PERSPECTIVES ON THE DIAGENETIC ALTERATION OF MARINE CARBONATES USING A MULTI-PROXY APPROACH: A MULTI-SITE COMPARISON OF Mg, Ca, AND Sr ISOTOPIC COMPOSITIONS OF CARBONATES

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ABSTRACT

Geochemical proxy-based reconstructions widely utilize the trace elemental and isotopic compositions of marine biogenic carbonates to interpret past climatic and oceanographic conditions. However, such proxy-based reconstructions are often challenged by marine diagenesis as carbonates are highly susceptible to diagenetic alteration, especially to partial dissolution and calcite recrystallization. Thus, quantifying diagenetic effects is a prerequisite for the development of any carbonate-based geochemical proxy. Among the metal isotopes, Mg isotopic composition ($\delta^{26}\text{Mg}$) of foraminiferal carbonates is a promising proxy to reconstruct secular seawater $\delta^{26}\text{Mg}$ variability, which is useful in understanding long-term changes in the Mg geochemical cycle. However, Mg in marine carbonates is particularly susceptible to diagenetic alterations due to its low abundance in carbonates compared to pore fluids. Hence, the development of $\delta^{26}\text{Mg}$ of marine carbonates as a proxy demands a thorough understanding of the isotopic systematics of Mg in marine sedimentary systems, which to date has not been accomplished.

The primary goal of this dissertation is to quantify the effect of diagenesis on metal isotopes, in particular, the $\delta^{26}\text{Mg}$ of marine carbonates from various depositional settings. Multiple marine sites are investigated to evaluate the effect of advection, diffusion, and lithological variation within the sedimentary column on the extent of calcite diagenesis. The first two chapters are focused on comparing the extent of diagenetic alteration among various marine sites and quantifying the impact of such diagenetic reactions on carbonate-based proxies.

In the first study, the effect of diagenetic recrystallization on bulk carbonate $\delta^{26}\text{Mg}$ is quantified from an open marine site (ODP Site 1171, Hole A), which is influenced by upward advection. Trace elemental (e.g., Mg/Ca and Sr/Ca) and isotopic compositions ($\delta^{26}\text{Mg}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) of pore fluids and bulk carbonates are analyzed from Hole 1171A using an ICP-AES and a Neptune Plus MC-ICP-MS, respectively. A systematic decrease in bulk carbonate $\delta^{26}\text{Mg}$ (\ldots
0.8 to -2.0 ‰) with depth is observed, which was not entirely explained by the changes in nannofossil and foraminiferal assemblages in the bulk sediments documented by smear slide observations. Application of a 1-D depositional reactive transport model to the pore fluid and bulk carbonate chemistry demonstrates that calcite recrystallization can account for the observed downcore shift in carbonate δ²⁶Mg. Additionally, downcore trends in ${}^{87}$Sr/${}^{86}$Sr, Mg/Ca, and Sr/Ca ratios of bulk carbonates also correlate well with the inferred diagenetic shift in the carbonate δ²⁶Mg.

In the second chapter, the δ²⁶Mg, δ⁴⁴/⁴⁰Ca, and ${}^{87}$Sr/${}^{86}$Sr ratios of pore fluids and bulk carbonates are analyzed from three marine carbonate-rich sites (ODP Holes 762B, 806B, and 807A) of comparable age that are not influenced by advection. The purpose of this study was to evaluate the impact of a diffusive lower boundary and intracolumn lithological variability on the extent of carbonate diagenesis and its impact on the preservation of geochemical proxies such as carbonate δ²⁶Mg. Two adjacent holes (Hole 807A and 806B) are studied to evaluate the impact of a variable diffusive lower boundary on the calcite recrystallization rate and its influence on carbonate δ²⁶Mg. Numerical modeling of Ca and Sr geochemistry suggest that the carbonates from Hole 806B have experienced higher recrystallization rates (~5%/Ma) compared to the Hole 807A (~2%/Ma). The diagenetic shift in bulk carbonate δ²⁶Mg at both sites is -0.5 to -1.0‰ over the 800 meters. The investigation of Hole 762B demonstrates the potential of pore fluid δ²⁶Mg to diagnose the increasing abundance of clays in the carbonate-rich sediments. An increase in bulk carbonate δ²⁶Mg by ~0.6 ‰, along with increase in Mg/Ca, Sr/Ca, and Na/Ca ratios within the clay-rich layer indicate that the presence of clay enhances the preservation of proxy archives. Therefore, this study significantly contributes towards the understanding of the major controls on marine pore fluids from carbonate-rich sediments.
In the final chapter, the exchange rates of foraminiferal calcite recovered from the Cariaco Basin sediment traps and from deep marine sediment cores (ODP Hole 807A) are quantified through a series of batch exchange experiments using a radioactive $^{45}$Ca tracer technique. As foraminiferal calcites are extensively utilized in geochemical proxy-based reconstruction, quantifying the exchange rates helps to evaluate the extent of recrystallization on foraminiferal geochemical proxies. The exchange experiments suggest the modern foraminiferal tests exchange faster ($6.50 \cdot 10^{-4}$ to $0.30 \cdot 10^{-4}$ mol/m$^2$/d) than the fossil foraminiferal tests ($2.50 \cdot 10^{-4}$ to $0.40 \cdot 10^{-4}$ mol/m$^2$/d). The increase in $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, and $[\text{Sr}^{2+}]$ in the fluid of a set of parallel non-tracer experiments indicates that dissolution-precipitation is the dominant mechanism of the atom exchange in foraminiferal calcite. Interestingly, in the presence of aqueous silica in some of the reactors the exchange rate of modern foraminifera decreases ($3.70 \cdot 10^{-4}$ to $0.13 \cdot 10^{-4}$ mol/m$^2$/d). This observation indicates that the presence of dissolved silica in the system can inhibit calcite-fluid exchange, which enhances the preservation of foraminiferal tests and minimizes the extent of alteration of foraminiferal proxies.
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Chapter 1

Introduction

1.1. Significance of marine carbonates in geochemical proxy reconstructions

The understanding of the natural processes responsible for the physical, chemical, and biological evolution of the Earth over multi-billion year timescales, indirectly from the geologic record, is one of the biggest challenges in Geoscience. As there is no direct manner of measuring the physical and chemical conditions of the past climate and ocean, geologists have to rely on the so-called geochemical proxies. Geochemical proxies are tools that utilize the elemental or isotopic composition of geologic materials (e.g., mineral) to infer the chemical and physical conditions (e.g., temperature, pressure, solution chemistry) at the time of formation. Accurate interpretations of geochemical proxies require precise calibrations of proxies to the specific environmental parameters of interest. For instance, the $\delta^{18}O$ of foraminiferal calcite is used to determine past surface seawater temperature (Urey, 1947; McCrea, 1950; Epstein et al., 1953; Emiliani, 1955; Shackleton, 1974; Erez and Luz, 1983). Because the temperature sensitivity of foraminferal $\delta^{18}O$ is also dependent on seawater $\delta^{18}O$, salinity, pH, $CO_3^{2-}$, and biological factors, numerous species-specific calibrations are developed using modern foraminifera under variable ranges of solution chemistry to reconstruct temperature in the past (e.g., Berger, 1971; Wafer and Berger, 1991; Spero and Lea, 1993, 1996; Duplessey et al., 1992; Spero et al., 1997; Rohling and Bigg, 1998; Zeebe, 1999).
Marine biogenic carbonates are one of the most extensively utilized proxy materials to reconstruct the physical and chemical conditions of the ocean and atmosphere. Numerous geochemical proxies have been developed from both the isotopic (e.g., $\delta^{18}O$, $\delta^{13}C$, $\delta^{44/40}Ca$, $^{87}Sr$/$^{86}Sr$, $\delta^{11}B$ and $\delta^{26}Mg$) and trace elemental (e.g., Mg/Ca, Sr/Ca, Ba/Ca, B/Ca) composition of marine foraminiferal calcite to reconstruct a range of physico-chemical conditions of the ocean (e.g. ocean ice volume, sea surface and bottom water temperature, ocean circulation, pH, elemental cycling) (Burke, 1982; DePaolo, 1985; Shackleton, 1987; Hemming and Hanson, 1992; Nurnberg et al., 1996; Rosenthal et al., 1997a; Lear et al., 2000; Billups and Schrag, 2002, 2003; Martin et al., 2002; Pekar et al., 2002; Hönisch et al., 2007; Hodell et al., 2007; Fantle and DePaolo, 2007; Foster et al., 2008; Hönisch et al., 2008; Katz et al., 2008; Miller et al., 2008; Higgins and Schrag, 2010; Higgins and Schrag, 2012; Fantle and Higgins, 2014).

However, extensive research on the development of geochemical proxies from foraminiferal carbonates in last few decades has revealed that the interpretation of a proxy from the geologic record is often complicated by diagenesis and multiple factors that contribute to the signal. A typical example of the latter is foraminiferal Mg/Ca paleothermometry. The Mg/Ca ratio of foraminiferal calcite is sensitive to the sea surface temperature and seawater Mg/Ca ratio at the time of calcification. Therefore, accurate reconstruction of paleotemperature from foraminiferal Mg/Ca ratio requires decoupling the temperature signal from the seawater Mg/Ca ratio. Additionally, foraminiferal tests are susceptible to post-depositional recrystallization via dissolution and reprecipitation that can impact Mg/Ca ratios significantly and thereby can complicate proxy interpretations. Such complications can be resolved by either developing new proxies that are explicitly sensitive to diagenesis, by utilizing multiple proxy records developed from the same geologic material to identify and decouple diagenetic signals from primary depositional signals.
1.2. The Mg isotope proxy

Magnesium is one of the most abundant elements in the Earth’s lithosphere and hydrosphere, and the geochemical cycling of Mg through surface and subsurface processes plays a vital role in the chemical evolution of the Earth’s land and ocean. The Mg cycle involves remobilization of Mg by weathering of Ca-Mg silicate and carbonate rocks in the terrestrial systems (Eq. 1.1 to 1.4) followed by transportation of dissolved Mg\(^{2+}\) via rivers and groundwater to the ocean. In the ocean, where the Mg is reincorporated into the solid earth by high-temperature basalt-seawater interactions at the mid-oceanic ridges, precipitation of marine carbonates (dolomite and biogenic calcite), and by formation of clay minerals during low temperature basalt-seawater interaction (Tipper et al, 2006; Tipper et al., 2006b; Higgins and Schrag, 2010). The Mg-geochemical cycle is directly linked to the global C cycle via continental weathering which sequesters atmospheric CO\(_2\), and through biogenic precipitation of carbonates that incorporate Mg from the seawater (Eq.1.5 and 1.6). Because the global C cycle regulates long-term changes in climate (e.g., temperature), by controlling the long-term variability of atmospheric CO\(_2\), understanding the Mg-geochemical cycle can provide useful insight to the paleoclimatic reconstruction.

\[
\begin{align*}
\text{CaSiO}_3 + 2\text{CO}_2 + 3\text{H}_2\text{O} & = \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{H}_4\text{SiO}_4 \quad \text{---- (1.1)} \\
\text{MgSiO}_3 + 2\text{CO}_2 + 3\text{H}_2\text{O} & = \text{Mg}^{2+} + 2\text{HCO}_3^- + \text{H}_4\text{SiO}_4 \quad \text{---- (1.2)} \\
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} & = \text{Ca}^{2+} + 2\text{HCO}_3^- \quad \text{---- (1.3)} \\
\text{CaMg(CO}_3)_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} & = \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^- \quad \text{---- (1.4)} \\
\text{Ca}^{2+} + 2\text{HCO}_3^- & \rightleftharpoons \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad \text{---- (1.5)} \\
\text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^- & \rightleftharpoons \text{CaMg(CO}_3)_2 + \text{CO}_2 + \text{H}_2\text{O} \quad \text{---- (1.6)} 
\end{align*}
\]
The ocean is one of Earth’s largest reservoirs of Mg with a long residence time (~13-20 Ma) (Broecker and Peng, 1982). Thus it records the long-term variability in the source and the sinks of Mg. The primary sink of Mg from the ocean, i.e., high-temperature hydrothermal circulation removes Mg from seawater quantitatively (i.e., no isotopic fractionation). As a consequence, the Mg isotopic composition (δ²⁶Mg) of seawater is mainly dictated by the mass fluxes and the δ²⁶Mg of the source (riverine discharge: -1.09‰) and the secondary sinks involving carbonate precipitation (dolomite: -2.0 ‰; biogenic calcite: -3.5 to -5.0 ‰;) and low-temperature clay formation (-0.05 to 0.3‰) (Tipper et al, 2006; Tipper et al., 2006b; Higgins and Schrag, 2010) (Fig. 1.1, Table 1). Therefore, variability in seawater δ²⁶Mg can reflect changes in the proportions of Mg incorporated into calcite, dolomite, and clays that fractionate Mg isotopes. In this context, the δ²⁶Mg of marine carbonates show promises to document such long-term changes in seawater δ²⁶Mg provided that the post-depositional diagenetic alteration has a negligible impact on carbonate δ²⁶Mg.

1.3. Diagenetic alteration of geochemical proxies

Diagenesis is defined as post-depositional physical and chemical changes in the initial sedimentary column. In case of carbonates, such processes usually involve dissolution of primary minerals (e.g. aragonite, high-Mg-calcite) and precipitation of secondary minerals (e.g. low-Mg-calcite). Diagenesis is known to have a substantial influence on the elemental and isotopic composition of marine carbonates (e.g., Lorens, 1981; Banner, 1995; Fantle and Higgins, 2014; Fantle, 2015). In particular, elements that are present in trace abundances (e.g., Mg, Sr, Ba, B) are more sensitive to diagenetic alteration relative to the major elements (Baker et al., 1982; Hampt and Delaney, 1997; Fantle and DePaolo, 2006; Fantle et al., 2010; Fantle, 2015; Edgar et al., 2015). Such alteration, if not well constrained, can cause a sizeable bias in proxy reconstructions.
For instance, the Mg/Ca ratio of foraminiferal calcite, utilized as a paleo-temperature proxy, is highly susceptible to dissolution because the incorporation of Mg^{2+} increases the solubility of calcite (Lohmann, 1995; Brown and Elderfield, 1996). Preferential removal of Mg-rich calcite from the bulk tests during partial dissolution can reduce the Mg/Ca ratio of the residual tests resulting in an underestimation of the paleo-temperature (Lorens, 1977; Rosenthal and Boyle, 1993; Lohmann, 1995; Brown and Elderfield, 1996; Lea et al., 2000; Rosenthal et al., 2000; Dekens et al., 2002; Benway et al., 2003). While in seawater column dissolution is the dominant process in the sedimentary column biogenic carbonates are altered by diagenetic calcite recrystallization via dissolution and reprecipitation of calcite, which can also modify Mg/Ca ratio in the foraminiferal tests (e.g., Boussetta et al., 2011; Kozdon et al., 2011; Kozdon et al., 2013; Fantle and Higgins, 2014). Therefore, it is crucial to quantify the effects of both dissolution and recrystallization on foraminiferal tests for accurate interpretation of elemental and isotopic proxies.

In marine sediments, due to the low abundance of Mg in biogenic carbonates relative to the pore fluids, (carbonate: pore fluid Mg mass ratio ~1.3 at 60% porosity) pore fluids have strong potential to alter the Mg in carbonates during diagenetic recrystallization. Studies on metal isotopes to date have documented a broad spectrum of δ^{26}Mg in biogenic calcite (-2.0 to -5.0 ‰) formed from seawater (-0.84 ‰), suggesting that Mg isotopes fractionate strongly during calcite precipitation (Galy et al, 2002; Young and Galy, 2004; Chang et al., 2004; Pogge von Strandmann, 2008; Wombacher et al., 2011) (Fig. 1.2). The extent of diagenetic alteration of the solid isotopic composition (dδ_s) is estimated by the following expression, which involves the diagenetic recrystallization rate (R), isotopic composition of the solid (dδ_s) and the fluid (dδ_f), the fractionation factor (Δ^{diag}_{δ_s-δ_f}) and the duration (dt) (Fantle and DePaolo, 2007; Fantle et al., 2010; Fantle, 2015):
\[ d\delta_s = -R[(\delta_s - \delta_r) - \Delta_{s-r}^{\text{diag}}]dt \quad \text{(1.7)} \]

If the fractionation factor of Mg associated with the diagenetic calcite crystallization is distinct from the fractionation factor associated with biogenic calcification, the $\delta^{26}$Mg of marine carbonate can be modified. Moreover, the extent of alteration of the isotopic composition in the solids is a function of the rate of recrystallization, isotopic disequilibrium between the solid and the pore fluid, and age. The recrystallization rate and degree of isotopic equilibrium between carbonates and pore fluids in a marine sedimentary column can be influenced by transport processes (e.g., advection) and lithological variations (e.g. the presence of silicate layers). Therefore, diagenetic calcite recrystallization has a strong potential to alter the Mg isotopic composition of marine carbonates.

Another potential way of altering the $\delta^{26}$Mg of the individual foraminiferal tests is partial dissolution. Growth-related heterogeneity in the distribution of Mg in biogenic calcite has been identified in some calcifying species (Benway et al., 2003; Eggins et al., 2003; Eggins et al., 2004). Such heterogeneity can result in alteration of the Mg content of the bulk test by selectively dissolving the Mg-rich parts of the tests. Such a process is also capable of altering the $\delta^{26}$Mg of the calcite test if the intra-test heterogeneity in Mg concentration is associated with different isotopic compositions. Comparison between the $\delta^{26}$Mg of various biogenic carbonates indicates that calcite with high Mg content tends to have lower $\delta^{26}$Mg values (-1.0 to -3.0 ‰) compared to the $\delta^{26}$Mg value of low-Mg calcite (-4.0 to -5.0 ‰) relative to seawater (Fig. 1.2). Therefore, partial dissolution induced by the intra-test heterogeneity of Mg has the potential to alter the initial $\delta^{26}$Mg of biogenic calcite.

Despite knowing very little about the diagenetic limitations on carbonate $\delta^{26}$Mg, the global records of Cenozoic variability in seawater $\delta^{26}$Mg have already been inferred from foraminiferal $\delta^{26}$Mg (Higgins and Schrag, 2012; Pogge von Strandmann et al., 2014). However, a
comparison between the age profiles of the $\delta^{26}\text{Mg}$ of planktonic foraminifera from multiple marine sites (ODP Holes 807A, 1263A, and 1264A) (Fig.1.3a) over the last ~40 Ma reveals a significant (-0.5 to -1.0 ‰) disagreement resulting in a large uncertainty (2SD $\geq \pm0.5\%$) in the reconstruction of the Cenozoic seawater $\delta^{26}\text{Mg}$ (Fig.1.3b). Due to the long residence time of Mg (~13-20 Ma) the ocean is well mixed with respect to Mg (Broecker and Peng, 1982). As foraminiferal $\delta^{26}\text{Mg}$ does not show any resolvable sensitivity to temperature, pH and/or salinity (Chang et al., 2004; Pogge von Strandmann, 2008; Wombacher et al., 2011) in a multi-site comparison, the variability among the coeval records of foraminiferal $\delta^{26}\text{Mg}$ could only imply different extents of diagenetic alteration. Hence quantifying the extent of diagenesis on carbonate chemistry from multiple marine sites and its impact on geochemical proxies (e.g. $\delta^{26}\text{Mg}$) is an essential step in proxy-based reconstructions.

