that are easily discernable from an average trend. Again, this interpretation is predicated on the assumption that all components in the sediment react to some extent and that the distribution is not bimodal (i.e., that some components of the bulk sediment are substantially less (or un-) reactive relative to others). If this is true, then this example calculation highlights the value that bulk sediment studies can have in providing geochemical content for the interpretation of proxy data produced from picked components such as foraminiferal tests and nannofossils.

Additionally, our analysis of the diagenetic shift in bulk carbonate $\delta^{26}\text{Mg}$ suggests a systematic ~ 1.3 mmole/mole increase in bulk carbonate Mg/Ca ratios at Site 1171 over ~ 33 Ma. Because foraminiferal tests contribute $\sim 50\%$ of the total Mg to the bulk carbonate sediment, it stands to reason that the measured bulk carbonate trend reflects alteration of the foraminiferal fraction to some degree. As a consequence, the paleo-sea surface temperatures derived from foraminiferal Mg/Ca (e.g., Lea et al, 1999; Lear et al., 2000; Nürnberg et al., 1996; Martin et al, 2002; Dekens et al., 2002; Anand et al., 2003) may be overestimated at this particular site by as much as $\sim 14^\circ\text{C}$ (Fig. 6c).

More generally, the analysis above hints at mechanisms that can explain apparent discrepancies between proxy records that share common controlling parameters (see Fantle, 2015 for additional discussion). Perhaps the best example is the constraint on temperature offered by Mg/Ca and $\delta^{18}\text{O}$. These tools have been used in a complementary manner to solve for unknowns in an underdetermined system (i.e., solving for seawater $\delta^{18}\text{O}$ assuming that Mg/Ca-based temperatures are robust). In some cases, the disagreement between Mg/Ca and $\delta^{18}\text{O}$ has even generated alternate hypotheses regarding the fundamental controls on foraminiferal Mg/Ca (e.g., Billups and Schrag, 2003).

While such approaches are useful and appropriate in some systems, they can be inappropriate in systems that are considerably impacted by diagenesis. This is especially true considering the differential leverage of Mg and O to alter in the sedimentary column. The results of this study indicate not only that diagenetic alteration of Mg is sizeable, but also suggests that alteration can vary considerably from site to site. Accurate interpretations of the past, therefore, appear to require fundamental, quantitative constraints on diagenesis on a site by site basis.

Two critical outstanding questions that remain to be answered are how the diagenetic alteration of bulk sediment (1) occurs mechanistically and (2) is accommodated in a heterogeneous sediment. Regarding the former, dissolution-reprecipitation is the most obvious candidate and abundant evidence exists for the operation of this process in marine carbonate sediments. Growth-related intra-test heterogeneity in foraminiferal Mg/Ca ratios (e.g., Eggins et al., 2003; Eggins et al., 2004) may drive such reactions at small spatial scales, with preferential dissolution of regions with elevated Mg/Ca and reprecipitation of low Mg/Ca carbonate. In this case, one key question when dealing with picked proxy archives is the length scale over which reprecipitation occurs. If precipitation is not local, then high fidelity material may be recovered from the sediment. If reprecipitation occurs local to the dissolving particle, and the altered material is not physically or chemically separable from the high fidelity material, then diagenesis can impact proxy records. Relatedly, recent laboratory work suggests that minerals can undergo extensive atom exchange with the surrounding aqueous medium over extremely short time scales (e.g., Curti et al., 2010; Lestini et al., 2013). In some cases, this exchange (termed “atom exchange”) seems to occur without any overt change in the mineral phase or morphology of the mineral (see recent review by Gorski and Fantle, 2017).

If either local dissolution-reprecipitation or stable mineral recrystallization operates in the sedimentary column, then this has significant implications for the assumption of pristine,

cleanable tests. Even in cases in which reprecipitation does not occur local to the test, dissolution may still discriminate elementally or isotopically via preferential dissolution of more soluble (and perhaps isotopically distinct) Mg-rich carbonates. In addition, though traditionally held to be too slow to be relevant at low temperatures, solid-state diffusion may operate over million-year time scales in defect-rich biogenic carbonates (Davis et al., 1987; Stipp et al., 1992; Stipp et al., 1998; Watson, 2004). In this case as well, alteration occurs at the individual test level and has the potential to impact picked proxy archives.