Several qualitative and semi-quantitative techniques are developed to identify the effect of partial dissolution and diagenetic recrystallization on the Mg/Ca ratios of biogenic calcites (e.g., Le and Shackleton, 1992; Pearson et al., 2001; Pearson et al., 2007; Mekik et al., 2007; Johnstone et al., 2010; Johnstone et al., 2011). However, the effects of such diagenetic processes on the $\delta^{26}\text{Mg}$ of biogenic carbonates are not extensively explored except for a couple of recent studies where a systematic decrease in the bulk carbonate $\delta^{26}\text{Mg}$ has been interpreted as diagenetic in origin (Higgins and Schrag, 2012; Fantle and Higgins, 2014). Hence a comprehensive study is required that involves comparing proxy records from multiple carbonate-rich sedimentary sections from different marine settings experiencing variable degrees of diagenetic calcite recrystallization. As the rates and extent of diagenetic recrystallization can be influenced by multiple parameters (e.g., age, thickness, relative influence of diffusion and advection, lithological variation), characterizing the impact of these factors on the extent of diagenetic alteration of carbonates is a critical step for developing geochemical proxies.
1.4. Objectives and research questions

The primary objective of this research is to investigate the impact of diagenesis (i.e., calcite recrystallization via dissolution and precipitation) on geochemical proxies, especially, the \( \delta^{26}\text{Mg} \) of marine pelagic carbonate ooze. The extent to which diagenetic recrystallization can modify the primary trace elemental and isotopic compositions of carbonates depends on the chemical and isotopic dissimilarity between carbonates and pore fluids (Fantle and DePaolo, 2007; Fantle et al., 2010; Fantle, 2015). Therefore, understanding the primary controls of marine pore fluid chemistry is critical. In a marine section, transport processes (i.e., diffusion and advection) and reactions are key controlling factors that dictate the pore fluid chemistry. In open marine sites, influenced by active advection, the pore fluid chemistry is continuously modified by the external fluid resulting in a prolonged chemical and isotopic disequilibrium between pore fluids and coexisting carbonates. Thus, the sediments from advection-influenced sites experience an enhanced extent of alteration due to the long duration of the diagenetic exchange. In addition, carbonate-rich sedimentary columns often contain interspersed silicate-bearing layers, which may also impact the chemistry of pore fluids and thus also can influence the extent of diagenetic alteration of sediments. Since the variation of lithology and influence of transport processes can differ between multiple sites, the extent of diagenetic alteration of marine carbonates and its impact on proxies is also expected to vary among sites.

An accurate estimation of the diagenetic effects on carbonate \( \delta^{26}\text{Mg} \) requires a multi-site investigation where the effects of different transport processes and variable lithology on diagenesis can be examined. Therefore, the overall focus of this dissertation is to quantify the effect of diagenetic recrystallization on the \( \delta^{26}\text{Mg} \) of marine carbonates via case studies from two different categories of marine settings: 1) open marine settings, influenced by advection and diffusion and 2) closed marine settings, influenced only by diffusion. Among the closed marine
sites, the influence of variable lithology is also explored by comparing multiple sites with variable carbonate and silicate contents.

Additionally, this dissertation explores the potential of short-term calcite-fluid exchange to alter the chemistry of foraminiferal tests. Trace elemental and isotopic composition of foraminiferal tests hand-picked from bulk sediments are extensively studied for paleoceanographic and paleoclimatic reconstructions. In the ocean, foraminiferal tests have ample opportunity to interact with seawater while settling through the water column (few days to weeks) and residing near the sediment-water interface (few months to years). Thus it is critical to evaluate their susceptibility to exchange with seawater near calcite saturation even over short time scales. Therefore, in this work, the rate of exchange of foraminiferal tests and its implication on foraminifera-based proxy alteration is determined via laboratory exchange experiments.

The main research questions that motivate this work are:

- How important are transport processes (advection and diffusion) when considering the effect of diagenesis on carbonate δ²⁶Mg?
- How do lithological changes in the sedimentary section influence the δ²⁶Mg of marine carbonates and pore fluids?
- Are foraminiferal tests susceptible to short-term mineral-fluid exchange? At what rate does foraminiferal calcite exchange with solutions that are saturated with respect to calcite? What are the implications of such exchange on the geochemical proxies developed from foraminiferal tests?

The proposed research involved analytical, experimental, and modeling approaches in investigating these research questions.

In the first project, the δ²⁶Mg and ⁸⁷Sr/⁸⁶Sr ratio of bulk carbonates and pore fluids from an open marine site (ODP Hole 1171A) on the South Tasman Rise are analyzed to quantify the
effect of calcite recrystallization on carbonate $\delta^{26}$Mg. This system is influenced by active advection, which is inferred to maintain the isotopic disequilibrium between the solids and coexisting pore fluids (Fantle, 2015). Thus, carbonate-rich sediments from open marine sites have the potential to display a significant extent of diagenetic exchange of the trace elements and isotopes between carbonates and pore fluids.

A systematic decrease in bulk carbonate $\delta^{26}$Mg (-0.8 to -2.0‰) with depth is observed. Application of a simple reactive transport model shows that the variability in sediment composition (abundance of nannofossils and foraminifera) cannot explain the observed shift in $\delta^{26}$Mg; thus diagenetic calcite recrystallization must be considered. Diagenetic trends observed from the down-core changes in the $^{87}$Sr/$^{86}$Sr, Mg/Ca, and Sr/Ca ratios of bulk carbonates also correlate well with the inferred diagenetic shift in the carbonate $\delta^{26}$Mg. Therefore, this study demonstrates that carbonate $\delta^{26}$Mg can be significantly altered by calcite recrystallization, especially in an advection-influenced marine sedimentary column.

The second project involves comparison of Ca, Mg, and Sr isotopic composition of bulk carbonates and pore fluids to explore the primary controls of marine pore fluids in closed marine settings and their influence on the extent of diagenetic alteration of the bulk carbonates. In this project, the $\delta^{26}$Mg, $\delta^{44/40}$Ca, and $^{87}$Sr/$^{86}$Sr ratios of pore fluids, bulk carbonates, and bulk clays are analyzed from multiple marine carbonate-rich sedimentary sites (ODP Holes 762B, 806B, and 807A) that are not influenced by external fluid flow. The influence of diffusion and lower boundary conditions on pore fluid chemistry and thus on the extent of diagenetic alteration of bulk carbonates are examined using two adjacent Pacific sites (ODP Holes 806B and 807A). These two sites exhibit some differences in pore fluid chemistry (Mg/Ca, $[\text{Mg}^{2+}]$, $[\text{Ca}^{2+}]$, $[\text{Sr}^{2+}]$) despite their similar thickness, age, lithology, and depositional history (Kroenke et al., 1991). Application of a reactive-transport model to the Ca and Sr geochemistry suggests different calcite recrystallization rates between Holes 806B and 807A and the difference is possibly due to the
dissimilarity in lower boundary conditions (i.e., whether pore fluids can interact with the lower boundary) between these two holes. The modeling exercise also indicates that the carbonate $\delta^{26}\text{Mg}$ in these two holes are less altered (-0.5 to -1.0‰) compared to the advection-influenced hole (ODP Hole 1171A).

The influence of lithological variation on pore fluid chemistry and carbonate $\delta^{26}\text{Mg}$ are explored using the Indian Ocean site (ODP Site 762). Hole 762B has mostly carbonate-rich with some interval containing ~10% clays (Wilkens et al., 1992). This study demonstrates the potential of pore fluid $\delta^{26}\text{Mg}$ to identify the increasing abundance of clay minerals in a carbonate-rich sedimentary column. The bulk carbonate $\delta^{26}\text{Mg}$ shows a general decreasing trend, which is generally consistent with other sites. However, an increase in the $\delta^{26}\text{Mg}$ of bulk carbonates (0.6 to 1.0‰) within the clay-bearing layer is interpreted to represent sediment that has experienced less alteration compared to the carbonate-rich layers above and below. Other geochemical data (Na/Ca, Mg/Ca, and Sr/Ca) also indicate less alteration of carbonates within the clay-bearing interval. Therefore, this study suggests that lithological variation has a significant impact on the alteration of carbonates. The extent of diagenesis is greater within the carbonate-rich sediments than that in the sediments containing clays, which implies better preservation of carbonate-based proxies within clay-rich sediments.

In the third project, the exchange rates of foraminiferal calcite near calcite saturation are quantified through a series of batch exchange reactions using the radioactive $^{45}\text{Ca}$ tracer. Modern and fossil foraminiferal tests are used to explore the influence of age on the rate of exchange. A set of experiments using inorganic calcite to explore the difference in the exchange rates between biogenic and inorganic calcite is also conducted. In addition, the influence of dissolved silica on the exchange rates of foraminiferal calcite is examined via another set of experiments.

The exchange experiments demonstrate that modern foraminiferal tests exchange faster than the fossil foraminiferal tests. However, in the presence of dissolved silica, the exchange rates
of modern foraminifera are slower compared to the foraminiferal tests in reactors without silica. This suggests that the presence of dissolved silica can significantly influence the extent of alteration of foraminifera-based proxies. Since most of the carbonate-based geochemical proxy records (e.g., $\delta^{26}\text{Mg}$, $\delta^{44/40}\text{Ca}$, Mg/Ca, and Sr/Ca) are developed from hand picked foraminiferal tests, constraining exchange rates involving foraminiferal archives will provide valuable insight in evaluating the fidelity of proxy material recovered from geologic records and quantifying the extent to which the exchange can modify proxies.

As little knowledge is available regarding the diagenetic effect on carbonate $\delta^{26}\text{Mg}$, this research directly contributes to the field of geochemical proxy development by quantifying the effect of diagenesis on carbonate $\delta^{26}\text{Mg}$. The site-by-site comparison of multiple geochemical records in bulk carbonates helps to evaluate the effect of transport processes and lithological variability on calcite recrystallization and its impact on geochemical proxies (e.g., carbonate $\delta^{26}\text{Mg}$). For Mg isotopes, foraminiferal $\delta^{26}\text{Mg}$ only shows sensitivity to seawater $\delta^{26}\text{Mg}$, which is homogeneous due to the long residence time of Mg in seawater. Thus, foraminiferal tests from all contemporary sites are expected to exhibit the same temporal variability assuming a constant fractionation factor for Mg associated with biogenic calcification. Therefore, any mismatch between the temporal trends in foraminiferal $\delta^{26}\text{Mg}$ can be attributed to diagenesis. In this regard, the study of different sites located in different marine settings is useful to evaluate the difference in diagenetic alteration between sites and the factors that influence the extent of alteration. Additionally, laboratory based exchange rates of foraminiferal tests demonstrates the susceptibility of foraminiferal tests to short-term mineral-fluid exchange, and suggests that foraminiferal tests may be altered in the water and/or sedimentary column. Ultimately, this research contributes both to the development of the Mg isotope proxy to reconstruct the past and to identify the sites with the greatest potential to generate reliable proxy records.
Table 1. Mg budget for modern ocean

<table>
<thead>
<tr>
<th>Source</th>
<th>Flux $^a$</th>
<th>Reference</th>
<th>Sinks</th>
<th>Flux $^a$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riverine</td>
<td>5.6</td>
<td>Tipper et al., 2006</td>
<td>Hydrothermal circulation at MOR</td>
<td>4.48 to</td>
<td>Tipper et al., 2006</td>
</tr>
<tr>
<td></td>
<td>6.1</td>
<td>Holland, 2005</td>
<td>Hydrothermal circulation at MOR</td>
<td>5.6</td>
<td>Holland, 2005</td>
</tr>
<tr>
<td>Riverine</td>
<td>5.64</td>
<td>Berner and Berner, 1996</td>
<td>Hydrothermal circulation at MOR</td>
<td>4.896</td>
<td>Berner and Berner, 1996</td>
</tr>
<tr>
<td>Riverine</td>
<td>5.2</td>
<td>Wilkinson and Algeo, 1989</td>
<td>Hydrothermal circulation at MOR</td>
<td>5.1</td>
<td>Wilkinson and Algeo, 1989</td>
</tr>
<tr>
<td>Ground water</td>
<td>&lt;0.56</td>
<td>Tipper et al., 2006</td>
<td>Biogenic carbonates</td>
<td>0.62</td>
<td>Berner and Berner, 1996</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dolomite</td>
<td>1.7</td>
<td>Holland, 2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Carbonate-dolostone</td>
<td>0 to 0.84</td>
<td>Tipper et al., 2006</td>
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<td></td>
<td></td>
<td></td>
<td>Clays + seafloor</td>
<td>&lt;0.06</td>
<td>Tipper et al., 2006</td>
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<td></td>
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<td>Basalt-alteration</td>
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<td>Low T seafloor</td>
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<td>Holland, 2005</td>
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<td></td>
<td>Basalt-alteration and reverse</td>
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<td>cation exchange</td>
<td>0.3</td>
<td>Holland, 2005</td>
</tr>
</tbody>
</table>

$^a$ Fluxes are in Tmole of Mg/year

Total Mg in the modern ocean: $71 \times 10^6$ Tmole (Tipper et al., 2006)
Fig. 1.1. Schematic diagram to show the main source and sinks of geochemical cycle of Mg. The numbers in the parentheses are referred to the $\delta^{26}$Mg of the input and output fluxes.
Fig. 1.2. Variability in $\delta^{26}$Mg in natural material including silicates, carbonate, seawater and riverine discharge (Galy et al, 2002; Young and Galy, 2004; Chang et al., 2004; Tipper et al., 2006a, 2006b; Pogge von Strandmann, 2008; Hipper et al., 2009; Ra et al., 2010; Wombacher et al., 2011; Higgins and Schrag, 2012; Pogge von Strandmann et al., 2014).
Fig. 1.3. (a) Comparison between foraminiferal $\delta^{26}\text{Mg}$ records from ODP Site 807, Site 1263 and Site 1264 (Higgins and Schrag, 2012[1]; Pogge von Strandmann et al., 2014[2]), (b) Seawater $\delta^{26}\text{Mg}$ reconstruction from ODP Sites 1263 and 1264 foraminiferal $\delta^{26}\text{Mg}$ (Pogge von Strandmann et al., 2014) records and estimated uncertainty envelop based on variability in carbonate $\delta^{26}\text{Mg}$ records among different sites.
1.5. References


Tipper E. T., Galy A. and Bickle M. J. (2006a) Riverine evidence for a fractionated reservoir of


Chapter 2

Quantifying the effect of diagenetic recrystallization on $\delta^{26}$Mg in marine carbonates

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2.1. Abstract

The Mg and Sr isotopic compositions ($\delta^{26}$Mg$_{DSM3}$ and $^{87}$Sr/$^{86}$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. The $\delta^{26}$Mg of marine carbonates is a promising proxy for reconstructing secular variations in seawater $\delta^{26}$Mg, which helps elucidate the long-term changes in the global Mg cycle. Given the trace amounts of Mg in marine carbonates, diagenesis has the potential to alter $\delta^{26}$Mg substantially. Hence, constraints on diagenetic effect on carbonate $\delta^{26}$Mg are critical to accurate proxy interpretations. This study focuses on quantifying the effect of diagenetic recrystallization on bulk carbonate $\delta^{26}$Mg in an open marine sedimentary section that is influenced by advection, which provides the context for assessing the fidelity of geochemical proxy-reconstructions generated from the primary components (i.e., foraminiferal and nannofossils tests) of bulk carbonate sediments.

Accordingly, we find that pore fluid $\delta^{26}$Mg values at Site 1171 increase systematically with depth (from -0.72‰ to -0.39‰ in upper ~260 m), while the $\delta^{26}$Mg of bulk carbonates decrease systemically with depth (from -2.23‰ to -4.01‰ in upper ~120 m). This variability is
ascribed primarily to carbonate diagenesis, with a fraction of the variability being accounted for by nannofossil and foraminiferal composition. The inferred diagenetic effect on bulk carbonate $\delta^{26}\text{Mg}$ correlates with down-core changes in Mg/Ca, Sr/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 (0.9955) and partition coefficient (1.5) consistent with previous work, assuming calcite recrystallization rates of $\leq 7\%/\text{Ma} (R=0.07e^{-\text{age}/6})$ constrained by Sr geochemistry. Ultimately, this study contributes significantly to the development of $\delta^{26}\text{Mg}$ as a proxy for temporal variability in seawater $\delta^{26}\text{Mg}$ by demonstrating the susceptibility of carbonate $\delta^{26}\text{Mg}$ to diagenetic alteration, especially in sediments in open marine systems. Furthermore, this study suggests that carbonate $\delta^{26}\text{Mg}$ can, in certain systems, be used to quantify the impact of diagenesis on carbonate-based geochemical proxies.

2.2. 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 organic 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; Hönisch et al., 2007; Foster, 2008; Hönisch 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; Hodell 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., δ¹⁸O, δ¹³C, δ⁴⁴/⁴⁰Ca, δ²⁶Mg, δ¹¹B, ⁸⁷Sr/⁸⁶Sr) 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 geochemical processes (i.e., the “calibration”), 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., ⁸⁷Sr/⁸⁶Sr, Sr/Ca, Mg/Ca, and B/Ca), especially those developed from 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 (δ²⁶Mg) of marine carbonates is an emerging proxy for reconstructing secular variations in seawater δ²⁶Mg (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 δ²⁶Mg variability in foraminiferal tests primarily reflects seawater δ²⁶Mg, with the ultimate proviso that foraminiferal δ²⁶Mg 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‰) 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 coexisting pore fluids ($\delta_s - \delta_f - \Delta_{s-f}^{\text{diag}}$) and the duration of the reaction ($dt$; Fantle and DePaolo, 2007; Fantle et al., 2010; Fantle, 2015):

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

where $\delta_s$ and $\delta_f$ represent the isotopic compositions of solid and fluid respectively and $\Delta_{s-f}^{\text{diag}}$ 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. In carbonate-rich sections, disequilibrium exists for elements such as Mg, which can be influenced both by temperature (i.e., as temperature impacts the partition coefficient) and changes in the fractionation factor. Moreover, the degree of local chemical disequilibrium between sediments and pore fluids is also 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 (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.
Accordingly, 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). Magnesium isotopic measurements are conducted on bulk carbonates and coexisting pore fluids, and interpreted using a one-dimensional depositional reactive transport model. Recent Ca and Sr isotope work at Site 1171 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). In addition, 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 Sr/Ca and Mg/Ca ratios. Altogether, these observations provide us with a rationale for selecting 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 overall conditions to which proxy archives such as foraminiferal tests and nannofossils are exposed. Such context can be used to estimate errors in proxy interpretation, and perhaps even correct for systematic offsets due to diagenesis.

2.3. Materials and Methods

2.3.1. 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. 2.1a) on a southwesterly dipping slope. The composite stratigraphic section of ~960 m thick sediments, comprised of three holes (A, C, and D) comprises sediments ranging from the late Paleocene (~58 Ma) to the Quaternary (Fig. 2.1b). The Neogene section of the sedimentary column, characterized by high carbonate content (>90% CaCO$_3$) and low organic carbon content (<1 wt %), is mostly continuous with an exception of a
hiatus present in the uppermost Miocene (Fig. 2.1b). 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. Below 276 mbsf (Units IV and V), sediments 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 ± 3%) to the carbonate-silicate transition (Fig. 2.1b). 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. 2.1b).

The ages of the sediments from Site 1171 are assigned based on previously reported biostratigraphic and magnetostratigraphic data (Fig. A1; Exon et al., 2001; 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., 2001; 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 Holes 1171A, 1171C, and 1171D are summarized in Fig. 2.2. 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., 2001).

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 [Mg$^{2+}$] at the bottom boundary condition) and silicate diagenesis in the silicate-rich section is the plausible explanation for the rapid decrease in Mg in the siliciclastics (Exon et al., 2001). 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.

2.3.2 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$_2$O$_2$) 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 preweighed polypropylene centrifuge tubes. To each tube was added 10 ml of reducing solution, prepared by dissolving 25 g of NH$_2$OH·HCl (hydroxylamine hydrochloride) into 200 ml of concentrated NH$_3$OH 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 NH₄OH 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.

2.3.3. 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 by a single step method 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 (Fig. A.2a).
Bulk carbonate-derived Mg was purified by passing 1-2 µg of Mg through Bio-Rad polypropylene columns filled with 1.5 ml TODGA resin to remove Ca; Ca-free cuts were collected in 24 ml of 4 N HNO₃. The Ca-free elution cuts were dried down, resuspended in 0.1 ml 0.4 N HCl, and loaded onto 1.9 ml AG-50WX-8 columns. Finally, Mg from the carbonate samples was purified using a similar method as that employed for the pore fluid samples (Fig. A.2b and c).

Our column separation procedure successfully separated Mg from both marine pore fluid and carbonate matrices with an average recovery of 99.2 ± 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. Thoroughly 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 ²⁴Mg⁻ 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 were conducted after methods described by 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 the column, washed 6 times alternately with 1 ml of 4 N HCl and deionized water, and conditioned with 1 ml of 3 N HNO₃. The filtered pore fluid samples were dried down and resuspended in 3 N HNO₃ 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 HNO₃. After loading the samples the columns were rinsed with 3.5 ml of 3N HNO₃ followed by collection of Sr in 2.5 ml of deionized water (Fig. A.2d). The procedural blank for the entire column separation was 0.2 to 0.5 ng (i.e., <0.05%) and the average Sr yield was 98.5±0.5%.

2.3.4. Mass Spectrometry

Precise and accurate measurements of Mg isotopic composition were performed using a Thermo Scientific Neptune Plus multi-collector ICP-MS. Our mass spectrometric approach was designed to minimize the impact of polyatomic interferences (\(^{12}\)C\(^{14}\)N\(^+\), \(^{12}\)C\(^2\)H\(^+\), \(^{23}\)Na\(^1\)H\(^+\)) and interferences from doubly charged ions (e.g., \(^{48}\)Ca\(^2\)\(^+\), \(^{50}\)Cr\(^2\)\(^+\), \(^{52}\)Mn\(^2\)\(^+\)) on 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 \(^{24}\)Mg\(^+\) ion beam of ~15 to 20 volts in medium mass resolution (M/ΔM ~7000). 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 detail in Table A.2.

Instrumental mass bias corrected delta values were calculated using a sample standard bracketing method, with DSM3 as a reference standard (e.g., Galy et al., 2002). The delta notation used to report Mg isotopic composition is:
\[ \delta^{3}\text{Mg} = \left( \frac{\langle \text{xMg}/24\text{Mg} \rangle_{\text{sample}}}{\langle \text{xMg}/24\text{Mg} \rangle_{\text{DSM3}}} - 1 \right) \times 1000 \] ---- (2.2)

where \( \text{x} \) represents either mass 25 or 26. Multiple measurements of in-house laboratory standards (not put through column chemistry) and seawater (that was purified) relative to DSM3 resulted in \( \delta^{26}\text{Mg} \) and \( \delta^{25}\text{Mg} \) values identical to their published values (Table 2.1). 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 \( \leq 0.10\% \) (Table 2.2). On an isotope-isotope plot (\( \delta^{26}\text{Mg} \) vs. \( \delta^{25}\text{Mg} \); Fig. 2.3c), all mass bias corrected delta values fell along a line with slope 0.515± 0.02, similar to the slope of the mass dependent fractionation line (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 Thermo Scientific Neptune Plus (Penn State MIL) in the low mass resolution mode under wet plasma conditions, yielding ~10 to 12 V \( ^{88}\text{Sr}^{+} \) at 200 ppb Sr (Balashov et al., 2015; Fantle, 2015). Peaks 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 Kr from its expected values (1.008) using an exponential law:

\[ \left( \frac{\text{int}}{\text{in}} \right)_{\text{meas}} = \left( \frac{\text{int}}{\text{in}} \right)_{\text{actual}} \times \left( \frac{\text{m}_1}{\text{m}_1} \right)^p \] ---- (2.3)
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 $^{84}\text{Kr}$ and $^{86}\text{Kr}$ ion beam intensities from the measured intensities on 84 and 86 masses, as they are not otherwise resolvable from the $^{84}\text{Sr}$ and $^{86}\text{Sr}$ ion beams on the Neptune. The fractionation-corrected values of $^{84}\text{Kr}$ and $^{86}\text{Kr}$ 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 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 seawater samples yield an average $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.709141 ± 0.000008 (2SD), which is comparable to the reported modern seawater value (0.709175 ± 0.00002). 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 $^{87}\text{Sr}/^{86}\text{Sr}$.

2.3.5. Description of 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:

$$\frac{\partial C_{pf}}{\partial t} = D_i \frac{\partial^2 C_{pf}}{\partial z^2} - v \frac{\partial C_{pf}}{\partial z} + RM (C_{i,s} - K_i C_{pf}) \quad ---- (2.4)$$

$$\frac{\partial C_{ls}}{\partial t} = -V \frac{\partial C_{ls}}{\partial z} - R (C_{ls} - K_i C_{pf}) \quad ---- (2.5)$$

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 $\rho$ is density and $\phi$ is porosity), $V$ is compaction, $z$ 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 deep marine carbonate sections (Richter and DePaolo, 1987; Richter and DePaolo, 1988; Richter, 1993, 1996; Richter and Liang, 1993; Fantle and DePaolo, 2006; and DePaolo, 2007; Fantle, 2015):

$$R(\text{age, Ma}) = \alpha + \beta \cdot e^{-\text{age}/\gamma} \quad ---- (2.6)$$
where, $\alpha + \beta$ is the initial recrystallization rate, and $\gamma$ reflects the rate at which the total rate approaches the long-term rate ($\alpha$).

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 fluid ($C_f$) to its concentration in the solid ($C_s$):

$$K_i = \frac{C_f}{C_s} \quad ---- (2.7)$$

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

$$\alpha_{s-f}^{\text{diag}} = \frac{K_i^j}{K_i^k} \quad ---- (2.8)$$

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

$$K_{Mg/Ca}^{\text{calcite}} = \frac{(Mg/Ca)_{calcite}}{(Mg/Ca)_{fluid}} = \frac{(m_{Ca})_{calcite}}{(m_{Ca})_{fluid}} \cdot \frac{(m_{Ca})_{calcite}}{(m_{Ca})_{calcite}} \quad ---- (2.9)$$

$$K_{Mg/Ca}^{\text{calcite}} = \frac{(Mg/Ca)_{calcite}}{(Mg/Ca)_{fluid}} = K_{Mg} \cdot \frac{(m_{Ca})_{fluid}}{(m_{Ca})_{calcite}} \quad ---- (2.10)$$

This equation (10) can be re-written as:

$$K_{Mg}^n = K_{Mg}^m \cdot \frac{m_{Ca}^{\text{fluid},n}}{m_{Ca}^{\text{fluid},m}} \quad ---- (2.11)$$

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 $K_{Mg}^{calcite}$ (depth-independent value) to calculate the $K_{Mg}$ at each depth 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 $[\text{Mg}^{2+}]$ are not expected to be in steady state with the coexisting carbonates in the sedimentary column due to its large diffusive reactive length scale (Fantle and DePaolo, 2006).

The diffusion coefficient of element $i$ ($D_i$) is a function of porosity and $D^0$ (the diffusion coefficient of the element at infinite dilution):

$$D_{Mg} = \frac{D^0}{\theta^2} \quad \text{---- (2.12)}$$

where $\theta^2$, the tortuosity, is defined by:

$$\theta^2 = 1 - \ln(\phi^2) \quad \text{---- (2.13)}$$

The diffusion coefficient of Mg at infinite dilution ($D^0$) is calculated from the temperature profile of the borehole using the following equation:

$$D^0 = M_1 + M_2 \times T \quad \text{---- (2.14)}$$

where $M_1$ and $M_2$ are constants representing the coefficients of linear regression of $D^0$ of a cation against temperature (T,°C; Boudreau, 1997).

2.4. Results

2.4.1. 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 2.2 and 2.3 and Fig. 2.3. The $\delta^{26}\text{Mg}$ values of pore fluids are generally higher than modern seawater (-0.84 ± 0.04‰), and exhibit a systematic increase with
depth from -0.72 ± 0.08‰ (~1.45 mbsf) to -0.39 ± 0.03‰ (~262.9 mbsf). In Hole A, within the upper ~78 mbsf, pore fluid $\delta^{26}$Mg increases with depth from -0.72 ± 0.08‰ to -0.52 ± 0.06‰ followed by a slight decrease to -0.61 ± 0.10‰ at 117.7 mbsf. In Hole C (below 120 mbsf), pore fluid $\delta^{26}$Mg increases gradually with depth (-0.39 ± 0.03‰ at 262.9 mbsf), except between ~177 and ~210 mbsf where pore fluid $\delta^{26}$Mg shifts slightly towards a lower value (-0.58 ± 0.10‰ at ~205 mbsf).

Compared to the pore fluids, bulk carbonates exhibit substantial variability in $\delta^{26}$Mg over the depth range investigated, generally decreasing from -2.23 ± 0.05‰ at 0.735 mbsf to -4.01 ± 0.05‰ at 115.53 mbsf with some variability. There are two depth intervals over which bulk carbonate $\delta^{26}$Mg shifts towards higher values by ~0.2 to 0.4‰ relative to the depth above: i) between 3.73 and 21.145 mbsf, the carbonate $\delta^{26}$Mg increases from -2.72 ± 0.08‰ to -2.26 ± 0.09‰ and ii) between 30.635 and 49.635 mbsf the carbonate $\delta^{26}$Mg increases from -3.36± 0.04‰ to -3.16 ± 0.05‰.

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

The $^{87}$Sr/$^{86}$Sr ratios of bulk carbonates from Site 1171A systematically decrease from the modern seawater $^{87}$Sr/$^{86}$Sr ratio (0.709174 ± 0.000005) near the sediment-water interface to 0.708834 ± 0.0000023 at 115.53 mbsf (Table 2.4, Fig. 2.4a-b). Shallower carbonates (0 to 50 mbsf depth) exhibit a monotonic decrease in $^{87}$Sr/$^{86}$Sr with an increasing offset from the seawater $^{87}$Sr/$^{86}$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 $^{87}$Sr/$^{86}$Sr shifts towards the pore fluid $^{87}$Sr/$^{86}$Sr (Fantle, 2015). However, below ~50 mbsf, bulk carbonates from the deeper section (67 to 115 mbsf) exhibit a relative increase in $^{87}$Sr/$^{86}$Sr that approaches the seawater curve (McArthur et al., 2001; McArthur and Howarth, 2004; Fig. 2.4).
2.4.3. Trace element composition of bulk carbonates

The trace elemental compositions of bulk carbonates are summarized in Table 2.5 and Fig. 2.4c-f and Fig. 2.6a-b. The Sr concentrations of the acetate-digested carbonate fractions from Hole 1171A exhibit a systematic decrease with depth from 1488.95 ± 13 ppm near the sediment-water interface to 980.49 ± 8 ppm at 67.275 mbsf, followed by a gradual increase to 1494.80 ± 18 ppm at 115.53 mbsf. By comparison, Mg concentrations exhibit an increasing trend with depth, from 477.66 ± 8 ppm at 0.735 mbsf to 762.32 ± 9 ppm at 49.635 mbsf, followed by a decrease (398.91 ± 10 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 ~1.12 at 67.135 mbsf, followed by an increase to 1.71 at 115.53 mbsf. The Mg/Ca ratio exhibits a general increase from ~1.97 (0.735 mbsf) to ~3.15 (49.635 mbsf), followed by a subsequent decrease to 1.64 at 115.53 mbsf. The Na/Ca ratio and Na concentration of the bulk carbonates show overall decrease with depth from ~4.61 (0.735 mbsf) to ~1.61(115.53 mbsf) and from 1055.87 ± 58.8 ppm to 368.75± 2.4 ppm, respectively (Fig. 2.6 a-b).

2.5. Discussion

The advent and spread of multi-collector plasma source instruments over the past fifteen years has opened up the periodic table and allowed for the exploration of previously unexplored isotopic systems at high analytical precision. While this technical revolution has diversified the geochemical toolbox for reconstructing the past, it has also brought to the fore many elemental and isotopic proxies that are present in trace abundance in the primary recording phase, CaCO₃. Given the relative ease with which trace elements such as Mg, Sr, Cd, and B may be altered in
CaCO$_3$ during diagenesis, it has consequently made the need for understanding and quantifying
diagenetic effects even more critical.

Accordingly, the current study investigates bulk carbonate diagenesis in a deep marine
sedimentary section (ODP 1171), a site drilled with the purpose of reconstructing past climate
(Exon et al., 2001; Fantle, 2015). This study focuses on $\delta^{26}$Mg, given the paucity of data to date
from deep sea carbonate sections (Higgins and Schrag, 2010; Higgins and Schrag, 2012). Marine
carbonate $\delta^{26}$Mg is a promising tool to reconstruct paleo-seawater $\delta^{26}$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) provided evidence for 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 deep sea 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
$\delta^{26}$Mg in an open marine system compare to $\delta^{26}$Mg in a relatively closed system? Are the
fractionation factor ($\alpha_{\text{diag}}^{\text{Mg}}$) and partition coefficient ($K_{\text{Mg}}$) associated with diagenesis constrained
by studies of closed systems applicable to more open systems? Could $\delta^{26}$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, site comparisons, and the temporal
evolution of carbonate-rich sections. More directly, such answers inform whether or not $\delta^{26}$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 $\delta^{26}$Mg increases systematically downcore, while (2) bulk carbonate $\delta^{26}$Mg
decreases systematically downcore. Qualitatively, both trends are similar to those observed at
Hole 807A (Higgins and Schrag, 2012), most notably in the upper ~100-150 m in which there is a rapid decrease in bulk carbonate δ²⁶Mg at both sites. More quantitatively, the pore fluid and bulk carbonate δ²⁶Mg trends are not identical in Holes 807A and 1171A (Fig. 2.3a-b). Over the upper 800 meters at 807A, pore fluid δ²⁶Mg increases from seawater values to -0.15‰; in Hole 1171A, by contrast, the pore fluid only increases to about -0.4‰ at the bottom of the carbonate-rich section. Over similar depth ranges, pore fluids in Hole 1171A are isotopically heavier than in Hole 807A. This difference, we contend, reflects the influence of advection at Site 1171. Further, we suggest that the influence of advection is also observed in the bulk carbonate δ²⁶Mg, which decreases drastically from about -2.23‰ to -4.01‰ over ~125 meters at Site 1171. By comparison, the δ²⁶Mg of the <65 µm fraction only decreases by -1‰ over the uppermost 150 m in Hole 807A.

In the Discussion below, our observations are used to form hypotheses that are subsequently tested using geochemical and paleontological evidence and numerical simulations. In particular, we present evidence of geochemical alteration of bulk carbonates and suggest that δ²⁶Mg is strongly influenced by diagenesis. We then evaluate the alternate hypothesis that the measured bulk carbonate δ²⁶Mg reflects the abundance and species composition of the sediment, concluding that these factors don’t entirely account for the observations. Finally, we apply the numerical model to demonstrate the consistency of the hypothesis that diagenesis controls bulk carbonate δ²⁶Mg with measured pore fluid and solid chemical data.

2.5.1. Geochemical evidence of bulk carbonate diagenetic alteration

The interpretation of a distinguishable diagenetic effect in bulk carbonates at Site 1171 is supported by multiple geochemical datasets, including Sr/Ca, Mg/Ca, Na/Ca, and ⁸⁷Sr/⁸⁶Sr 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 Hole 1171A. Above ~67 mbsf, bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ deviates significantly from the global seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve (McArthur and Howard, 2004), approaching pore fluid $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 2.4a and b). Over the same depth range, bulk carbonate Sr/Ca decrease from ~1.7 to 1.12 while Sr concentrations decrease from ~1488 ppm to ~980 ppm (Fig. 2.4c and d). The $^{87}\text{Sr}/^{86}\text{Sr}$ offset from the seawater curve is reasonably correlated with Sr/Ca ($r^2 = 0.684$; Fig. 2.5a).

Both Sr/Ca and Sr concentrations are consistent with the preferential loss of Sr from biotic carbonates during recrystallization, though the extent to which this occurs is considerably higher than is seen at sites such as 807A. Recently, Fantle (2015) suggested that the more open system dynamics in Hole 1171A influenced recrystallization rates and that advection maintained local chemical disequilibrium (with respect to the $[\text{Sr}^{2+}]$ 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 Hole 1171A.

Over the same depth interval described above (<67 mbsf), bulk carbonate Mg/Ca increases from ~1.97 to ~3.0 while Mg concentrations increase from ~400 to 800 ppm (Fig. 2.4e and f), the former correlating quite well with both the offset in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the seawater curve ($r^2 = 0.776$) and Sr/Ca ($r^2 = 0.707$; Fig. 2.5b and c). Both correlations imply that the Mg in the bulk carbonates is affected by the same process responsible for the observed decrease in Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 2.5d, e, and f). We suggest that this process is diagenetic recrystallization, which in this case increases 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.

Below 67 mbsf, bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ values approach the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve (Fig. 2.4a and b) while Sr concentrations (from ~1093 ppm to ~1498 ppm) and Sr/Ca ratios (from ~1.25 to ~1.71; Fig. 2.4c and d) increase. These trends coincide with a decrease in bulk carbonate
Mg concentrations (from ~762 ppm to ~399 ppm) and Mg/Ca ratios (from ~3.14 to ~1.64; Fig. 2.4e and f). Quite interestingly, these trends are the opposite of what one would expect in older carbonates, assuming that the integrated extent of recrystallization increases with age. Consequently, the data at Site 1171 suggest that reaction rates, and/or pore fluid composition (in particular the lower boundary), and/or the advection regime have changed over time. It seems most likely that the latter has perhaps driven the former two. The importance of this observation is in its implication for proxies, specifically that diagenetic alteration may vary between systems (and over time in a given system) due to fundamental changes in the dynamics of the system.

Given the support for the presence of distinguishable and clear diagenetic effects in bulk carbonates, we interpret the Mg isotope trend primarily as a diagenetic signal. Such a hypothesis is directly supported by $^{87}$Sr/$^{86}$Sr (and is consistent with Sr/Ca, Mg/Ca, and Na/Ca; Fig. 2.5 and Fig. 2.6), 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. From an isotopic perspective, there is likely also reasonable leverage in the fractionation factor ($\alpha_{x-f}^{diag}$) to alter Mg isotopically, provided that the initial offset in delta values between pore fluid and bulk carbonate is ~1.5‰ while the theoretical equilibrium value is about -5‰ (~0.9950; Rustad et al., 2010). Additionally, the decrease in bulk carbonate Na/Ca ratio correlates with the increase in Mg/Ca and decrease in Sr/Ca ratios above ~100 m depth suggesting the diagenetic alteration to be the potential cause for the observed loss of Na in bulk carbonates. Therefore, the strong correlation ($r^2=0.858$) between the decrease in Na/Ca ratio and $\delta^{26}$Mg of bulk carbonates from Hole 1171A over the entire 120 m depth interval also support the inference that the decrease of bulk carbonate $\delta^{26}$Mg is a result of diagenesis (Fig. 2.6c).
2.5.2. 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 $\delta^{26}\text{Mg}$ in Hole 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 abundance and species composition of the bulk sediment. Since the bulk carbonates are comprised of both foraminiferal and nannoplankton fossils, 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 address this hypothesis, we conducted a smear slide study of the bulk sediments and compiled previously published observations (Exon et al., 2001, 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. 2.7a and Fig. A.3). In the upper ~21 m of the section, nannofossil abundance is ~48%, increases to ~80% between 21 and 40 mbsf, and remains high (~80±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 Hole 1171A, suggesting lower bulk carbonate $\delta^{26}\text{Mg}$ values associated with higher nannofossil abundances. The nannofossil assemblages, that also change somewhat with depth, are also noted in Fig. 2.7.

Previous work has demonstrated that *Emiliania huxleyi* and *Gephyrocapsa oceanica* $\delta^{26}\text{Mg}$ measured in culture experiments and natural sediments (Ra et al., 2010a; Ra et al., 2010b; Müller et al., 2011) are generally heavier (-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 the 1171 section, 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 (Fig. A.4).

Given our limited understanding of coccolithophore $\delta^{26}\text{Mg}$, and the relative amount of Mg in benthic and planktonic foraminifera and nannofossils, we estimated a range of bulk carbonate $\delta^{26}\text{Mg}$ expected at Hole 1171A. The initial bulk carbonate $\delta^{26}\text{Mg}$ is constrained by the following mass balance calculation:

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

where the subscripts carb and $i$ refer to the bulk carbonate and the endmember components. The term $X_i$ is 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 each endmember component and bulk carbonate, respectively. The terms mass$_i$ and mass$_{\text{carb}}$ refer to the masses (g CaCO$_3$) of individual components and bulk carbonate, respectively.

The relative proportions of each endmember are constrained by observations of foraminiferal and nannofossil abundance at Hole 1171A (Exon et al., 2001; 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., 2001). Accordingly, we assign an average planktonic abundance of 60% of the total foraminiferal fraction, with a normally distributed variability of ±10% based on the uncertainty in the smear slide counting.

The variability in each endmember $\delta^{26}\text{Mg}$ is taken into account in a similar fashion, with average values assigned to each component, assuming a normal distribution based on the published measurements of natural samples (Table A.3, Fig. A.5). Average values for Mg/Ca ratios of foraminiferal and nannofossil tests are chosen based on the range of foraminiferal Mg/Ca
ratios at Site 1171 (Shevenell et al., 2004; Shevenell et al., 2008) and range of coccolith Mg/Ca ratios 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 accounted for 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. 2.7b), the opposite of the measured trend. This suggests that the observed trend in $\delta^{26}\text{Mg}$ with depth is not entirely explained by species composition, and likely reflects an integrated signal of diagenesis.