5. Conclusions

Isotopic and geochemical data from ODP Site 1171 (Holes A and C) demonstrate the effects of diagenetic recrystallization on bulk carbonate $\delta^{26}\text{Mg}$, which allows for an evaluation of the potential of carbonate $\delta^{26}\text{Mg}$ to act as a proxy for the secular variation of seawater $\delta^{26}\text{Mg}$. At Site 1171, the $\delta^{26}\text{Mg}$ of bulk carbonates decrease by a considerable ~ 0.8 to 2.0‰ over ~ 120 meters. In the same sediments, $^{87}\text{Sr}/^{86}\text{Sr}$ deviates significantly from contemporaneous seawater, while Sr/Ca and Na/Ca ratios decrease and Mg/Ca ratio increases. These geochemical data support the hypothesis that calcite recrystallization controls downcore variability in bulk carbonate $\delta^{26}\text{Mg}$, a hypothesis that is also supported by reactive transport modeling.

Ultimately, this study demonstrates that diagenetic recrystallization of carbonate sediments can substantially impact the concentrations and isotopic compositions of trace elements (e.g., Mg, Sr, B). Recrystallization can cause systematic biases in proxy records that influence interpretations from site to site, and between proxies that are influenced by common factors (e.g., Mg/Ca and $\delta^{18}\text{O}$ as $f(\text{temperature})$). Given the potential magnitude of diagenetic effects, quantifying alteration is critical to any proxy-based interpretation of the past. Studies of bulk carbonates provide important context to interpretations based on picked components of the bulk sediment. Finally, the sensitivity of carbonate $\delta^{26}\text{Mg}$ to diagenetic alteration suggests that the $\delta^{26}\text{Mg}$ may be useful for fingerprinting diagenesis, especially in studies in which bulk carbonate is the primary proxy archive.

Acknowledgements

This work was supported by NSF Grant EAR-OCE-1154839 to M.S.F. The authors would like to thank Prof. Timothy J. Bralower for assistance with imaging and identification of nannofossils in smear slides. The authors also sincerely thank three anonymous reviewers and associate editor Silke Severmann for constructive comments that improved the original manuscript. This research used samples and data provided by the Ocean Drilling Program (ODP).

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Appendix: Description of the reactive transport model

The reactive transport model used in the current study to interpret the Mg isotope data is a one-dimensional depositional model in which the sedimentary column grows with time and samples contemporaneous seawater as pore fluid upon deposition (Richter and DePaolo, 1987; Richter and DePaolo, 1988; Richter and Liang, 1993; Richter, 1996; Fantle and DePaolo, 2006; Fantle and DePaolo, 2007; Fantle, 2015). The basic assumptions made in this model are:

1. The solid is monominerallic (i.e., calcite);
2. The modeled reaction is calcite recrystallization, in which the dissolution and precipitation mass fluxes of Ca are equal (i.e, no net gain or loss of calcite); and
3. Compaction is insignificant ($V=0$).

For a monomineralic sedimentary section the temporal evolution of the elemental concentration in the fluid ($\frac{\partial C_{pf}}{\partial t}$) and the solid ($\frac{\partial C_s}{\partial t}$) are:

$$\frac{\partial C_{i,pf}}{\partial t} = D_i \frac{\partial^2 C_{i,pf}}{\partial z^2} - v \frac{\partial C_{i,pf}}{\partial z} + RM (C_{i,s} - K_i C_{i,pf}) \quad [A1]$$

$$\frac{\partial C_{i,s}}{\partial t} = -R(C_{i,s} - K_i C_{i,pf}) \quad [A2]$$

where C_i is the concentration of element i in the pore fluid (pf) and solid (s), D_i is the tortuosity-corrected diffusion coefficient of element i in sedimentary column (m^2/Ma); R is the recrystallization rate of the solid (Ma^{-1}), K_i is the equilibrium partition coefficient of element i between solid and pore fluid, M is the solid/fluid mass ratio ($= \rho_s (1-\phi)/\rho_f \phi$; where ρ is density and ϕ is porosity), z is depth, and v is the pore fluid advection velocity (m/Ma).

The 1-dimensional spatial reference frame is defined such that $z=0$ at the sediment-basement interface and z increases in the upward direction. By this convention, upward fluid advection is positive and downward advection is negative. The rate of recrystallization (R) is formulated as a function of sediment age as suggested by previous studies of carbonate ooze diagenesis (Richter and DePaolo, 1987; Richter and DePaolo, 1988; Richter, 1993, 1996; Richter and Liang, 1993; Fantle and DePaolo, 2006; and DePaolo, 2007; Fantle, 2015):

$$R(\text{age}, Ma) = \alpha + \beta \cdot e^{-\text{age}/\gamma} \quad [A3]$$

where, $\alpha + \beta$ is the initial (age=0) recrystallization rate, and γ reflects the rate at which the total rate approaches the long-term rate (α).