### 2.5.3. Model exploration of bulk carbonate diagenesis

We have proposed that bulk carbonate $\delta^{26}\text{Mg}$ at Site 1171 is primarily controlled by 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 use of $\delta^{26}\text{Mg}$ in carbonate-rich sediments as a proxy. Our suggestion is that the diagenetic overprint can be quite substantial, and thus 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, 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 mechanism. The modeling was conducted given reasonable estimates for the partition coefficient of Mg in calcite ($K_{\text{Mg}}$), the fractionation factor associated with recrystallization ($\alpha_{\text{s-f}}^{\text{diag}}$), the diffusion coefficient ($D_{\text{Mg}}$), and...
the pore fluid advection velocity (v). Recrystallization rates at Site 1171 have been previously constrained by pore fluid Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ (Fantle, 2015). Sensitivity tests were conducted to help constrain the limits of our interpretations (Appendix A.1.1; Figs. A.6 – A.14).

Using recrystallization rates of $\leq 7\%$/Ma ($R = 0.07e^{-age/6.6}$), a partition coefficient ($K_{\text{Mg}}$) of 1.5, and a diagenetic fractionation factor ($\alpha_{s-f}^{\text{diag}}$) of 0.9955, the model reproduced the observed trends in the pore fluid and bulk carbonate $\delta^{26}\text{Mg}$ and Mg concentrations (Fig. 2.8). Although the estimate for $K_{\text{Mg}}$ 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 $K_{\text{Mg}}$ used 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 (0.9955) 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 limestone diagenesis (Fantle and Higgins, 2014).

The modeling exercise suggests that the calculated initial and pore fluid $\delta^{26}\text{Mg}$ data are consistent with diagenetic recrystallization as a controlling mechanism at Site 1171. The simulations indicate that the “characteristic” increase in pore fluid $\delta^{26}\text{Mg}$ observed in multiple carbonate-rich sections can be interpreted as a result of recrystallization. Interestingly, the simulations indicate that some amount of the initial variability in bulk carbonate $\delta^{26}\text{Mg}$ is still reflected in the bulk carbonate after reaction, despite being altered by ~0.8 to 2.0‰ during recrystallization.

Further, the modeling suggests that bulk carbonate Mg concentrations increase by 5 to 10 mmole/kg and Mg/Ca ratios by ~1.3 mmole/mole during recrystallization (Fig. 2.9). Thus, diagenetic recrystallization can significantly modify the long-term trend in carbonate Mg/Ca over hundreds of meter length scales, similar to previous suggestions (Fantle et al., 2010).
2.5.4. Implications for geochemical proxies

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.

To illustrate this concept, and its implications for Mg isotope-based reconstructions, a Monte Carlo simulation is presented in which 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. 2.7b). The distribution is assumed to be a gamma distribution (Fig. 2.10a), uniquely determined for each depth, the mean of which is identical to the measured bulk sediment. From 5000 datums in this distribution, four are randomly selected at each depth (downsampled to n=25 to reflect a realistic dataset) and plotted as a function of depth (Fig. 2.10b).

The simulation suggests that a random sampling of such a heterogeneous substrate has the potential to generate Mg isotope records that are not representative of either the initial or final
states. Instead, as expected, 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. 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 tests.

Additionally, our analysis of the diagenetic shift in bulk carbonate $\delta^{26}\text{Mg}$ suggests a systematic $\sim1.3$ mmole/mole increase in bulk carbonate Mg/Ca ratios at Site 1171 over $\sim33$ Ma. Because foraminiferal tests contribute $\sim50\%$ of the total Mg to the bulk carbonate, 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 $\sim7.5^\circ\text{C}$ (Fig. 2.7c).

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 those 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.

One critical outstanding question that remains to be answered is how the diagenetic alteration of bulk sediment (1) occurs mechanistically and (2) is accommodated in the heterogeneous sediment (Fig. 2.11). Recent laboratory work has suggested 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. If such a mechanism operates in the sedimentary column, then this has significant implications for the assumption of pristine, cleanable tests. 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 material on the same test (Fig. 2.11). It is also possible to imagine that reprecipitation does not occur local to the test, and that the lost material accretes elsewhere in the sediment (Fig. 2.11). In this case, 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.
2.6. Conclusions

Isotopic and geochemical data from ODP Site 1171 demonstrate the effects of diagenetic recrystallization on bulk carbonate $\delta^{26}$Mg, which allows for an evaluation of the potential of carbonate $\delta^{26}$Mg to act as a proxy for the secular variation of seawater $\delta^{26}$Mg. At Hole 1171A, bulk carbonates $\delta^{26}$Mg values decrease by a considerable ~0.8 to 2.0‰ over ~120 meters. In the same sediments, $^{87}$Sr/$^{86}$Sr deviates significantly from contemporaneous seawater, while Sr/Ca ratio decreases and Mg/Ca ratio increases. These geochemical data supports the hypothesis that calcite recrystallization is a controlling factor on bulk carbonate $\delta^{26}$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 $\delta^{18}$O as $f(temperature)$). Given the potential magnitude of diagenetic effects, quantifying alteration is critical to any proxy-based interpretations 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 $\delta^{26}$Mg to diagenetic alteration suggests that the $\delta^{26}$Mg may be a useful tool to fingerprint diagenesis, especially in studies in which bulk carbonate is the primary proxy archive.

2.7. Acknowledgements

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identification of nannofossils in smear slides. This research used samples and data provided by the Ocean Drilling Program (ODP).

**Data Tables**

Table 2.1: Mg isotopic compositions of seawater and standards measured in this study

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<tr>
<th>Samples /Standards</th>
<th>δ²⁶Mg_DSMM3 (%) Measured</th>
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<th>n</th>
<th>δ²⁶Mg_DSMM3 (%) Accepted</th>
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<td>-0.84</td>
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Table 2.2. Magnesium isotopic composition of pore fluids from ODP Site 1171

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<th>Sample Core-section interval (cm)</th>
<th>Depth mbf a</th>
<th>δ²⁶Mg_DSMM3 %</th>
<th>2σ %</th>
<th>δ²⁶Mg_DSMM3 %</th>
<th>2σ %</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Leg 189 Hole 1171A-</em></td>
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</tr>
<tr>
<td>1H-1W(145-150)</td>
<td>1.45</td>
<td>-0.72</td>
<td>0.08</td>
<td>-0.36</td>
<td>0.03</td>
</tr>
<tr>
<td>2H-3W(140-150)</td>
<td>11.55</td>
<td>-0.62</td>
<td>0.07</td>
<td>-0.32</td>
<td>0.02</td>
</tr>
<tr>
<td>3H-3W(140-150)</td>
<td>21.05</td>
<td>-0.67</td>
<td>0.06</td>
<td>-0.35</td>
<td>0.02</td>
</tr>
<tr>
<td>4H-3W(140-150)</td>
<td>30.55</td>
<td>-0.62</td>
<td>0.08</td>
<td>-0.32</td>
<td>0.01</td>
</tr>
<tr>
<td>5X-2W(140-150)</td>
<td>40.05</td>
<td>-0.56</td>
<td>0.09</td>
<td>-0.28</td>
<td>0.05</td>
</tr>
<tr>
<td>6H-3W(145-150)</td>
<td>49.55</td>
<td>-0.53</td>
<td>0.03</td>
<td>-0.28</td>
<td>0.05</td>
</tr>
<tr>
<td>9H-3W(140-150)</td>
<td>78.0</td>
<td>-0.52</td>
<td>0.06</td>
<td>-0.27</td>
<td>0.05</td>
</tr>
<tr>
<td>10H-3W(140-150)</td>
<td>87.5</td>
<td>-0.55</td>
<td>0.08</td>
<td>-0.28</td>
<td>0.05</td>
</tr>
<tr>
<td>11H-3W(140-150)</td>
<td>97.0</td>
<td>-0.58</td>
<td>0.10</td>
<td>-0.31</td>
<td>0.05</td>
</tr>
<tr>
<td>14X-2W(140-150)</td>
<td>117.7</td>
<td>-0.61</td>
<td>0.10</td>
<td>-0.31</td>
<td>0.06</td>
</tr>
<tr>
<td><em>Leg 189 Hole 1171C-</em></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>17X-3W(140-150)</td>
<td>148.5</td>
<td>-0.52</td>
<td>0.09</td>
<td>-0.27</td>
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</tr>
<tr>
<td>20X-3W(140-150)</td>
<td>177.3</td>
<td>-0.43</td>
<td>0.02</td>
<td>-0.22</td>
<td>0.01</td>
</tr>
<tr>
<td>23X-3W(140-150)</td>
<td>205.9</td>
<td>-0.58</td>
<td>0.10</td>
<td>-0.30</td>
<td>0.03</td>
</tr>
<tr>
<td>26X-3W(140-150)</td>
<td>234.7</td>
<td>-0.52</td>
<td>0.10</td>
<td>-0.28</td>
<td>0.04</td>
</tr>
<tr>
<td>29X-3W(140-150)</td>
<td>262.9</td>
<td>-0.39</td>
<td>0.03</td>
<td>-0.19</td>
<td>0.03</td>
</tr>
</tbody>
</table>

a As reported in Exon et al. (2001).
Table 2.3 Magnesium isotopic composition of bulk carbonates from ODP Hole 1171A

<table>
<thead>
<tr>
<th>Sample Core-section interval (cm)</th>
<th>Depth mbsf a</th>
<th>Age Ma b</th>
<th>$\delta^{26}$Mg DSM3 ‰</th>
<th>2σ</th>
<th>$\delta^{25}$Mg DSM3 ‰</th>
<th>2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg 189 Hole 1171A-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H-1W(73-74)</td>
<td>0.735</td>
<td>0.03</td>
<td>-2.23</td>
<td>0.05</td>
<td>-1.10</td>
<td>0.02</td>
</tr>
<tr>
<td>1H-3W(73-74)</td>
<td>3.73</td>
<td>0.22</td>
<td>-2.72</td>
<td>0.08</td>
<td>-1.41</td>
<td>0.04</td>
</tr>
<tr>
<td>3H-4W(3-4)</td>
<td>21.145</td>
<td>1.50</td>
<td>-2.26</td>
<td>0.09</td>
<td>-1.16</td>
<td>0.04</td>
</tr>
<tr>
<td>4H-4W(3-4)</td>
<td>30.635</td>
<td>2.46</td>
<td>-3.56</td>
<td>0.09</td>
<td>-1.83</td>
<td>0.08</td>
</tr>
<tr>
<td>5H-4W(3-4)</td>
<td>40.135</td>
<td>3.55</td>
<td>-3.36</td>
<td>0.04</td>
<td>-1.72</td>
<td>0.04</td>
</tr>
<tr>
<td>6H-4W(3-4)</td>
<td>49.635</td>
<td>4.94</td>
<td>-3.16</td>
<td>0.05</td>
<td>-1.63</td>
<td>0.04</td>
</tr>
<tr>
<td>8H-4W(3-4)</td>
<td>67.275</td>
<td>6.52</td>
<td>-3.98</td>
<td>0.04</td>
<td>-2.06</td>
<td>0.03</td>
</tr>
<tr>
<td>11H-4W(3-4)</td>
<td>97.135</td>
<td>10.65</td>
<td>-3.88</td>
<td>0.08</td>
<td>-2.00</td>
<td>0.06</td>
</tr>
<tr>
<td>14X-4W(73-74)</td>
<td>115.53</td>
<td>11.07</td>
<td>-4.01</td>
<td>0.05</td>
<td>-2.07</td>
<td>0.02</td>
</tr>
</tbody>
</table>

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

Table 2.4 Strontium isotopic composition of bulk carbonates from ODP Hole 1171A

<table>
<thead>
<tr>
<th>Sample Core-section interval (cm)</th>
<th>Depth mbsf a</th>
<th>Age Ma b</th>
<th>$^{87}$Sr/$^{86}$Sr c</th>
<th>2SE internal d</th>
<th>SD external d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg 189 Hole 1171A-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H-1W(73-74)</td>
<td>0.735</td>
<td>0.03</td>
<td>0.70916200*</td>
<td>0.000010</td>
<td></td>
</tr>
<tr>
<td>1H-3W(73-74)</td>
<td>3.73</td>
<td>0.22</td>
<td>0.70912807</td>
<td>0.000006</td>
<td>0.000023</td>
</tr>
<tr>
<td>2H-4W(4-5)</td>
<td>11.645</td>
<td>0.72</td>
<td>0.70912500*</td>
<td>0.000010</td>
<td></td>
</tr>
<tr>
<td>3H-4W(3-4)</td>
<td>21.145</td>
<td>1.50</td>
<td>0.70907800*</td>
<td>0.000010</td>
<td></td>
</tr>
<tr>
<td>4H-4W(3-4)</td>
<td>30.635</td>
<td>2.46</td>
<td>0.70903193</td>
<td>0.000008</td>
<td>0.000018</td>
</tr>
<tr>
<td>5H-4W(3-4)</td>
<td>40.135</td>
<td>3.55</td>
<td>0.70899100*</td>
<td>0.000010</td>
<td>0.000105</td>
</tr>
<tr>
<td>6H-4W(3-4)</td>
<td>49.635</td>
<td>4.94</td>
<td>0.70891700*</td>
<td>0.000013</td>
<td></td>
</tr>
<tr>
<td>8H-4W(3-4)</td>
<td>67.275</td>
<td>6.53</td>
<td>0.708917248</td>
<td>0.000007</td>
<td>0.000019</td>
</tr>
<tr>
<td>10H-4W(3-4)</td>
<td>87.635</td>
<td>9.55</td>
<td>0.708869854</td>
<td>0.000007</td>
<td>0.000014</td>
</tr>
<tr>
<td>11H-4W(3-4)</td>
<td>97.135</td>
<td>10.65</td>
<td>0.70885400</td>
<td>0.000006</td>
<td>0.000009</td>
</tr>
<tr>
<td>14X-4W(73-74)</td>
<td>115.53</td>
<td>11.07</td>
<td>0.70883351</td>
<td>0.000008</td>
<td>0.000023</td>
</tr>
</tbody>
</table>

a As reported in Exon et al. (2001).
b Based on age-depth model using magneto- and biostratigraphy (Stickley et al., 2004).
c Measured using Penn State Metal Isotope Laboratory’s Neptune Plus MC-ICPMS.
d In cases where replicates (2 - 4) were analyzed, the external reproducibility (2-standard deviation) is reported. In cases where no replicates were analyzed, the internal reproducibility (2-standard error) is reported. * $^{87}$Sr/$^{86}$Sr ratios of bulk carbonates are reported in Fantle (2015).
Table 2.5. Trace elemental composition of bulk carbonates from ODP Holes 1171A

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth</th>
<th>[Sr] ppm</th>
<th>SD ppm</th>
<th>Sr/Ca mmol/mol</th>
<th>[Mg] ppm</th>
<th>SD ppm</th>
<th>Mg/Ca mmol/mol</th>
<th>[Na] ppm</th>
<th>SD ppm</th>
<th>Na/Ca mmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H-1W(73-74)</td>
<td>0.735</td>
<td>1488.95</td>
<td>9.72</td>
<td>1.70</td>
<td>477.66</td>
<td>4.54</td>
<td>1.97</td>
<td>1055.87</td>
<td>58.78</td>
<td>4.61</td>
</tr>
<tr>
<td>1H-3W(73-74)</td>
<td>3.73</td>
<td>1171.89</td>
<td>10.03</td>
<td>1.34</td>
<td>553.39</td>
<td>6.58</td>
<td>2.28</td>
<td>934.48</td>
<td>12.28</td>
<td>4.08</td>
</tr>
<tr>
<td>3H-4W(3-4)</td>
<td>21.145</td>
<td>1168.76</td>
<td>17.63</td>
<td>1.34</td>
<td>675.25</td>
<td>8.41</td>
<td>2.78</td>
<td>1074.20</td>
<td>8.43</td>
<td>4.69</td>
</tr>
<tr>
<td>4H-4W(3-4)</td>
<td>30.635</td>
<td>1053.01</td>
<td>13.07</td>
<td>1.20</td>
<td>621.39</td>
<td>18.11</td>
<td>2.56</td>
<td>907.00</td>
<td>6.51</td>
<td>3.96</td>
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<tr>
<td>5H-4W(3-4)</td>
<td>40.135</td>
<td>1124.62</td>
<td>6.60</td>
<td>1.29</td>
<td>683.93</td>
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<td>836.00</td>
<td>37.48</td>
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<tr>
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<td>49.635</td>
<td>1135.59</td>
<td>16.98</td>
<td>1.30</td>
<td>762.97</td>
<td>6.39</td>
<td>3.15</td>
<td>783.32</td>
<td>14.39</td>
<td>3.42</td>
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<tr>
<td>8H-4W(3-4)</td>
<td>67.275</td>
<td>980.49</td>
<td>4.93</td>
<td>1.12</td>
<td>732.32</td>
<td>5.56</td>
<td>3.02</td>
<td>547.41</td>
<td>14.15</td>
<td>2.39</td>
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<tr>
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<td>1423.00</td>
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<td>1.63</td>
<td>558.11</td>
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<td>2.30</td>
<td>540.53</td>
<td>26.68</td>
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<td>1198.03</td>
<td>19.64</td>
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<td>632.33</td>
<td>5.57</td>
<td>2.92</td>
<td>513.05</td>
<td>2.74</td>
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<td>1494.80</td>
<td>15.87</td>
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<td>398.91</td>
<td>0.96</td>
<td>1.64</td>
<td>368.75</td>
<td>2.41</td>
<td>1.61</td>
</tr>
</tbody>
</table>

* As reported in Exon et al. (2001).

* Estimated concentrations in the acetic digested bulk calcite (µg/g CaCO₃) fraction of total solids.