The equilibrium partition coefficient (K_i) of the element of interest between the pore fluid and solid is defined as the ratio of the concentration of the element in the solid (C_s) to that in the fluid (C_f):

$$K_i = \frac{C_{i,s}}{C_{i,f}} \quad [A4]$$

For reactions that involve mass dependent isotopic fractionation, the fractionation factor between two stable nuclides j and k of element i is expressed as:

$$\alpha_{s-f}^{diag} = \frac{j_{K_i}}{k_{K_i}} \quad [\text{A5}]$$

In model used herein, K_{Mg} is formulated as described in Fantle et al. (2006):

$$K_{Mg/Ca}^{calcite} = \frac{(Mg/Ca)_{calcite}}{(Mg/Ca)_{fluid}} = \frac{(m_{Mg})_{calcite}}{(m_{Mg})_{fluid}} \cdot \frac{(m_{Ca})_{fluid}}{(m_{Ca})_{calcite}} \quad [\text{A6}]$$

$$K_{Mg/Ca}^{calcite} = \frac{(Mg/Ca)_{calcite}}{(Mg/Ca)_{fluid}} = K_{Mg} \cdot \frac{(m_{Ca})_{fluid}}{(m_{Ca})_{calcite}} \quad [\text{A7}]$$

Or:

$$K_{Mg}^n = K_{Mg}^m \cdot \frac{m_{Ca}^{fluid,n}}{m_{Ca}^{fluid,m}} \quad [\text{A8}]$$

where m and n are two different depths. The mass of any element i in calcite and pore fluid are represented by the terms $(m_i)_{calcite}$ and $(m_i)_{fluid}$, respectively. This formulation for K_{Mg} requires the Ca concentration in pore fluids from different depths and a reference $K_{Mg}^{calcite}$ (at the reference depth m) in order to calculate K_{Mg} at each grid point in the model. Unlike Sr, the reference value of the K_{Mg} cannot be calculated from the $[Mg^{2+}]$ of deeper pore fluids and carbonates because the pore fluid $[Mg^{2+}]$ are not expected to be in steady state with the co-existing carbonates in the sedimentary column due to its large diffusive reaction length scale ($\sim \sqrt{D_i/RMK_i}$; Fantle and DePaolo, 2006).

The diffusion coefficient of element i (D_i) is a function of porosity and D^o (the diffusion coefficient of the element at infinite dilution):

$$D_{Mg} = \frac{D^o}{\theta^2} \quad [\text{A9}]$$

where θ^2 , the tortuosity, is estimated from porosity (ϕ) by: $\theta^2 = 1 - \ln(\phi^2)$. The diffusion coefficient of Mg at infinite dilution (D^o) is calculated from the temperature profile of the borehole using:

$$D^o = M_1 + M_2 \cdot T \quad [\text{A10}]$$

where M_1 and M_2 are constants taken from the literature ($T, ^\circ\text{C}$; Boudreau, 1997).

Figure captions

Fig. 1. (a) Locations of Ocean Drilling Program Sites 1171 and 807A and (b) simplified lithostratigraphic sections of ODP Site 1171 (Holes A, C, and D), including major lithological units, wt. % CaCO_3 , porosity, and bore hole temperature as a function of depth (mbsf). Data are from Exon et al. (2001a); depositional hiatuses are denoted by .

Fig. 2. Chemistry of ODP Site 1171 in terms of (a) wt. % CaCO_3 of bulk sediments, as well as pore fluid (pf) (b) pH, (c) alkalinity, (d) calcium concentration, (e) magnesium concentration, (d) strontium concentration, (f) sulfate concentration and (g) ammonium ion concentration as a function of depth (Exon et al., 2001b).

Fig. 3. Magnesium isotopic composition ($\delta^{26}\text{Mg}$, in the DSM3 scale) of (a) pore fluids and (b) bulk carbonates from ODP Site 1171 (this study) and from ODP Site 807A (Higgins and Schrag, 2012). (c) Three-isotope plot ($\delta^{25}\text{Mg}$ vs. $\delta^{26}\text{Mg}$) illustrating measured data ($m=0.518 \pm 0.005$) relative to the mass dependent fractionation line ($m=0.520$).

Fig. 4. (a) Strontium isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}$) and (b) depth-detrended $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of bulk carbonates and pore fluids from ODP Site 1171, as well as the global seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve (McArthur and Howarth, 2004) as a function of depth. Depth profiles of bulk carbonate (c) molar Sr/Ca, (d) molar Mg/Ca, and (f) molar Na/Ca from Site 1171 (Holes A and C). Solid blue and gray circles in Figure (a) and (b) represent data measured in this study and previously (Fantle, 2015), respectively. Solid dark blue circles and light blue squares in Figure (c), (d), and (e) represent bulk carbonates from Holes A and C, respectively.

Fig. 5. Cross plots relating the percent deviation of bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ from the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve (McArthur and Howarth, 2004) and (a) molar Sr/Ca and (b) molar Mg/Ca. Cross plots of bulk carbonate (c) Mg/Ca and Sr/Ca ratios, (d) $\delta^{26}\text{Mg}$ and deviation of $^{87}\text{Sr}/^{86}\text{Sr}$ from the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve, (e) $\delta^{26}\text{Mg}$ and Sr/Ca, and (f) $\delta^{26}\text{Mg}$ and Na/Ca. The dark and light blue symbols represent samples above and below 67 mbsf. The circles and squares signify Hole A and Hole C sediments. The linear correlation is derived using the samples above 67 mbsf; outliers are marked with black open circles.

Fig. 6. (a) Variation of the nannofossil (closed symbols) and foraminiferal (open symbols) percent abundance in bulk carbonates with depth at ODP Site 1171. Grayscale shading indicates different nannofossil assemblages inferred from smear slide observations in this study (Supplementary Material, Fig. A3) and previously (Exon et al., 2001b; Stickley et al., 2004). (b) The measured and expected (calculated using mass balance) down-hole trends in bulk carbonate $\delta^{26}\text{Mg}$ at Site 1171, including the standard deviation (gray area) of the calculated $\delta^{26}\text{Mg}$. (c) Initial (calculated using mass balance) and final (model derived)

Mg/Ca of bulk carbonates and sea surface temperatures derived using various published temperature-foraminiferal Mg/Ca calibrations.

Fig. 7. Model simulations of recrystallization at Site 1171, with comparisons to measured (a) pore fluid $[Mg^{2+}]$, (b) pore fluid $\delta^{26}Mg$, (c) bulk carbonate Mg concentration, and (d) bulk carbonate $\delta^{26}Mg$. All model runs assumed a depth-invariant $D_{Mg} = 6900 \text{ m}^2/\text{Ma}$. The upper boundary $[Mg^{2+}]$ and $\delta^{26}Mg$ are fixed to the modern seawater values ($[Mg^{2+}] = 53.1 \text{ mmole/kg}$; $\delta^{26}Mg = -0.84\text{‰}$). The $[Mg^{2+}]$ of the lower boundary is assumed to be 40 (model i) and 43 mmole/kg (model ii to vi). The $\delta^{26}Mg$ of lower boundary and advecting fluid is assumed to be -0.4‰ (model i to v) and -0.55‰ (model vi). Open and closed symbols represent measured pore fluids and bulk carbonates, respectively. The solid gray and colored dashed and dotted lines numbered (i) to (vi) indicate different model scenarios in which initial conditions and/or rates have been changed. The subscripts “pf” and “carb” are shorthands for pore fluid and bulk carbonate.

Fig. 8. Modeled effects of diagenetic calcite recrystallization on bulk carbonate (a) $\delta^{26}Mg$ and (b) Mg concentration at Site 1171. Model parameters utilized: reaction rate expression, $R = 0.07 * e^{-age/6.6}$, $v = 250 \text{ m/Ma}$, and $D_{Mg} = 6900 \text{ m}^2/\text{Ma}$. Open and solid circles indicate the measured pore fluid and bulk carbonates, respectively. The solid gray lines indicate initial conditions and model results are shown by solid black and dotted green lines. The subscript “carb” is shorthand for “bulk carbonate”.

Fig. 9. Monte Carlo simulations of Mg isotope proxy records, assuming (a) a gamma distribution unique to each depth ($shape=1$, $scale$ is proportional to permil difference between final and initial $\delta^{26}Mg$ curves). (b) Four depth trends randomly selected from the 5000 datums at each depth interval; a subset of the Monte Carlo dataset at 25 depths is used to represent a typical Mg isotope dataset from such a section. In (b), the assumed final (solid curve) and initial (dashed curve) bulk sediment $\delta^{26}Mg$ curves are noted.