* Calculated from the analytical uncertainty in ICP-AES data.
Fig. 2.1. (a) Location map, (b) simplified lithostratigraphic column including major lithological units, wt. % of CaCO₃ in the sediments and the stratigraphic hiatus marked by wiggle lines, % porosity, and bore hole temperature as a function of depth (mbsf) from ODP Site 1171 (Leg 189). Data are adopted from Exon et al. (2001).
Fig. 2.2. Chemistry of ODP Site 1171 in terms of (a) wt. % of CaCO$_3$ of bulk sediments and pore fluid (b) pH, (c) alkalinity, (d) calcium, (e) magnesium, (d) strontium, (f) sulfate, and (g) ammonium ion concentration as a function of depth (Exon et al., 2001). The abbreviation “pf” stands for pore fluid.
Fig. 2.3. Magnesium isotopic composition ($\delta^{26}\text{Mg}_{\text{DSM3}}$) of (a) pore fluids and (b) bulk carbonates from ODP Site 1171 (this study) and from ODP Hole 807A (Higgins and Schrag, 2012). (c) Mg three-isotope plot to show that all measured data fall on the straight line with slope $\sim0.515 \pm 0.005$ which is identical to the slope of equilibrium mass dependent fractionation line (0.520).
Fig. 2.4. (a) The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and (b) the depth-detrended values of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of bulk carbonates, pore fluids from ODP Site 1171, and the global seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve (McArthur and Howarth, 2004) as a function of depth, the depth profiles of (c) Sr/Ca ratios, (d) Sr concentrations, (e) Mg/Ca ratios, and (f) Mg concentrations of bulk carbonates from Site 1171. Solid black and grey circles represent data measured in this study and from previous publication (Fantle, 2015), respectively.
Fig. 2.5. The correlation between percent deviation of bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve (McArthur and Howarth, 2004) and (a) Sr/Ca ratios and (b) Mg/Ca ratios from ODP Site 1171 are presented. The correlation between bulk carbonate (c) Mg/Ca and Sr/Ca ratios, (d) $\delta^{26}\text{Mg}_{\text{DSM3}}$ and Sr/Ca ratios, (e) $\delta^{26}\text{Mg}_{\text{DSM3}}$ and Mg/Ca ratios and (f) $\delta^{26}\text{Mg}_{\text{DSM3}}$ and percent deviation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve from Site 1171 are presented. The dark and light blue symbols represent the data with good linear correlation ($r^2$) and the outliers in the correlation, respectively.
Fig. 2.6. (a) The Na/Ca ratios (b) the Na concentration as a function of depth, and (c) the correlation between bulk carbonate Na/Ca and $\delta^{26}$Mg of bulk carbonates from ODP Site 1171 are presented.
Fig. 2.7. (a) Variation of the nannofossil (closed circles) and foraminiferal percent abundance (open circles) in bulk carbonates with depth at ODP Hole 1171A with different shades of grey representing different nannofossil assemblages inferred from the smear slide observation in this study (Fig. A.3) and previous data (Exon et al., 2001 and Stickley et al., 2004), (b) the observed and expected (calculated using mass balance) down-hole trends in bulk carbonate $\delta^{26}\text{Mg}$ at Site 1171 with the standard deviation (grey area) of the calculated $\delta^{26}\text{Mg}$, and (c) the initial (calculated using mass balance) and final (model derived) Mg/Ca of bulk carbonates and sea surface temperatures derived from the initial and final Mg/Ca of bulk carbonates using temperature calibration for various foraminiferal Mg/Ca.
Fig. 2.8. The model fits to the measured data of (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 used 6900 m$^3$/Ma as diffusion coefficient ($D_{Mg}$) and 43 mmole/kg as lower boundary [Mg$^{2+}$]. The upper boundary [Mg$^{2+}$] and $\delta^{26}$Mg are fixed to the modern seawater composition ([Mg$^{2+}$] = 53.1 mmole/kg and $\delta^{26}$Mg$_{DSM3}$ = -0.84‰). The open and closed symbols represent measured pore fluids and bulk carbonates, respectively. The solid grey and colored dotted lines from (i) to (v) represent the initial conditions and model results, respectively. The model result # (iii) indicates the preferred fit to the measured data. The subscripts “LB”, “adv”, “pf”, and “carb” represent lower boundary, advection, pore fluid and bulk carbonate, respectively.
Fig. 2.9. The effect of calcite recrystallization during diagenesis on (a) $\delta^{26}\text{Mg}$ and (b) Mg concentration of the bulk carbonates from the Site 1171 using the reaction rates $\sim 7\%/\text{Ma}$ ($R = 0.07* e^{-0.6/6.6}$) with $K_{\text{Mg}} = 1.5$, $\alpha_{s-f}^{\text{diag}} = 0.9955$, $v = 250 \text{ m/Ma}$, and $D_{\text{Mg}} = 6900 \text{ m}^2/\text{Ma}$. The open and solid circles represent the measured pore fluid and bulk carbonates respectively. The solid grey and red lines represent the initial condition and final model outcomes respectively. The subscript “carb” represents the bulk carbonates.
Fig. 2.10. 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; the Monte Carlo dataset is sub-selected at 25 depths to simulate 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.
Fig. 2.11. Schematic diagram showing diagenetic processes in the bulk sediment. (a) The upper and lower diagonal halves of the rectangular box are showing the external and internal structures of the foraminiferal and coccolith tests. (b) The dissolution-precipitation (“Diss-ppt”) and solid-state diffusion (“Diff”) processes involving foraminiferal tests are shown. Intra-test heterogeneity in foraminiferal Mg/Ca is shown by dark and light grey alternate bandings. K and α represent the partition coefficient and fractionation factor of Mg associated with each process.
2.7. References


Lestini L., Beaucaire C., Vercouter T., Descostes M. (2013); Radium uptake by recrystallized gypsum: an incorporation study; *Procedia Earth Planet. Sci.* 7, 479-482


Chapter 3

Elucidating primary controls on marine pore fluid $\delta^{26}$Mg from multiple sites to evaluate the extent of diagenetic alteration on carbonates and its impact on geochemical proxies

3.1 Abstract

The Mg, Ca, and Sr isotopic compositions of pore fluids, bulk carbonates, and bulk clays from ODP Holes 762B, 806B, and 807A are analyzed. The main purpose of this study is to elucidate the major controls on marine pore fluid $\delta^{26}$Mg, specifically the effect of calcite recrystallization and authigenic clay precipitation in sedimentary sections containing a variable amount of carbonates. Such studies are critical for evaluating the potential of pore fluids in carbonate section to drive diagenetic alteration and its implication on the preservation of geochemical proxies.

The pore fluid $\delta^{26}$Mg at each site shows a systematic increase with depth. In the upper ~108 m sections of all three sites, the pore fluid $\delta^{26}$Mg gradually increases from the modern seawater value (-0.80 ± 0.04 ‰) to -0.54 ± 0.08 ‰ (Holes 807A and 806B) and -0.39 ± 0.04 ‰ (Hole 762B). Below ~110 mbsf in both Holes 807A and 762B, pore fluid $\delta^{26}$Mg decreases noticeably by ~0.2‰, while pore fluids in the 806B exhibit a continual, gradual increase in $\delta^{26}$Mg to -0.17‰ at 679.9 mbsf.

Simple reactive transport modeling suggests that the general increase in the pore fluid $\delta^{26}$Mg with depth results from diffusion and calcite recrystallization. The difference between pore fluid Mg/Ca ratios between Holes 807A and 806B is explained by different rates of calcite recrystallization and lower boundary conditions. However, diffusive communication with an isotopically distinct lower boundary alone cannot entirely explain the observed decrease by ~0.2‰ in the pore fluid $\delta^{26}$Mg between 200 and 300 m depth.
Lithological and mineralogical evidence from Hole 762B indicates that the Mg isotopic shift in the pore fluids occurs at a depth interval (between ~120 and 144 mbsf) where clay (mainly illite and smectite) content increases from 3% to 11%, CaCO$_3$ content decreases from 87% to 63%, and porosity decreases by ~10%. The isotopic and mineralogical data are consistent with the formation of secondary clays that preferentially sequester isotopically heavy Mg, implying that clay precipitation is relevant to the geochemical evolution of pore fluids even in carbonate-rich sediments. Reactive transport models using the Stella and CrunchTope software packages, which include reactions between pore fluids and both calcite and clay minerals, are used to evaluate the impact of clay precipitation within the carbonate-rich sediments on pore fluid and carbonate $\delta^{26}$Mg. The model results also indicate that the increase in carbonate $\delta^{26}$Mg within the clay-rich layer in Hole 762B cannot be explained by calcite recrystallization. Instead, the observed increase may reflect less alteration of carbonates within the clay-rich interval. The increase in bulk carbonate Na/Ca, Sr/Ca, and Mg/Ca in this depth interval (120-144 mbsf) also supports this hypothesis that the presence of clay enhances proxy preservation.

Combined analytical data and model results suggest that pore fluid $\delta^{26}$Mg can identify deep diagenetic reactions like clay precipitation in carbonate-rich sediments. Identifying such variation in lithology within the carbonate-rich section is important because precipitation of clay can also minimize the impact of calcite recrystallization on the carbonate-based geochemical proxies. This study also demonstrates the significance of bulk carbonates in quantifying the diagenetic impact on geochemical proxy records, especially in studies involving rock records from the deep time where isolating small-scale proxy archives (e.g. foraminiferal tests) from bulk sediment is not a viable option.
3.2 Introduction

The geochemical cycling of Mg is directly related to the global carbon cycle via continental weathering and precipitation of marine carbonates and hence is invaluable for reconstructing variability in past climatic conditions (e.g. pCO$_2$ and temperature) (e.g., Berner et al., 1983; Berner, 1994; Berner and Berner, 1996). The Mg budget in the ocean is regulated by continental weathering via riverine discharge and by reincorporation of Mg into lithosphere primarily via hydrothermal circulation at the mid-oceanic ridges and also through marine carbonate deposition (biogenic carbonates and dolomites) and authigenic clay formation during low-temperature seawater-basalt interaction as secondary sinks (Edmond et al., 1979; Berner and Berner, 1997; Holland, 2005; Tipper et al., 2006). The primary sink of Mg, i.e., high-temperature hydrothermal circulation is known to remove Mg from the seawater quantitatively (Tipper et al., 2006; Higgins and Schrag, 2012). However, Mg isotopes are fractionated at the source (weathering flux: -1.09 ± 0.05‰) and at the secondary sinks (i.e., dolomite = -1.8 to -2.0 ‰, biogenic carbonates = -4.0 to -5.0‰, and clays = 0.3 to -0.05‰) (Tipper et al., 2006a; Tipper et al., 2006b; Shen et al., 2009). Therefore, reconstructing past variability of seawater δ$^{26}$Mg offers a unique opportunity to decouple the long-term changes in the input and output fluxes of Mg to the ocean, which helps us to solve the long-standing problems related to dolomite formation and the steady state of Mg in the ocean.

The δ$^{26}$Mg of marine carbonates, especially foraminiferal calcite is a promising proxy for seawater δ$^{28}$Mg (Higgins and Schrag, 2012; Pogge von Strandmann et al., 2014) because fractionation of Mg isotopes in low-Mg foraminiferal calcite shows negligible correlation with carbonate ion concentration, salinity, growth rate, and temperature (range: 5-35°C) (Pogge von Strandmann, 2008; Saulnier et al., 2012; Pogge von Strandmann, 2008; Chang et al., 2004; Wombacher et al., 2011; Saenger and Wang, 2014). Therefore, foraminiferal δ$^{26}$Mg has potential
to record the secular variability of seawater $\delta^{26}\text{Mg}$ and thus can be used to determine the temporal variation in the global Mg cycle.

The effectiveness of any isotopic proxy depends on accurate calibrations of the fractionation factor to the environmental conditions of interest and on the knowledge of the susceptibility of the primary isotopic signal to diagenesis. Post-depositional diagenetic recrystallization via dissolution of primary carbonates and precipitation of secondary carbonates is known to impact the trace elemental and isotopic composition of carbonates significantly and thus can complicate the carbonate-based geochemical proxy interpretation (Fantle and DePaolo, 2006; Fantle et al., 2010; Fantle and Higgins, 2014; Fantle, 2015). Therefore, it is critical to quantify the diagenetic effect on the trace elemental and isotopic composition of carbonates to facilitate accurate proxy reconstruction. This is especially true for Mg isotopes in carbonates, as foraminiferal $\delta^{26}\text{Mg}$ has already been used to interpret the global Mg cycle (Higgins and Schrag, 2012; Pogge von Strandmann et al., 2014) despite the fact that very little is known about the susceptibility of marine carbonate $\delta^{26}\text{Mg}$ to diagenetic alteration.

Marine pore fluids play a vital role in altering the concentration and isotopic compositions of trace metals in carbonate during diagenetic recrystallization. Especially, Mg in carbonates is more sensitive to diagenetic exchange than the Mg in pore fluids. In a given amount of sediment with 50-60% porosity molar mass of Mg in pore fluids is 2-3 times higher than the molar mass of Mg in carbonates. Moreover, the extent to which the isotopic compositions of an element in carbonates get altered ($d\delta_s$) is dictated by the following expression (Eq. 3.1.), which involves rate ($R$) and the duration ($dt$) of the recrystallization and the isotopic disequilibrium between the solid and coexisting pore fluids $\left(\delta_s - \delta_f - \Delta_{s-f}^{\text{diag}}\right)$ (Fantle and DePaolo, 2007; Fantle et al., 2010; Fantle, 2015) (Eq. 3.1).

$$d\delta_s = -R \left[ (\delta_s - \delta_f) - \Delta_{s-f}^{\text{diag}} \right] dt \quad \text{---- (3.1)}$$
Here, the isotopic compositions of the solid and the pore fluid are represented by $\delta_s$ and $\delta_f$ respectively and the isotopic fractionation associated with the diagenetic recrystallization is represented by $\Delta_{s-f}^{diag}$. Because the $\delta^{26}$Mg of marine pore fluids and bulk carbonates differ significantly (pore fluid: -0.2 to -0.8 ‰ and carbonates: -3.5 to -5.5‰) (Higgins and Schrag, 2010; Higgins and Schrag, 2012) diagenetic exchange between carbonates and pore fluids is also likely to alter the $\delta^{26}$Mg of carbonates.

Additionally, in a carbonate-rich section, the reactive length scale ($L_d$) of Mg is larger (~1100-2000 m) than that of Ca and Sr (~20 mbsf and ~200 mbsf, respectively). The reactive length scale is the spatial extent, i.e., depth in this case, over which the pore fluid reacts with the sediment to reach local equilibrium with respect to a certain element in the system. In a sedimentary column, where the effect of advection is negligible to none, the reactive length scale ($L_d$) of an element is defined by the following equation (Fantle and DePaolo, 2006; Fantle and DePaolo, 2007; Fantle et al, 2010; Fantle, 2015):

$$L_d = \sqrt{\frac{D}{RKM}}$$

--- (3.2)

Here, the terms $D$ and $K$ stand for the diffusion coefficient and partition coefficient of that element in the sediment, respectively, and $R$ and $M$ represent the reaction rates and solid to fluid mass ratio, respectively. As a result, Mg in carbonates, due to a large reactive length scale, is susceptible to a greater extent of alteration compared to Ca and Sr in carbonates. Therefore, Mg in marine carbonates not only has a higher susceptibility to alteration and the extent of alteration of carbonate Mg is also larger than other elements.

Marine sedimentary sites may undergo a variable degree of diagenetic recrystallization depending on their location (i.e., water depth), sedimentation rate, thickness, the influence of transport process, and variation in the lithology (i.e., carbonate-silicate intercalation) (Richter and
Liang, 1993; Fantle and DePaolo, 2006; Fantle, 2015). Transport processes (e.g., advection and diffusion) modify the pore fluid chemistry in a sedimentary column and thus enhance the local chemical disequilibrium between the pore fluids and bulk carbonates. The greater the chemical mismatch between the carbonates and pore fluids the higher the extent of recrystallization in marine carbonates. Additionally, lithological variability within carbonate-rich sediments, especially the presence of clay can also influence the concentration and isotopic composition of pore fluid Mg. Biogenic calcification preferentially sequesters light Mg nuclide ($^{24}\text{Mg}$) while silicate minerals tend to incorporate heavy Mg nuclides ($^{25}\text{Mg}$ and $^{26}\text{Mg}$) favorably (e.g., Galy, 2002; Young and Galy, 2004; Cheng et al., 2003; Cheng et al., 2004; Tipper et al., 2006b; Pogge von Strandmann, 2008; Wombacher et al., 2011; Wimpenny et al., 2014). The theoretical equilibrium fractionation factor for Mg during calcite precipitation is 0.9950 (ab initio technique; Rustad et al., 2010) while laboratory precipitation of brucite suggests a fractionation factor of 1.0005 (Wimpenny et al., 2014). Since clay incorporates more Mg than carbonates, authigenic precipitation of clay within carbonate-rich sediments has the potential to modify both pore fluid Mg concentration and $\delta^{26}\text{Mg}$. Because pore fluid chemistry dictates the extent of carbonate diagenesis, the presence of clay-bearing intervals within carbonate-rich sediments can influence the rate and extent of carbonate diagenesis.

Given the high susceptibility of carbonate Mg (both Mg/Ca ratio and $\delta^{26}\text{Mg}$) to diagenetic recrystallization selecting the ideal marine site with high preservation potential is a fundamental requirement of developing proxy records based on carbonate Mg. In this regard, comparison of marine carbonate $\delta^{26}\text{Mg}$ between multiple sites influenced by transport processes and lithological variation is useful in identifying sites with potential to generate high-fidelity proxy records. As seawater is homogeneous with respect to Mg and as $\delta^{26}\text{Mg}$ of biogenic carbonates are only sensitive to seawater $\delta^{26}\text{Mg}$, differences in the contemporaneous records of marine carbonate $\delta^{26}\text{Mg}$ can be attributed to differences in diagenesis. Therefore, site-to-site
comparisons of marine carbonate $\delta^{26}\text{Mg}$ also can be useful in isolating diagenetic signals from primary depositional signals.

In this study, we investigated the effect of diagenesis on the $\delta^{26}\text{Mg}$ of deep-sea carbonates using Ca, Sr, and Mg isotopic compositions of marine pore fluids and bulk carbonates from three ODP sites (762, 806, and 807) (Fig. 3.1). Variability in the CaCO$_3$ content and pore fluid chemistry between these three sites provide an opportunity to evaluate the influence of these parameters on calcite recrystallization and its impact on the preservation of geochemical proxies. Here we present the $\delta^{26}\text{Mg}$ measurements from bulk carbonates and pore fluids from ODP Holes 806B and 762B, along with $\delta^{26}\text{Mg}$ of bulk clays from Hole 762B and high-resolution pore fluid $\delta^{26}\text{Mg}$ data from Hole 807A. Due to the difference in reactive length scales between Ca, Sr, and Mg, these elements have different sensitivity to carbonate diagenesis (Fantle and DePaolo, 2006; Fantle et al., 2010; Fantle, 2015). Consequently, studying multiple proxies from the same sites provides the scope to elucidate the impact of diagenetic alteration on the carbonate-based proxies over different depth scales. Using Mg isotopes along with Ca and Sr has an additional advantage as Mg isotopes can identify reactions involving silicate minerals in the deeper part of the sedimentary column (Higgins and Schrag, 2010). Therefore, comparing multiple proxy records between different marine sites helps to estimate the diagenetic effect on carbonate-based geochemical proxies.

This is the first study to compare and contrast the $\delta^{26}\text{Mg}$ records of both bulk carbonates and pore fluids from two adjacent Sites (ODP 806 and 807). Despite their similarity in age, sediment thickness, depositional history, these two sites show significant difference in pore fluid chemistry, especially in the downcore Mg/Ca, and Sr/Ca profiles (Kroenke et al., 1991; Delaney and Linn, 1993). Given the similarity between the two sites, such contrast in pore fluid chemistry can be attributed to carbonate diagenesis. In this study, we investigated the effect of post-
depositional diffusive communication with the lower boundary on calcite recrystallization rates and evaluated the diagenetic effect on geochemical proxies.

The Site 762 is chosen to investigate the impact of lithological variability on carbonate diagenesis and its implication on proxy preservation. The lithological contrast between two Pacific holes (806B and 807A) and the Indian Ocean Hole 762B helps evaluate the influence of reactions involving silicates on the $\delta^{26}\text{Mg}$ of marine pore fluids and bulk carbonates. Ultimately, the primary objectives of this study are: 1) to evaluate the diagenetic effect on Mg isotopes in marine pore fluids and carbonates from thick carbonate-rich sections that only experience diffusion and 2) to investigate the influence of lithological variability on the extent of alteration of carbonate-based geochemical proxies, especially, carbonate $\delta^{26}\text{Mg}$.

3.3 Materials and Methods

3.3.1 Study Sites

The ODP sites selected for this study are located in different depositional settings. The two adjacent Sites, 807 (3°36.420 N, 156°37.490 E) and Site 806 (0°19.11’N, 159°21.68’E) are situated on the northeastern side of the Ontong Java Plateau at water depths of 2804 m and 2520 m, respectively (Fig. 3.1). The Quaternary and Neogene sections from both of these sites are represented by ~800 m thick foraminifera and nannofossil bearing carbonate-rich sediments. The lowermost sediments in the two holes range from early Oligocene (Hole 807A) to late Oligocene (Hole 806B) (Kroenke et al., 1991). The maximum thickness of the sediment cover at these sites is more than 1200 m. The upper ~800 m of the sedimentary columns in Holes 807A and 806B are represented by relatively continuous sedimentary section with high CaCO$_3$ content (~85-95 wt. %), low organic-carbon content (0.02 – 0.6 wt. %), porosity (~70% near sediment-water interface
to ~50% near ~800 mbsf) and presence of trace amount of biogenic (radiolarian, diatom, sponge) and terrigenous (clay, quartz, and feldspar) silicate components (Kroenke et al., 1991, Bassinot et al., 1993).

The age-depth relationships constructed from biostratigraphy and magnetostratigraphy shows that the average sedimentation rate for Hole 807A is 24.6 m/Ma, which is slightly lower the sedimentation rate for Hole 806B (~30 m/Ma) (Appendix Fig. B.1a). The sedimentation rate in Hole 806B exhibits a decrease from ~33 m/Ma to ~20 m/Ma in lower Miocene followed by an increase to ~46 m/Ma in upper Miocene (5-10 Ma). However, during the Pliocene-Pleistocene Period the sedimentation rate decreased to ~21 m/Ma (Kroenke et al., 1991).

The Site 762 is located on the western margin of the Exmouth Plateau (19°53.24’S, 112°15.24’E) at a water depth of 1360 m (Haq et al., 1990) (Fig. 3.1). The upper ~176 m thick section of the sedimentary column (Hole 762B) is primarily composed of foraminifera and nannofossil-bearing carbonate ooze although the CaCO₃ content is quite variable over the depth (~60 to 86 wt%) with variable amount of radiolarians, sponge spicules, quartz and clay minerals (1-10%) (Haq et al., 1990; de Carlo, 1992). The sedimentary section in Hole 762B is relatively continuous spanning from middle Miocene to Quaternary in age with an exception of a brief unconformity at ~130 mbsf. The average sedimentation rate in Hole 762B is 1-2 m/Ma, which is significantly slower than the sedimentation rates observed at Sites 807A and 806B (Haq et al., 1990) (Appendix Fig. B.1b).

The geochemistry of the pore fluids exhibits a significant difference between the three sites (Fig. 3.2, Appendix Fig. B.2) (Kroenke et al, 1991; Haq et al., 1990; de Carlo, 1992; Delaney and Linn, 1993). An increase in alkalinity is observed at all three sites above ~200 m depth, but the magnitude of the increase is higher in Holes 807A and 806B (from ~3.6 to 7 mM) compared to Hole 762B (~3.6 to 5 mM). Below 200 mbsf the alkalinity at all three sites decrease to ~3.6 mM. In upper 200 m depth the calcium concentration ([Ca²⁺]) in the pore fluids increases
down-depth in both Holes 807A and 806B to ~18 mM. However, below 200 m depth the pore
fluid [Ca\(^{2+}\)] shows a monotonic increase to ~30 mM at ~700 mbsf in Hole 806B while in Hole
807A the gradient of pore fluid [Ca\(^{2+}\)] becomes steeper and [Ca\(^{2+}\)] increases only up to ~20 mM
over the same depth interval. In contrast, the pore fluid [Ca\(^{2+}\)] in Site 762 only increases to ~11
mM over 940 m depth. The Mg concentration ([Mg\(^{2+}\)]) in pore fluids at all three sites exhibits a
systematic down-hole decrease although below 200 mbsf the gradient of the decrease in pore
fluid [Mg\(^{2+}\)] in Hole 807A is steeper than that in other two sites. In Holes 807A and 806B the
pore fluid Sr concentration ([Sr\(^{2+}\)]) increases rapidly to ~1000 uM in upper 200 m depth followed
by almost no change in the deeper part in Hole 807A and a very slow increase in Hole 806B to
~1200 µM. Contrastingly, the pore fluid [Sr\(^{2+}\)] in Site 762 only increases to ~400 uM in the upper
200 m depth followed a very slow increase to 450 uM at ~600 mbsf and almost a constant
concentration below that depth. The potassium concentration ([K\(^{+}\)]) exhibits a slow but
monotonic increase over the similar depth range in Holes 807A and 806B while the decrease in
pore fluid [K\(^{+}\)] is more rapid and significant at Site 762 (Kroenke et al., 1991; Haq et al., 1990; de
Carlo, 1992; Delaney and Linn, 1993).

The pore fluid SO\(_4^{2-}\) concentration ([SO\(_4^{2-}\)]) in Holes 807A and 806B decreases in a
similar fashion from seawater SO\(_4^{2-}\) to ~22 and 18 mM, respectively. In contrast, the [SO\(_4^{2-}\)] at
Site 762 decreases rapidly with depth to a much lower value (~2 mM at 700 mbsf) that the other
two sites. In both Holes 807A and 806B the dissolved silica concentration [SiO\(_2\)] in pore fluid
shows a steady increase from ~600 µM near sediment-water interface to ~1500 µM at ~800 mbsf
depth (Kroenke et al., 1991; Delaney and Linn, 1993). On the contrary, in Site 762 the pore fluid
[SiO\(_2\)] decreases to 200 µM in upper 200 mbsf depth followed by an increase to ~900 µM
between 200 and 400 mbsf and another subsequent decrease to ~200 µM below 400 mbsf (Haq et
3.3.2 Sample Preparation

The pore fluids samples were processed were filtered and processed with an oxidizing mixture of of 25% hydrogen peroxide (H$_2$O$_2$) and 6N HNO$_3$ at 80°C for 40 minutes (3 to 5 times) to remove the organic matter. Digested aliquotes were then dried down and reserved for chemical and isotopic analyses. The bulk carbonates were cleaned and selectively digested using a digestion procedure adopted from a previously developed method (Apitz, 1991; Delaney and Linn,1993). The method involves reductive cleaning of bulk sediments followed by selective digestion of the carbonates using 0.1 M ammonium acetate-acetic acid buffer (pH ~ 4.7) solution. An aliquot of the acetate-digested sample was then filtered, weighed, and stored for later analysis. A Perkin-Elmer Optima 5300 UV ICP-AES was utilized to analyze elemental concentration of the digested samples prior to ion exchange chromatography. The detailed method is described in the Appendix B (Section B.1.1).

The residual silicate fraction from the previous selective digestion step of the bulk solid is filtered and digested using a combination of concentrated HCl, HNO$_3$, HF, and HClO$_4$ acid to dissolve the silica and remove organic matters (Appendix B, Section.B.1.2).

3.3.3. Ion Chromatographic Purification of Mg, Ca, and Sr

Aliquots of the digested pore fluids and carbonates were purified for Ca, Sr, and Mg sequentially using a three-stage ion-exchange chromatography developed using Eichrom’s TODGA resin (Horwitz et al., 2005; Pourmand and Dauphas, 2010, Harouaka et al., 2016), Eichrom’s Sr Spec resin (Fantine and DePaolo, 2006), and Bio-Rad’s AG-50W-X8 resin (Wombacher et al., 2009; Wombacher et al., 2011). The procedure is described in details in Appendix B (Section. B.1.3, Fig. B.3). The average yields of the Ca, Sr, and Mg from these
column separation methods are 98.5±0.5%, 98.3±0.5%, and 99.5±0.5%, respectively, which confirms near quantitative purification of Ca, Sr, and Mg.

3.2.4. Analyses of Ca, Mg, and Sr isotopes using MC-ICPMS

The Mg isotopic composition of pore fluids, bulk carbonates, and clays were measured using a Thermo Scientific Neptune Plus multi-collector ICP-MS. In order to reduce the effect of interference of polyatomic \((^{12}\text{C}^{14}\text{N}^+),^{12}\text{C}_2^+,^{12}\text{C}_2^2\text{H}^+,^{23}\text{Na}^3\text{H}^+)\) and doubly-charged ions (e.g., \(^{48}\text{Ca}^2+,^{48}\text{Ar}^2+,^{50}\text{Cr}^2+,^{52}\text{V}^2+,^{52}\text{Cr}^2+,^{52}\text{Mn}^2+)\) on masses 24, 25, and 26, in addition to the effective separation Mg from all other elements, Elemental Scientific’s (ESI) Apex IR desolvating nebulizer was used to introduce the purified samples to the plasma as dry aerosol. The Mg samples diluted to 200-250 ppb in 0.3N HNO\(_3\) produced \(^{24}\text{Mg}\) ion beam of ~15 volts intensity in medium mass resolution \((M/\Delta M \sim 7000)\) using a combination of Thermo H-skimmer cones and Spectron jet sample cones.

Sample standard bracketing technique with DSM3 as a reference standard is used to correct the delta values for the instrumental mass bias. The Mg isotopic composition of the sample is expressed using the following delta notation:

\[
\delta^x\text{Mg} = \left( \frac{X_{Mg}^{24}/X_{Mg}^{25}}{X_{Mg}^{24}/X_{Mg}^{25}}_{\text{DSM3}} \right) - 1 \times 1000

\text{---- (3.3)}
\]

where \(x\) stands for either mass 25 or 26. Several measurements of in-house laboratory standards (not put through column chemistry) and seawater (that was purified) relative to DSM3 resulted in \(\delta^{26}\text{Mg}\) and \(\delta^{25}\text{Mg}\) values identical to their published values (Table 3.1). The isotopic composition of each sample is reported as the average \(\delta^{26}\text{Mg}\) of three to five 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).
The quality of the analysis was assessed by measuring multiple in-house standards (Cambridge-1 and Fang-Zhen Teng’s laboratory standard, FZT-Mg) in several replicates within each analytical session (Appendix Table B.1). The typical external reproducibility (2SD) of \( \delta^{26}\text{Mg} \) is in each analytical session was \( \leq 0.10\% \). In addition, all samples were plotted on the \( \delta^{26}\text{Mg} \) vs. \( \delta^{25}\text{Mg} \) line to ensure that all data points fall along the equilibrium mass dependent fractionation line of slope ~0.520.

The \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratios were measured on the Thermo Scientific Neptune Plus MC-ICPMS in low-resolution mode using wet plasma conditions. The 200 ppb Sr solutions in 0.3N HNO3 resulted ~10-12 volts signal on \( ^{88}\text{Sr}^+ \) (Balashov et al., 2015; Fantle, 2015). Intensities were monitored at mass 82, 83, 84, 85, 86, 87, and 88. The instrumental mass bias and Kr interference corrections were performed off-line (Appendix B, Section. B.1.4). Multiple measurements of the standard SRM-987 over two years produce an average \( ^{87}\text{Sr}/^{86}\text{Sr} \) value of \( 0.710223 \pm 0.000038 \) (2\( \sigma \)) (NIST certified value: 0.71034± 0.00026). Besides, several measurements of Sr purified from seawater samples yield an average \( ^{87}\text{Sr}/^{86}\text{Sr} \) of 0.709110 ± 0.000042 (comparable to the reported modern seawater value: 0.709175± 0.00002) within the analytical uncertainty. In this contribution, the \( ^{87}\text{Sr}/^{86}\text{Sr} \) values are linearly de-trended with respect to depth to help in comparison for relatively small-scale variability in the depth profile.

The Ca isotope analysis was performed using the Thermo Scientific Neptune Plus MC-ICPMS. The analytical technique, adopted from Harouaka et al., 2016, involves introduction of the ~3.5 ppm of purified Ca samples in 1% HNO3 to the plasma using Cetac Aridus II desolvation system as a dry aerosol. The purpose of using Aridus is to effectively remove the polyatomic interference (e.g., \( ^{40}\text{ArH}_2 \), \( ^{14}\text{N}_3 \), \( ^{14}\text{N}_2^{16}\text{O} \)) generated from the sample matrix and the carrier gas. A combination of Thermo Scientific jet cone and Spectron skimmer H cone was used to enhance sensitivity and stability of the signal. The resulting intensity on mass 44 was ~8 volts using ~3.5 ppm of Ca samples in medium resolution (M/\( \Delta M \) ~7000-8000). The signal at mass 48, 46, 43,
and 42 were monitored on the H4, H2, L1, L2, and L4 Faraday cups, respectively. Another cup (H3) was set to monitor for mass 47 ($^{47}$Ti$^+\). The primary polyatomic interferences on mass 44 were $^{14}$N$_2$$^{16}$O$^+$ and $^{40}$ArH$_2^+$ and on mass 42 was $^{14}$N$_3^+$ in dry plasma mode in medium resolution. Typical background intensities at masses 44 and 42 measured in blank 1% HNO₃, were <6 and <2 mV, respectively. A plateau test is performed before each analysis to identify the interference-free plateau on the mass 44 and 42 by analyzing $^{44}$Ca/$^{42}$Ca and $^{43}$Ca/$^{42}$Ca ratios of NIST SRM-915b at several masses along the plateau. The typical interference-free plateau width is <0.01 amu). Ideally the plateau mass to measure isotope ratios is approximately the mid point between the shoulder of the plateau and the rise of the interference peak ($^{40}$ArH$_2^+$) on the mass 42. The mass difference (amu) between the half width full maximum (HWFM) and the plateau mass was measured and considered as a constant offset, which then applied to select the plateau masses with respect to the HWFM to ensure that the measurements were done at interference-free plateau masses.

Isotope ratios were collected in a single block of 40 cycles, with an 8.39 s integration time and a 5 s idle time. Each measurement was followed by a 5 minute rinse with clean 1% HNO₃. To correct for the instrumental mass bias, each sample was bracketed by Sr-purified NIST SRM-915a standard. The delta notation of Ca isotopic composition of the sample relative to the NIST standard SRM-915a is expressed as follows:

$$\delta^{44/42}\text{Ca} = \left(\frac{(44\text{Ca}/42\text{Ca})_{\text{sample}}}{(44\text{Mg}/42\text{Mg})_{\text{SRM-915a}}} - 1\right) \times 1000$$ ---- (3.4)

In this paper, the Ca isotopic composition of reported as $\delta^{44/40}\text{Ca}$ with respect to both NIST SRM-915a and bulk earth scales (BE). The conversion of $\delta^{44/42}\text{Ca}$ to $\delta^{44/42}\text{Ca}$ is done by multiplying the measured $\delta^{44/42}\text{Ca}$ values by a factor 2.15.

The precision and accuracy of the analysis was assessed by analyzing multiple isotope standards (NIST SRM-915b and SRM 3109) 4-6 times in every analytical sessions along with
each sample measured at least in three replicates (Table B.2). The typical analytical uncertainty expressed in 2 times the standard deviation of all replicates of each sample (i.e., external 2SD) is <0.1‰. Additionally, to ensure that the measurements were not affected by Sr interference, all samples were plotted on the δ^{44/42}\text{Ca} - δ^{43/42}\text{Ca} isotope-isotope plot where deviation from the mass dependent fractionation line is used to diagnose the presence of Sr impurity in the sample and standard. Instrument operating conditions are described in detail in Appendix Table B.3.

3.3.5. Depositional calcite recrystallization model

In order to interpret the Mg isotope data and constrain the calcite recrystallization rates using Sr and Ca isotopes the current study utilizes a depositional reactive transport model similar to the previous studies (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 model assumes a monomineralic sedimentary section (i.e. only calcite) where dissolution and precipitation fluxes of Ca are balanced. Also, the effect of compaction in the sedimentary column is considered to be negligible in this model (i.e. \( V=0 \)). The temporal evolution of the elemental concentration in the fluid (\( \frac{\partial C_{pf}}{\partial t} \)) and the solid (\( \frac{\partial C_{s}}{\partial t} \)) in a carbonate sedimentary section are defined by the following equations:

\[
\frac{\partial C_{pf}}{\partial t} = D_i \frac{\partial^2 C_{pf}}{\partial z^2} - v \frac{\partial C_{pf}}{\partial z} + RM (C_{s} - K_i C_{pf}) \quad \text{---- (3.5)}
\]

\[
\frac{\partial C_{s}}{\partial t} = -V \frac{\partial C_{s}}{\partial z} - R (C_{s} - K_i C_{pf}) \quad \text{---- (3.6)}
\]

where \( C_i \) stands for the concentration of element \( i \) in the pore fluid (pf) and solid (s). The term \( D_i \) represents the tortuosity-corrected diffusion coefficient of element \( i \) in sedimentary column.
(m²/Ma) and R stands for the recrystallization rate of the solid (Ma⁻¹). The equilibrium partition coefficient of element i between solid and pore fluid is $K_i$ and $M$ is the solid/fluid mass ratio (= $\rho_s (1-\phi)/\rho_f \phi$; where $\rho$ is density and $\phi$ is porosity). The term $V$ represents compaction, and $v$ is advection velocity (m/Ma) of the external fluid.

The 1-dimensional spatial reference frame is defined such that the depth, $z = 0$ at the sediment-basement interface. The recrystallization rate ($R$) is a function of sediment age (Richter and DePaolo, 1987; Richter and DePaolo, 1988; Richter, 1993, 1996; Richter and Liang, 1993; Fantle and DePaolo, 2006; and DePaolo, 2007; Fantle, 2015) and is defined by the following equation:

$$R (\text{age}, \text{Ma}) = \alpha + \beta \cdot e^{-\text{age}/\gamma} \tag{3.7}$$

Here, the background reaction rates are represented by $\alpha + \beta$ (age=0), and $\gamma$ reflects the rate at which the recrystallization rate approaches the long-term rate ($\alpha$).

The equilibrium partition coefficient ($K_i$) of the element between the solid and coexisting pore fluids is defined by the following expression where $C_f$ and $C_s$ are the concentrations of that element in the fluid solid:

$$K_i = \frac{C_f}{C_s} \tag{3.8}$$

The mass dependent isotopic fractionation is defined by two stable nuclides $j$ and $k$ of element $i$:

$$\alpha_{s-f}^\text{diag} = \frac{K_j^i}{K_k^i} \tag{3.9}$$

Detailed formulation of partition coefficient, fractionation factor and diffusion coefficients are described in Appendix B (Section. B.1.5).
3.4. Results

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

The general pore fluid $\delta^{26}$Mg trend at each of the three sites is a systematic increase with depth. In the upper ~108 m of all three sites, the pore fluid $\delta^{26}$Mg gradually increases from the modern seawater value (-0.80 ± 0.04 ‰) to -0.54 ± 0.08 ‰ (Holes 807A and 806B) and -0.39± 0.04 ‰ (Hole 762B). Below ~110 mbsf depth in both Holes 807A and 762B, pore fluid $\delta^{26}$Mg decreases noticeably by ~0.15 – 0.3‰, while pore fluids in Hole 806B exhibit a gradual increase in $\delta^{26}$Mg to -0.17‰ at 679.9 mbsf (Fig. 3.3a, and 4.4a and Table.3.1 and 3.8).

The bulk carbonates from ODP Hole 806B exhibit general decreasing trend from -3.75‰ to -5.0‰ with depth, similar to the $\delta^{26}$Mg of carbonates with <65um grain size from ODP Hole 807A (Higgins and Schrag, 2012) while the bulk carbonate $\delta^{26}$Mg from Site 762B shows an oscillatory trend with depth. The bulk carbonate $\delta^{26}$Mg values in Hole 762B initially increase from -4.45‰ to -4.22‰ in upper 25 m, followed by a decrease to -5.27‰ at ~80 mbsf. In between 100 – 140 mbsf the $\delta^{26}$Mg in bulk carbonates exhibit a significant increase by ~0.5 – 1.0‰ followed by a subsequent decrease to -4.57± 0.05 ‰ at 166.62 mbsf depth (Fig. 3.3b, and 3.4b, Table 3.2 and 3.9).

The $\delta^{26}$Mg value of the bulk clays measured from the depth interval between 100 and 150 mbsf in the Hole 762B are in general higher (range: -0.09 to 0.27‰) than the bulk carbonate $\delta^{26}$Mg (range: -4.01 to -5.27‰). However, the bulk clay $\delta^{26}$Mg exhibit a slight overall decrease with depth (from 0.27 ± 0.08‰ at 104.78 mbsf to -0.09± 0.03‰ at 144.11 mbsf) (Fig. 3.4c and Table.3.10).
3.4.2 Strontium isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}$) of bulk carbonates and pore fluids

The $^{87}\text{Sr}/^{86}\text{Sr}$ of the bulk carbonates from both Holes 806B and 762B systematically vary between modern seawater $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.709150 ± 0.000005) and 0.708773 at depth following the general trend of the Sr seawater curve (McArthur 2001; McArthur and Howarth, 2004). The pore fluid $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from both Holes 806B and 762B decrease from 0.70914 (close to modern seawater value: 0.70917) near the sediment-water interface to 0.70851 and 0.708211 in the deeper part of the sections respectively following the similar (though offset relatively) trend of the bulk carbonates (Fig. 3.5 and Appendix Fig. B.4; Tables 3.3, 3.4, 3.13, and 3.14).

3.4.3 Calcium isotopic composition ($\delta^{44/40}\text{Ca}$) of bulk carbonates and pore fluids

In Hole 806B, the bulk carbonate $\delta^{44/40}\text{Ca}_{\text{SRM-915a}}$ varies between 0.49 and 0.44 (± 0.1) ‰ over ~500 m depth. The $\delta^{44/40}\text{Ca}_{\text{SRM-915a}}$ of pore fluids in upper 50 m depth decreases rapidly from 1.27 ± 0.03‰ (at 4.45 mbsf) to 0.35 ± 0.05‰ (50.45 mbsf) followed by a slow decrease to 0.31 ± 0.03‰ at ~100 mbsf. Between 100 and 200 m depth interval, pore fluid $\delta^{44/40}\text{Ca}$ shows a sharp increase to 0.63 ± 0.03‰ (at 164.45 mbsf) followed by a subsequent gradual down-depth decrease (0.27 ± 0.1‰ at 509.3 mbsf) at a slower rate with some variability in the deeper part of the column (Fig. 3.6a, Table. 3.5 and 3.6).