Tables

Table 1. Mg isotopic compositions of seawater and standards measured in this study

Samples /Standards	$\delta^{26}\text{Mg}$ (‰, DSM3) Measured	2SD	n	$\delta^{26}\text{Mg}$ (‰, DSM3) Accepted
FZT Mg-Std	-2.26	0.06	25	-2.28
Cambridge-1	-2.59	0.07	30	-2.58
Modern seawater	-0.81	0.05	5	-0.84

Table 2. Magnesium isotopic composition of pore fluids from ODP Site 1171

Sample Core-section interval (cm)	Depth mbsf ^a	$\delta^{26}\text{Mg}$ (‰, DSM3)	2 σ ‰	$\delta^{25}\text{Mg}$ (‰, DSM3)	2 σ ‰
<i>Leg 189 Site 1171A-</i>					
1H-1W(145-150)	1.45	-0.72	0.08	-0.36	0.03
2H-3W(140-150)	11.55	-0.62	0.07	-0.32	0.02
3H-3W(140-150)	21.05	-0.67	0.06	-0.35	0.02
4H-3W(140-150)	30.55	-0.62	0.08	-0.32	0.01
5X-2W(140-150)	40.05	-0.56	0.09	-0.28	0.05
6H-3W(145-150)	49.55	-0.53	0.03	-0.28	0.05
9H-3W(140-150)	78.0	-0.52	0.06	-0.27	0.05
10H-3W(140-150)	87.5	-0.55	0.08	-0.28	0.05
11H-3W(140-150)	97.0	-0.58	0.10	-0.31	0.05
14X-2W(140-150)	117.7	-0.61	0.10	-0.31	0.06
<i>Leg 189 Site 1171C-</i>					
17X-3W(140-150)	148.5	-0.52	0.09	-0.27	0.04
20X-3W(140-150)	177.3	-0.43	0.02	-0.22	0.01
23X-3W(140-150)	205.9	-0.58	0.10	-0.30	0.03
26X-3W(140-150)	234.7	-0.52	0.10	-0.28	0.04
29X-3W(140-150)	262.9	-0.39	0.03	-0.19	0.03

^a As reported in Exon et al. (2001b)

Table 3. Magnesium isotopic composition of bulk carbonates from ODP Site 1171

Sample Core-section interval (cm)	Depth mbsf ^a	Age Ma ^b	$\delta^{26}\text{Mg}$ (‰, DSM3)	2σ ‰	$\delta^{25}\text{Mg}$ (‰, DSM3)	2σ ‰
<i>Leg 189 Site 1171A-</i>						
1H-1W(73-74)	0.735	0.03	-2.23	0.05	-1.10	0.02
1H-3W(73-74)	3.73	0.22	-2.72	0.08	-1.41	0.04
3H-4W(3-4)	21.145	1.50	-2.26	0.09	-1.16	0.04
4H-4W(3-4)	30.635	2.46	-3.56	0.09	-1.83	0.08
5H-4W(3-4)	40.135	3.55	-3.36	0.04	-1.72	0.04
6H-4W(3-4)	49.635	4.94	-3.16	0.05	-1.63	0.04
8H-4W(3-4)	67.275	6.52	-3.98	0.04	-2.06	0.03
11H-4W(3-4)	97.135	10.65	-3.88	0.08	-2.00	0.06
14X-4W(73-74)	115.53	11.07	-4.01	0.05	-2.07	0.02
<i>Leg 189 Site 1171C-</i>						
1171C 15X-1W	125.16	12.19	-4.78	0.06	-2.48	0.03
1171C 18X-1W	154.06	13.71	-4.94	0.10	-2.57	0.07
1171C 21X-1W	184.06	15.03	-4.96	0.10	-2.58	0.05
1171C 24X-1W	211.46	19.81	-4.99	0.08	-2.59	0.03
1171C 27X-1W	239.96	22.91	-5.10	0.08	-2.64	0.05
1171C 29X-1W	258.86	23.88	-5.00	0.03	-2.57	0.03

^a As reported in Exon et al. (2001b)^b Based on Age-model using magneto- and biostratigraphy (Stickley et al., 2004).