The pore fluid $\delta^{44/40}\text{Ca}_{\text{SRM-915a}}$ in Hole 762B decreases sharply from 1.75 ± 0.08‰ near sediment-water interface to 0.72 ± 0.05‰ in the upper ~50 mbsf. Below 50 mbsf, the pore fluid $\delta^{44/40}\text{Mg}$ shows a slight increase to 1.00 ± 0.05‰ (at ~106 mbsf) followed by a slow gradual decrease with depth to 0.43 ± 0.03‰ at ~163 mbsf. The bulk carbonate $\delta^{44/40}\text{Ca}_{\text{SRM-915a}}$ in this site exhibit a slow systematic increase from 0.50 ± 0.07‰ (at 1.02 mbsf) to 0.75 ± 0.02‰ (at 166.62 mbsf) over the upper ~167 m thick sedimentary column (Fig. 3.6.b, Table. 3.11 and Table 3.12).
3.4.4 Trace elemental composition of bulk carbonates, pore fluids, and bulk clays

The Sr/Ca, Mg/Ca and Na/Ca ratios of acetate digested bulk carbonates from Holes 806B and 762B are summarized in Tables 3.7 and 3.15, and Fig. 3.7. The bulk carbonate Sr concentration and Sr/Ca in both sites show systematic decrease with depth while the Mg concentration and Mg/Ca increase with depth. In Hole 806B the Sr/Ca ratio decrease gradually from 1.74 (at 1.11 mbsf) to 1.20 mmole/mole (at 698 mbsf) with depth. The Sr concentration in this hole also decreases from 1523 ppm to 1024 ppm over same depth interval. In contrast, the bulk carbonate Sr/Ca ratio in Hole 762B oscillates between 2.0 and 1.65 mmole/mole in the upper 100 m depth followed by a sharp decrease to 1.27 mmole/mole at ~120 mbsf. However, between 132 and 144 mbsf in Hole 762B the Sr/Ca ratio exhibit a slight increase to 1.67 mmole/mole followed by subsequent decrease with depth to 1.31 mmole/mole at ~167 mbsf. Similarly, the bulk carbonate Sr concentration in Hole 762B fluctuates between 1715 ppm to 1454 ppm in the upper ~100 mbsf followed by a sharp decrease to 1113 ppm at 120 mbsf and a subsequent increase to 1466 ppm at 144 mbsf. Below 144 mbsf the Sr concentration decreases again to 1147 ppm at ~167 mbsf.

The Mg/Ca ratio and Mg concentration in Hole 806B show slight increase from ~2.5 to ~3.6 mmole/mole and ~594 to 860 ppm respectively in the upper ~300 m depth. Below 300 m depth both Mg/Ca ratio and Mg concentration in bulk carbonate increase gradually to 2.65 mmole/mole and 626 ppm at ~700 mbsf. In Hole 762B, the Mg/Ca ratio and Mg concentration of bulk carbonates decrease from 2.95 mmole/mole and 715 ppm to 1.57 mmole/mole and 381 ppm respectively in the upper ~85 m depth. Below 85 m depth both Mg concentration and Mg/Ca ratio exhibit a sharp increase to 917 ppm and 3.77 mmole/mole, respectively at 120 mbsf followed by a gradual decrease to 707 ppm and 2.91 mmole/mole at ~167 mbsf.

The Na/Ca ratio of bulk carbonates from Hole 806B exhibit a sharp decrease in the upper 20 m depth from 4.04 to 2.30 followed by more or less constant values (~2.5±0.5) with some
variability over the ~167 m depth. Contrastingly, in Hole 762B, the upper ~100 m depth interval shows a systematic decrease in bulk carbonate Na concentration and Na/Ca ratio from 945 to 264 ppm and 4.11 to 1.15 mmole/mole, respectively followed by a subsequent increase to 976 ppm and 4.25 mmole/mole, respectively until ~140 mbsf. Below ~140 mbsf both Na/Ca and Na concentration exhibit a gradual decrease with depth to 2.2 mmole/mole and 505 ppm, respectively at ~167 mbsf.

3.5. Discussion

The main objective of this investigation is to elucidate the influence of pore fluid chemistry on the extent of diagenetic alteration of marine carbonates using the isotopic and elemental data from three different carbonate-rich marine sections. We used Ca, Mg, and Sr isotopes and trace elemental composition of sediments and coexisting pore fluids from multiple sites to address: (1) the extent to which the pore fluid chemistry is influenced by diffusion and how that impacts the diagenetic calcite recrystallization; and (2) the effect of lithological variability over depth on pore fluid $\delta^{26}$Mg and its implication on proxy preservation.

The two adjacent Holes (807A and 806B) on the Ontong Java Plateau in western equatorial Pacific Ocean are located well above the calcite compensation depth (CCD) which resulted in an accumulation of ~1200 m thick carbonate sediments that are not affected by significant net dissolution. The absence of geochemical evidence of active advection through the sedimentary columns makes these two sites ideal for investigating the effect of calcite recrystallization on carbonate $\delta^{26}$Mg in a “closed system” with respect to external fluid flow. The primary processes controlling the pore fluid chemistry are therefore diffusion and diagenetic calcite recrystallization. Given the proximity of these two sites (~475 km) it is reasonable to assume that they have experienced similar depositional history. Hence pore fluids from these sites
are expected to display similar elemental and isotopic composition with depth and any difference
in the observed trends can be attributed to the difference in post-depositional processes, i.e.,
reaction and diffusion.

Comparing the elemental concentrations of Ca, Mg, and Sr in pore fluids between ODP
Holes 807A and 806B, we found that rates of increase in $[\text{Ca}^{2+}]$ and $[\text{Sr}^{2+}]$ and rates of decrease in
$[\text{Mg}^{2+}]$ in pore fluids with depth are significantly higher in Hole 806B relative to Hole 807A (Fig.
3.2). Besides, the depth-profiles of pore fluid Mg/Ca ratios from Holes 807A and 806B also
differs significantly. We hypothesize that the observed differences in elemental concentration
profiles between two adjacent sites are the result of a difference in carbonate diagenesis. Unlike
Site 806, the presence of a low permeable layer composed of chert and chalk below ~1000 mbsf
at Site 807 (Gieskes and Lawrence, 1981) can impede the diffusion of pore fluids across that
layer, which can potentially influence the calcite recrystallization rates at Site 807. In this study,
we investigated the effect of different lower boundary conditions on pore fluid chemistry and how
that influences the carbonate diagenesis in the neighboring sites.

Site 762 on the Exmouth Plateau, situated above the modern CCD, is also comprised of
thick (~940 m) carbonate-rich sediments (Haq et al., 1990; de Carlo, 1992). However, unlike the
two sites on the Ontong Java Plateau, ODP Hole 762B has some depth intervals where carbonate-
rich sediments are intercalated with clay-rich sediments. Thus Hole 762B is an ideal site to
investigate the effect of lithological variation on pore fluid chemistry and calcite recrystallization.

The four key observations of this study that steer the subsequent discussions are:

(1) In all sites, pore fluid $\delta^{26}\text{Mg}$ increases with depth while carbonate $\delta^{26}\text{Mg}$ decreases with
depth.

(2) Hole 807A and 806B exhibit a mismatch (~0.2-0.3‰) between the depth profiles of pore
fluid $\delta^{26}\text{Mg}$ below ~300 mbsf.
(3) Between 100-150 mbsf in Hole 762B, carbonate $\delta^{26}\text{Mg}$ increases by ~0.6-1.0‰ and pore fluid $\delta^{26}\text{Mg}$ decreases by -0.15‰.

(4) Bulk clay $\delta^{26}\text{Mg}$ values (0.27 to -0.09‰) from Hole 762B are generally higher than the average pore fluid values.

The difference in depth trends of pore fluid $\delta^{26}\text{Mg}$ between Holes 806B and 807A indicate differences in post-depositional processes as hypothesized from the pore fluid chemistry. Moreover, we suggest that the ~ 1.0‰ decrease in bulk carbonate $\delta^{26}\text{Mg}$ at both sites reflects diagenetic alteration of bulk carbonates. Similarly, in Hole 762B, the down-depth increase in pore fluid $\delta^{26}\text{Mg}$ reflects a combination of diffusion and calcite recrystallization along with a decrease (-0.15 to -0.2‰) in pore fluid $\delta^{26}\text{Mg}$ between 100 and 150 mbsf, which suggests small scale lithological variability in the sedimentary column. Mineralogical evidence from this hole indicates that clay (mainly illite and smectite) content increases from 3% to 11%, CaCO$_3$ content decreases from 92% to 63%, and porosity decreases by ~20% in the same depth interval (Wilkens et al., 1992) which supports this hypothesis. Analysis of silicate fraction, which is mainly composed of illite and smectite clay, from Hole 762B shows that the clay mineral preferentially incorporates heavier Mg isotopes ($^{25}\text{Mg}$ and $^{26}\text{Mg}$). Therefore, we suggest that authigenic precipitation of Mg-clay, which can potentially deplete the pore fluids with $^{25}\text{Mg}$ and $^{26}\text{Mg}$, can cause the observed decrease in pore fluid $\delta^{26}\text{Mg}$, even within carbonate-rich sediments. Furthermore, we interpret the overall downcore decrease in bulk carbonate $\delta^{26}\text{Mg}$ from -4.0‰ to -4.75‰ as a result of diagenetic recrystallization while the increase in bulk carbonate $\delta^{26}\text{Mg}$ by ~ -1.0‰ from 10 to 150 mbsf is a result of lower recrystallization within the clay-rich layer.

In the subsequent sections, we discuss the validity of the proposed hypotheses utilizing several lines of geochemical evidence and employing multiple reactive-transport model simulations to the measured chemistry. The elemental and isotopic evidence and numerical modeling validate the notion that in “closed systems” with respect to advection, diffusion controls
the pore fluid chemistry, which dictates the extent of diagenetic recrystallization of the sediments. For sediments with variable carbonate and silicate contents, pore fluid $\delta^{26}$Mg often can fingerprint deeper diagenetic reactions involving silicate minerals and within clay-bearing sediments the extent of calcite recrystallization may differ from that within sediments comprised mostly of carbonates.

3.5.2. Quantifying calcite recrystallization rates using reactive-transport model

Quantifying recrystallization rates in marine carbonates is critical to determine the extent to which diagenesis altered the primary chemistry. The recrystallization rate in Hole 807A has been previously constrained (Fantle and DePaolo, 2006; 2007). Here we take a similar approach using pore fluid Ca and Sr concentrations, $\delta^{44/40}$Ca, and $^{87}$Sr/$^{86}$Sr to constrain reaction rates (e.g., Richter and DePaolo 1987, 1988; Richter and Liang, 1993; Fantle and DePaolo, 2006; Fantle et al., 2010; Fantle, 2015). A simple 1-D depositional calcite recrystallization model is employed to constrain the recrystallization rates of the carbonates from Holes 806B and 762B and the recrystallization rates are compared with the rate estimated from the Ca and Sr geochemistry from Hole 807A.

3.5.2.1. Sr geochemical constraints on recrystallization rates at Sites 806 and 762

The model simulations for Site 806 suggests that using reaction rates similar to Site 807 (base case scenario, R=0.023 e^{-age/15.686}; Fantle and DePaolo, 2006) can reproduce the depth profile of pore fluid $[\text{Sr}^{2+}]$ within the upper ~200 mbsf, but does not express the depth variability in pore fluid $^{87}$Sr/$^{86}$Sr. In order to reproduce the pore fluid $^{87}$Sr/$^{86}$Sr data from Site 806, the model requires higher reaction rate ($\leq$5%/Ma, R=0.05 e^{-age/6}; Appendix Fig. B.5b) than that estimated for Site
807. This observation supports the hypothesis that the rate of calcite recrystallization is different between the two adjacent sites. Likewise, the model iterations suggest that calcite recrystallization rates at Site 762 are not similar to Site 807 if the same $K_{Sr}$ is applied. Instead, calcite recrystallization rates similar to the rates in the Site 806 are required to explain both the concentration and isotope profiles of pore fluid Sr (i.e. $\leq 5%$/Ma, $R=0.0055+0.045e^{-age/2.1}$; Appendix Fig. B.6b). In both sites varying the $K_{Sr}$ value within a reasonable range (18.5 ±10%) can generate reasonable fits to the Sr isotope data but not without compromising the fits to the pore fluid Sr concentration. Therefore, the model simulations validate the hypothesis the diagenetic recrystallization rates in both sites (806 and 762) are different relative to the rates in Site 807 (Fantle and DePaolo, 2006; Fantle and DePaolo, 2007).

In the reactive-transport model simulations of the Sr geochemistry, we assumed a simple case scenario where the sedimentary column is considered as a closed system where the pore fluid chemistry is primarily influenced by diffusion and calcite recrystallization, as there is no physical or chemical evidence of advection at the studied sites. The basaltic basement at ~1200 mbsf depth is considered as the lower boundary of the sedimentary column in Hole 806B, similar to the Hole 807A. On the contrary, the lower boundary in Hole 762B is considered to be the transition between the carbonate-rich and silicate-rich layer at ~580 mbsf depth. However, unlike Hole 807A, the sedimentary columns in Holes (806B and 762B) do not show the presence of any low permeable chert layers above the lower boundary, which suggests that the diffusive communication of pore fluid at the lower boundary is not interrupted at these two holes. Therefore, in the model, we also allowed diffusive interaction of the pore fluid with lower boundary.
3.5.2.2. Ca isotope constraints on recrystallization rates at Sites 806B and 762

The pore fluid and bulk carbonate $\delta^{44/40}$Ca data from Holes 806B and 762B exhibit down-core variability similar to Hole 807A. In all three cases, the pore fluid $\delta^{44/40}$Ca values approach the bulk carbonate $\delta^{44/40}$Ca within upper ~10 mbsf. The reaction rates constrained by Sr geochemistry at Site 806 can generate depth-profiles similar to the measured $\delta^{44/40}$Ca. However, the sharp decrease in pore fluid $\delta^{44/40}$Ca from the seawater value (1.95‰) to 0.27 at ~4.5 mbsf in Hole 806B cannot be fully explained by the model fits using the Sr-derived reaction rates. Because there is no evidence of a sharp increase in pore fluid [Ca$^{2+}$] in the upper part of the sedimentary column, net carbonate dissolution is not a likely explanation. Instead, we hypothesize that carbonate recrystallization rates in sediments younger than 1 Ma are substantially higher than in older sediments. This is similar to previously studied sites (e.g., Site 807, 1170, and 1171) (Fantle and DePaolo, 2007; Fantle, 2015). Accordingly, the $\delta^{44/40}$Ca of pore fluids from Hole 806B are modeled with an age-dependent recrystallization rates in which reaction rates for age <1 Ma are set to ~30%/Ma and the reaction rates for age >1Ma are set to ~5%/Ma (Appendix Fig. B.5a).

In Hole 762B, the decrease in pore fluid $\delta^{44/40}$Ca in the upper ~3 mbsf from seawater value (1.95 ‰) is relatively slow (0.7‰ at 2.9 mbsf). The Sr-derived reaction rates (~5%/Ma) can reasonably reproduce the observed trend in $\delta^{44/40}$Ca in shallow pore fluids above 20 mbsf. This observation suggests that in Hole 762B carbonates younger than 1 Ma are significantly less altered than young carbonates from the two Pacific Sites (807 and 806) (Appendix Fig. B.6a).

3.5.3. Geochemical evidence of carbonate diagenesis in Holes 762B, 806B, and 807A

Calcite recrystallization is clearly evident is all three sites base on the pore fluid Ca and Sr concentrations and isotopic composition and numerical modeling. Bulk carbonate Mg and Sr
concentrations and elemental ratios also indicate the impact of calcite recrystallization to some extent. In Hole 807A, carbonates (<65 µm) from upper ~250 mbsf exhibit an increase in Mg/Ca ratio (from 2.68 to 3.73 mmole/mole) which correlates with a decrease in Sr/Ca ratio (from 1.85 to 1.45) ($r^2 = 0.69$). However, carbonates (<65 µm) below ~250 mbsf do not show any significant correlation between Mg/Ca and Sr/Ca ratios (Higgins and Schrag, 2012) (Fig. 3.8). This observation indicates that both Sr and Mg in Hole 807A carbonates above ~250 mbsf are influenced by calcite recrystallization. Since, the Sr/Ca and Mg/Ca ratios of carbonates below 250 mbsf do not correlate, we suggest that shallower carbonates (above ~ 250 mbsf) in Hole 807A are altered more than the deeper carbonates.

The difference in the extent of calcite recrystallization in Hole 807A can be explained by the lack of diffusive communication of pore fluids with lower boundary (i.e., sediment-basalt interface) due to the presence of an imperious chert layer above the lower boundary. Because of the lack of interaction of the pore fluids with the basalt at lower boundary the diffusive gradients in the pore fluid elemental concentrations in the deeper section are not strong. Hence, the chemical disequilibrium between pore fluids and bulk carbonates in Hole 807A is not maintained over a long period due to lack of strong diffusion. This reduces the extent of diagenetic exchange between carbonates and pore fluids in the deeper part of the section. However, in the shallower part of the section where the pore fluids continue to react with carbonates to attain chemical equilibrium, the extent of alteration is significant resulting the observed correlation between bulk carbonate Mg/Ca and Sr/Ca ratios (Higgins and Schrag, 2012).

In Hole 806B, the increase in Mg/Ca and decrease in Sr/Ca ratios of the bulk carbonates correlate well ($r^2 = 0.55$) over the entire 700 m depth interval indicating that carbonates in the entire section exchange with pore fluids. Due to the absence of any impermeable chert layer at Site 806, the pore fluids continue to interact with the basalt at the lower boundary resulting a strong diffusion gradient in the pore fluids’ elemental concentrations. Therefore, diffusion
continuously modifies the pore fluid chemistry, which helps to maintain the chemical and isotopic disequilibrium between the carbonates and pore fluids over the entire section. This results in a greater extent of diagenetic alteration of the carbonates in Hole 806B compared to the carbonates in Hole 807A. Therefore, this observation validates our hypothesis that due to the difference in lower boundary conditions pore fluids from two adjacent sites exhibit differences in elemental concentrations over depth, which also influences the extent of diagenetic alteration of carbonates in those sites. In Hole 762B, the overall increase in Mg/Ca ratio increases from samples between ~2.9 and ~115 mbsf and between ~144 and ~166.6 mbsf (from 2.95 to 3.88 mmole/mole) correlates to some extent (r² = 0.31) with the decrease in Sr/Ca ratios (from 1.94 to 1.31 mmole/mole) (Fig. 3.8). However, the Mg/Ca and Sr/Ca ratios of bulk carbonates between ~115 and ~144 mbsf interval and the carbonates from 166.62 mbsf show no correlation (r² <0.10). Since, the clay wt% containing illite and smectite clay in the depth interval between 115 and 144 mbsf interval increases to ~11%, and the carbonate Mg/Ca and Sr/Ca ratios show no correlation this layer, it can be suggested that carbonate chemistry within the clay-bearing interval are least affected by diagenesis.

The Na/Ca ratio of the shallow bulk carbonate (~above 20 mbsf) from Hole 806B exhibits a rapid decrease from 4.04 to 2.30 mmole/mole followed by more or less depth-invariant values. Since the decrease in Na/Ca ratios in carbonates has been interpreted as the effect of carbonate recrystallization in previous studies (Lorens, 1977; Graham et al., 1982; Delaney et al., 1985) the observed decrease in Na/Ca ratio in bulk carbonates from Hole 806B that has been proven to be partially recrystallized, also indicates an influence of diagenesis. In Hole 762B, the Na/Ca ratios of bulk carbonate decrease with depth in the upper ~104 m (from 4.11 to 1.15) interval. In this interval, the Na/Ca ratios also correlate with the Mg/Ca ratios (r² = 0.68) (Fig. 3.8). However, below 104.78 mbsf, the bulk carbonate Na/Ca ratios increase to 4.25 mmole/mole (at 138.0 mbsf) and the Na/Ca ratios exhibit no correlation with Mg/Ca ratios (r² <0.10). This also
suggests that the observed increase in Na/Ca, Mg/Ca, and Sr/Ca ratios in bulk carbonates in the clay-bearing interval (~115 to ~144 mbsf) in Hole 762B reflect primary depositional signals.