Table 4. Strontium isotopic composition of bulk carbonates from ODP Site 1171A

Sample Core-section interval (cm)	Depth mbsf ^a	Age Ma ^b	⁸⁷ Sr/ ⁸⁶ Sr ^c	2SE _{internal} ^d	2SD _{external} ^d
<i>Leg 189 Site 1171A-</i>					
1H-1W(73-74)	0.735	0.03	0.709162*	0.000010	
1H-3W(73-74)	3.73	0.22	0.709128	0.000006	0.000002
2H-4W(4-5)	11.645	0.72	0.709125*	0.000010	
3H-4W(3-4)	21.145	1.50	0.709078*	0.000010	
4H-4W(3-4)	30.635	2.46	0.709032	0.000008	0.000002
5H-4W(3-4)	40.135	3.55	0.708991*	0.000010	0.000105
6H-4W(3-4)	49.635	4.94	0.708917*	0.000013	
8H-4W(3-4)	67.275	6.53	0.708917	0.000007	0.000002
10H-4W(3-4)	87.635	9.55	0.708870	0.000007	0.000002
11H-4W(3-4)	97.135	10.65	0.708854	0.000006	0.000001
14X-4W(73-74)	115.53	11.07	0.708836	0.000008	0.000002

^a As reported in Exon et al. (2001b).

^b Based on age-depth model using magneto- and biostratigraphy (Stickley et al., 2004).

^c NBS-987 = 0.710243 ± 0.000008 (long-term average, Penn State Metal Isotope Laboratory's Neptune Plus MC-ICPMS).

^d External reproducibility (2·standard deviation) is reported where replicates (2 - 4) were analyzed. Internal reproducibility (2·standard error) is reported for samples analyzed once.

* ⁸⁷Sr/⁸⁶Sr ratios of bulk carbonates are reported in Fantle (2015).

Table 5. Trace elemental composition of bulk carbonates from ODP Site 1171

Sample Core-section interval (cm)	Depth mbsf ^a	Sr/Ca mmol/ mol	SD mmol/ mol ^b	[Sr] ppm ^c	Mg/Ca mmol/ mol	SD mmol/ mol ^b	[Mg] ppm ^c	Na/Ca mmol/m ol*	[Na] ppm ^c
<i>Leg 189 Site 1171A-</i>									
1H-1W(73-74)	0.735	1.70	0.01	1487.58	1.69	0.39	411.04	4.61	1059.38
1H-3W(73-74)	3.73	1.47	0.19	1289.69	2.03	0.36	492.20	4.08	937.58
3H-4W(3-4)	21.145	1.35	0.02	1186.59	2.51	0.38	610.52	4.69	1077.76
4H-4W(3-4)	30.635	1.25	0.07	1092.01	2.33	0.33	566.19	3.96	910.01
5H-4W(3-4)	40.135	1.27	0.02	1114.93	2.71	0.16	658.53	3.65	838.77
6H-4W(3-4)	49.635	1.25	0.06	1099.07	2.81	0.47	683.29	3.42	785.92
8H-4W(3-4)	67.275	1.19	0.09	1038.76	2.66	0.51	645.79	2.39	549.22
10H-4W(3-4)	87.635	1.64	0.02	1438.46	2.63	0.72	638.79	2.36	542.33
11H-4W(3-4)	97.135	1.40	0.08	1229.55	2.44	0.23	593.36	2.24	514.75
14X-4W(73-74)	115.53	1.83	0.17	1604.29	1.56	0.12	379.91	1.61	369.98
<i>Leg 189 Site 1171C-</i>									
15X-1W(36-37)	125.16	1.55 *		1355.53	1.81*		440.24	2.20	505.01
18X-1W(36-37)	154.06	1.60*		1400.22	1.91*		465.42	1.45	332.62
21X-1W(36-37)	184.06	1.47*		1285.45	2.04*		496.49	1.85	424.17
24X-1W(36-37)	211.46	1.53*		1344.14	1.74*		423.53	1.07	246.58
27X-1W(36-37)	239.96	1.62*		1419.33	1.67*		404.78	1.17	269.54
29X-1W(36-37)	258.86	1.25*		1092.75	2.47*		600.16	1.70	391.70

^a As reported in Exon et al. (2001a).

^b External standard deviation calculated from the ICP-AES data measured (this study) and previously reported (Fantle, 2015).

^c Estimated concentrations in the acetic digested bulk calcite ($\mu\text{g/g CaCO}_3$) fraction of total solids.

* External standard deviation is not available as the samples are measured once only in this study.

Fig.1

a

b

Fig.2

Fig.3

Fig .4

Fig. 5

a

b

c

d

e

f

Fig. 6.

Fig. 7

Fig. 8

Fig. 9