3.5.4. Impact of calcite recrystallization on the $\delta^{26}$Mg of marine pore fluids and carbonates

The elemental Mg in the carbonates from all three sites (762, 806, and 807) indicates the influence of calcite recrystallization to some extent. Therefore, it is likely that Mg isotopes in carbonates and pore fluids are also influenced in the sediments from the studied sites. Accordingly, we modeled the pore fluid and bulk carbonate Mg profiles in each site using the same depositional reactive-transport model and recrystallization rates constrained by Sr and Ca concentrations and isotope data. The model iterations assume a partition coefficient ($K_{Mg}$) and a fractionation factor ($\alpha_{Mg}^{dia}$) of Mg associated with diagenesis that is reasonably chosen from the previously published data (Mucci and Morse, 1983; Oomori et al., 1987; Huang and Fairchild, 2001; Rustad et al., 2010; Higgins and Schrag, 2012; Fantle and Higgins, 2014). The main purpose of this modeling exercise is to evaluate the potential of diagenetic recrystallization to alter Mg isotopes in carbonates from marine settings that are not influenced by active advection. Given the large reactive length scale of Mg ($L_D \sim 1100$ m) in carbonate-rich sediments (Fantle and DePaolo, 2006) closed to advection, Mg in pore fluids from ~800 mbsf thick sedimentary column never attains equilibrium with the bulk carbonates, which enhances the extent of diagenetic alteration of Mg. Besides, comparing the pore fluid [Mg$^{2+}$] and $\delta^{26}$Mg from two adjacent carbonate-rich sites also provides a unique way to identify diagenetic reactions involving silicate minerals in the deeper section.

The model simulations for Site 807 are performed using closed lower boundary, which does not allow any diffusive communication of pore fluids with the lower boundary. This condition is justified by the presence of impermeable chert layer ~1000 mbsf depth. The partition
coefficient (\(K_{\text{Mg}}\)) and fractionation factor (\(\alpha^{\text{diag}}_{\text{s-f}}\)) for Mg associated with diagenetic calcite recrystallization are estimated to be 1.65 and 0.9947, respectively, to reproduce the overall trends in pore fluid and bulk carbonate \(\delta^{26}\text{Mg}\) and Mg concentrations in Hole 807A using the reaction rates of \(\leq 2\%/\text{Ma} \quad (R= 0.023e^{-\text{age}/15.686})\) (Fig. 3.9a and b). The initial \([\text{Mg}^{2+}]\) in pore fluids are estimated based on the fluid inclusion data obtained from marine evaporites (Zimmermann, 2000; Horita et al., 2002). The initial \(\delta^{26}\text{Mg}\) values of pore fluids are assumed to be same as the upper boundary (i.e., modern seawater: -0.84 ‰).

Utilizing the reaction rates of \(\sim 5\%/\text{Ma} \quad (R=0.05exp^{-\text{age}/6})\) with a partition coefficient (\(K_{\text{Mg}}\)) of 2.5 and a fractionation factor (\(\alpha^{\text{diag}}_{\text{s-f}}\)) of 0.9950 in the reactive transport model we were able to reproduce the down-core variability in pore fluid \(\delta^{26}\text{Mg}\) and \([\text{Mg}^{2+}]\) observed at Site 806B (Fig. 3.10). However, unlike Site 807, the model requires an open lower boundary condition to fit the pore fluid and solid chemistry at Site 806 where the pore fluids maintain diffusive interaction with the lower boundary. The values of \(\delta^{26}\text{Mg}\) and \([\text{Mg}^{2+}]\) for lower boundary are chosen to be -0.15‰ and 15 mM respectively, similar to values observed at carbonate-basalt interface in marine sections. The model iterations demonstrate that both high reaction rates and open lower boundary condition are also required to explain the downhole pore fluid Mg profiles in Hole 806B. Therefore, the model results validate the hypothesis that the observed differences in pore fluid chemistry (i.e., \([\text{Mg}^{2+}], [\text{Sr}^{2+}], \) and Mg/Ca ratios) between two adjacent sites reflect the difference in diagenetic recrystallization which in this case is possibly triggered by different lower boundary conditions. The model outcomes also demonstrate that both concentration and isotopic composition of Mg in carbonates can be altered significantly (at least by -0.5 to -1.0 ‰) in an \(\sim 800\) m thick carbonate-rich marine section where diffusion is the only active transport.

At Site 762, the overall downhole increase of pore fluid \(\delta^{26}\text{Mg}\) and decrease of pore fluid \([\text{Mg}^{2+}]\) are successfully reproduced employing the calcite recrystallization model utilizing the reaction rates of \(\leq 5\%/\text{Ma} \quad (R= 0.0055+0.045\text{exp}^{-\text{age}/2.1})\), constrained by Ca and Sr geochemistry,
with reasonable estimates of $K_{\text{Mg}}$ (~2.5) and $\alpha_{s-f}^{\text{diag}}$ (0.9940) for calcite recrystallization (Fig. 3.11). The pore fluids are allowed to interact diffusively with the lower boundary (carbonate-silicate transition) and the values of $[\text{Mg}^{2+}]$ and $\delta^{26}\text{Mg}$ of lower boundary are selected to be -0.20 ‰ and 20 mM respectively, which is reasonable for the underlain silicate-rich sediments (Higgins and Schrag, 2010; Higgins and Schrag, 2012). The model simulations indicate that although the combination of diffusion and calcite recrystallize can reasonably reproduce the pore fluid $[\text{Mg}^{2+}]$, the depth profile of $\delta^{26}\text{Mg}$, especially, the pore fluid $\delta^{26}\text{Mg}$ between 115 and 144 mbsf in Hole 762B cannot by entirely explained by diffusion and calcite recrystallization. This suggests that within that depth interval the pore fluid chemistry is influenced by a different reaction other than calcite recrystallization.

3.5.5. Potential of marine pore fluid $\delta^{26}\text{Mg}$ to fingerprint authigenic clay precipitation

Because clay minerals incorporate a substantial amount of Mg (~2-5 wt %) and also sequester Mg enriched with $^{26}\text{Mg}$ and $^{25}\text{Mg}$ during precipitation, authigenic Mg-clay formation has potential to lower pore fluid $\delta^{26}\text{Mg}$. The model iterations with a constant $\alpha_{s-f}^{\text{diag}}$ of 0.9947 and $K_{\text{Mg}}$ of 1.65 can reproduce the observed increase in pore fluid $\delta^{26}\text{Mg}$ within upper ~200 mbsf depth in Hole 807A using the reaction rates of ~2%/Ma. However, the observed decrease by -0.20 to -0.30 ‰ in pore fluid $\delta^{26}\text{Mg}$ below 400 mbsf cannot be explained by these model iterations (Fig. 3.9). This observation implies that in the deeper part of the section in Hole 807A, a different diagenetic reaction is occurring with a sink enriched with $^{26}\text{Mg}$ and $^{25}\text{Mg}$ or a source depleted of $^{26}\text{Mg}$ and $^{25}\text{Mg}$. Our simple model is unable to quantify that effect as the model is designed only for calcite recrystallization. Because, no evidence of net dissolution is observed in Hole 807, the possibility of carbonate dissolution as a source of $^{24}\text{Mg}$ to the deep pore fluids in this site can be ignored. This suggests that the authigenic Mg-clay precipitation that preferentially incorporates
Mg enriched with $^{26}\text{Mg}$ and $^{25}\text{Mg}$ from pore fluids is occurring in the deeper part of the section in Hole 807A. Although the presence of clays in trace amounts in the deeper part of the Hole 807A is reported which makes the Mg-clay being another plausible sink in Hole 807A, the difficulty of analyzing such negligible amount of silicates for $\delta^{26}\text{Mg}$ made it impossible to quantify the effect of clay precipitation on pore fluid $\delta^{26}\text{Mg}$ in Hole 807A. Therefore, in order to illustrate the effect of clay precipitation on marine pore fluids from carbonate-rich sediments our investigation incorporated the third Site 762, where in certain depth-intervals the Mg-clay minerals are abundant enough for isotopic analysis.

Similar to Hole 807A, the pore fluid $\delta^{26}\text{Mg}$ in Hole 762B exhibit a -0.15 ‰ offset from the model fits the pore fluid $\delta^{26}\text{Mg}$ between 120 and 144 mbsf (Fig. 3.11). The XRD analyses of sediment from Hole 762B document an increase in clay (mainly illite and smectite) content from 3% to 11%, decrease in CaCO$_3$ content from 92% to 63% between 120 and 144 mbsf interval. A decrease in porosity by ~10% within the same depth interval is also observed (Fig. 3.12) (Wilkens et al., 1992). The analyses of bulk clays, from the clay-rich depth interval in Hole 762B, reveal that the $\delta^{26}\text{Mg}$ of bulk clay is in the range of -0.09 ± 0.03‰ to 0.27 ± 0.08‰. Based on such observations we suggest that the decrease in pore fluid $\delta^{26}\text{Mg}$ is related to the formation of Mg-clay at a certain depth in Hole 762B and therefore pore fluid $\delta^{26}\text{Mg}$ can be utilized to identify authigenic clay precipitation in carbonate-rich marine sections.

3.5.6. Geochemical models to investigate the effect of clay precipitation on pore fluid $\delta^{26}\text{Mg}$

A simple box model is used to simulate the effect of clay precipitation simultaneously with calcite recrystallization on pore fluid $\delta^{26}\text{Mg}$ to validate the hypothesis of authigenic clay precipitation in the deeper section of Hole 762B. Using this model we can estimate the amount of clay required to generate the observed shift in pore fluid $\delta^{26}\text{Mg}$ (Appendix B, Section.B.1.5).
Later, we utilized the ChrunchTope, a multi-component geochemical model to investigate the feasibility of authigenic precipitation of Mg-clay in a sedimentary column with the same geochemistry of pore fluids and sediments as observed in Hole 762B (Appendix B, Section.B.1.6). The ChrunchTope results demonstrate that the authigenic precipitation of Fe-Mg-rich smectite and illite is possible at a given depth in a Site 762-like carbonate-rich sedimentary column if enough dissolved Al\(^{3+}\), Fe\(^{2+}\), and SiO\(_2\) are available. As beneath the carbonate-rich sediments (~below 250) in Hole 762B, a significant amount of silicate minerals are present, it is reasonable to assume that the supply of Al\(^{3+}\), Fe\(^{2+}\), and SiO\(_2\) will be adequate for clay formation. The pore fluid chemistry of the Site 762 indicates that at least \(~4.2\times10^{-9}\) volume % (m\(^3\) of mineral per m\(^3\) of sediment) of Fe-Mg-smectite can precipitate over 1 year (\(\approx 1\)wt% of clay / Ma) within the sedimentary column in the same depth interval where the increased amount of clay % is reported (Fig. 3.13b).

In the Stella model, diffusion is simulated between three layers in which the calcite recrystallization is active at a rate of \(~5%/\)Ma in the upper and the lower most layer with a fractionation factor of 0.9950 and partition coefficient (\(K_{\text{Mg}}\)) of 2.5. In the middle layer, along with calcite recrystallization, a Mg-bearing clay (containing \(~5\) wt % of Mg) is precipitated with a fractionation factor of 1.0005. The model results show that only a small amount of clay precipitation (<1wt% in the sediment over 1Ma) is required to generate \(-0.2\) to \(-0.4\)‰ difference in the pore fluid \(\delta^{26}\text{Mg}\) from the layers above and below the clay-bearing layer (Fig. 3.13a). The model also demonstrates that a small difference (i.e., \(-0.2\) to \(-0.4\)‰) in pore fluid \(\delta^{26}\text{Mg}\) can only be maintained over longer timescales (million years) if the diffusion coefficient (\(D_{\text{Mg}}\)) in the clay-bearing interval is smaller (\(D_{\text{Mg}} = 4500\) m\(^2\)/Ma) than the diffusion coefficient in the rest of the sedimentary column (\(D_{\text{Mg}} = 7600\) m\(^2\)/Ma).

The above model simulation indicates that clay precipitation can occur at a reasonable rate in a carbonate-rich sediment and potentially generates a \(~0.2\)- \(0.4\)‰ shift in the pore fluid.
\(\delta^{26}\text{Mg}\) at a certain depth. The model also suggests that despite the continuous diffusive communication of the pore fluids with the upper and lower boundary, such shift in pore fluid \(\delta^{26}\text{Mg}\) can be maintained if the \(D_{\text{Mg}}\) is slower in the depth interval where clay is forming compared to the \(D_{\text{Mg}}\) in the rest of the column. Such assumption is justified as a significant porosity reduction (~20%) is observed in the clay-bearing depth interval in Hole 762B, which reduces the diffusivity of the cations in the pore fluids.

3.5.7. Implication of lithological variability on the preservation of carbonate-based proxies

The trace elemental ratios and isotopic composition of bulk carbonates exhibit sizeable shifts in the clay-bearing depth interval (120-140 mbsf) from the general downcore trends in Hole 762B. The lack of correlation between the observed increase in Na/Ca, Sr/Ca and Mg/Ca ratios in the same clay-rich interval indicates less impact of diagenesis on the carbonates within the clay-bearing interval. As the Mg concentration in the bulk carbonates appears to be less affected in the presence of clay, it is reasonable to consider that the \(\delta^{26}\text{Mg}\) of the same carbonates are less altered as well. Hence we suggest that the positive shift by ~0.6 to 1.0 ‰ in the bulk carbonate \(\delta^{26}\text{Mg}\) within the clay-bearing interval (~120 to 140 mbsf) indicates better preservation of the biogenic carbonates (e.g., foraminiferal calcites) in the presence of clay and hence reflects the primary depositional signal.

In clay-rich sediments, the fine-grained clays precipitated on the surface of biogenic calcite grains can effectively reduce the reaction of the calcite grains by preventing the exchange between the biogenic calcite and pore fluids. Hence, the presence of clay minerals in carbonate-rich sediments can potentially decrease the extent of diagenetic alteration in biogenic carbonates. Our geochemical and isotopic observations are also in agreement with the exceptionally good preservation of foraminiferal tests (i.e., “glassy tests”) reported from clay-rich sediments (e.g.,
Norris and Wilson, 1998; Wilson and Norris, 2001; Pearson et al., 2001; Wilson et al., 2002; Sexton et al., 2006). Therefore, the presence of clay increases the fidelity of carbonate-based geochemical proxies.

In a recent study, the δ²⁶Mg records of marine foraminiferal tests from deep marine sediments (Hole 1263A and Hole 1264A) are utilized to reconstruct the secular variability in seawater δ²⁶Mg over the Cenozoic period (Pogge von Strandmann et al., 2014). This study suggests that the seawater δ²⁶Mg varied significantly (by ~0.6 to 0.8 ‰) over the last 40 Ma. The age vs. δ²⁶Mg records from all three sites (762, 806, 807) are compared with the foraminiferal δ²⁶Mg from Hole 1263A and 1264A (Pogge von Strandmann et al., 2014) to estimate the error associated to the sediment diagenesis in reconstructing past seawater δ²⁶Mg record (3.14). The comparison reveals a rapid decrease (~1.0 ‰) in the carbonate δ²⁶Mg of age < 5 Ma in all four sites. The calcite recrystallization rates estimated from each site based on the Ca and Sr geochemistry indicates that the younger sediments exchange at a faster rate than the older sediments. Thus, it is reasonable to interpret such decrease in carbonate δ²⁶Mg as a result of the rapid exchange of calcite with pore fluids. In the sediments older than 5 Ma, the δ²⁶Mg of bulk carbonate in Hole 806B and Hole 807A exhibit very similar decrease with increasing age, which is quite the opposite of the foraminiferal δ²⁶Mg records from Hole 1264A.

Given, the proximity of these two sites (807 and 806) and extent of diagenetic recrystallization constrained by Ca and Sr geochemistry, such variability can be attributed to carbonate diagenesis. On the contrary, bulk carbonates from Hole 762B exhibit a sharp increase in δ²⁶Mg between ~9.5 and 25 Ma, which is similar to the foraminiferal δ²⁶Mg profiles from Hole 1263A and Hole 1264A. As there are multiple geochemical evidence in support of a lesser extent of diagenetic alteration of carbonates from the clay-bearing depth interval of Hole 762B, the values carbonate δ²⁶Mg observed within clay-bearing layers can be considered as primary signal. The presence of clay (~ 4-5 wt%) is also observed in the sediments of the Holes 1263A and
1264A (Zachos et al., 2004), which also indicates that less alteration of foraminiferal tests in the clay-bearing sediments from these holes are possible. Therefore, this study suggests that the clay-bearing sediments have more potential to generate high-fidelity proxies compared to carbonate-rich sediments.

3.6. Conclusions

Comparison of isotopic and trace elemental compositions of pore fluids and bulk carbonates between multiple sites reveals that the δ²⁶Mg of marine pore fluids are significantly controlled by both diffusion and reaction in the sedimentary column. The differences in elemental concentration profiles in neighboring Sites 807 and 806 can be explained by the difference in calcite recrystallization rates, which is influenced by different lower boundary conditions. However, the -0.2 to -0.3 ‰ contrast between the pore fluid δ²⁶Mg profiles in the deeper part of the section cannot be entirely explained by only calcite recrystallization and diffusion unless the diagenetic reaction involving Mg-bearing non-carbonate mineral is considered. Authigenic precipitation of Mg-clay is suggested to be the secondary diagenetic reaction occurring along with calcite recrystallization at a deeper level of the sedimentary column in Hole 807A.

Investigation of the δ²⁶Mg of pore fluids from the silicate-bearing carbonate sediments from Hole 762B supports that authigenic clay precipitation in the carbonate-rich sediments can have a sizeable impact on pore fluid δ²⁶Mg. Analysis of bulk clay from Hole 762B displayed the δ²⁶Mg value in the range of -0.09 to 0.27‰, validates the hypothesis that the presence of clay in the carbonate-rich sediments can influence the pore fluid δ²⁶Mg. Moreover, in the Hole 762B, bulk carbonates exhibit higher values of δ²⁶Mg, Mg/Ca, Sr/Ca, and Na/Ca ratios within the clay-bearing interval than the carbonates from the layer above and below the clay-bearing interval. This observed shift in bulk carbonate δ²⁶Mg couldn’t be reproduced using calcite recrystallization
model. Lack of correlation between Mg/Ca, Sr/Ca, and Na/Ca of bulk carbonates from Hole 762B suggests that these compositions are not affected by diagenesis.

Therefore, this study elucidates the main processes that dictate the Mg isotopes in marine pore fluids in carbonate-rich sediments. As in a marine carbonate-rich sedimentary column pore fluids controls the extent of diagenetic alteration of carbonates, understanding the factors that control the pore fluid chemistry, especially the type of lower boundary condition and lithological variation is useful in assessing the preservation of carbonate-based proxies in various marine sites. This study implies that the presence of clay in carbonate-rich sediments offers better preservation of proxy materials against diagenesis. Therefore in a clay-bearing interval within carbonate-rich sediments trace elemental and isotopic compositions of the bulk carbonates are likely to be less altered. Therefore, identifying sites with a variable amount of silicates and carbonate will improve proxy-based reconstruction by providing high-fidelity geochemical proxy records.

3.7. Acknowledgements

This work was supported by NSF Grant EAR-OCE-1154839 to M.S.F. The authors would like to thank Prof. Fangzhen Teng for assistance with analyzing Mg isotopic composition of the pore fluids from ODP 807A. This research used samples and data provided by the Ocean Drilling Program (ODP).

Data Tables

Table 3.1. Magnesium isotopic composition of pore fluids measured from ODP Hole 806B

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth mbsf</th>
<th>$\delta^{26}$Mg$_{DSM3}$</th>
<th>$\sigma$</th>
<th>$\delta^{25}$Mg$_{DSM3}$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg 130 Hole 806B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H-3W(145-150)</td>
<td>4.45</td>
<td>-0.83</td>
<td>0.06</td>
<td>-0.43</td>
<td>0.05</td>
</tr>
<tr>
<td>2H-4W(145-150)</td>
<td>12.45</td>
<td>-0.80</td>
<td>0.12</td>
<td>-0.41</td>
<td>0.06</td>
</tr>
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</table>
### Table 3.2. Magnesium isotopic composition of bulk carbonates measured from ODP Hole 806B

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth mbsf</th>
<th>δ²⁶Mg&lt;sub&gt;DSM3&lt;/sub&gt;</th>
<th>2σ</th>
<th>δ²⁵Mg&lt;sub&gt;DSM3&lt;/sub&gt;</th>
<th>2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg 130 Hole 806B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3H-4W(145-150)</td>
<td>21.95</td>
<td>-0.76</td>
<td>0.01</td>
<td>-0.39</td>
<td>0.03</td>
</tr>
<tr>
<td>6H-4W(145-150)</td>
<td>50.45</td>
<td>-0.65</td>
<td>0.05</td>
<td>-0.34</td>
<td>0.03</td>
</tr>
<tr>
<td>9H-4W(145-150)</td>
<td>78.95</td>
<td>-0.56</td>
<td>0.04</td>
<td>-0.29</td>
<td>0.03</td>
</tr>
<tr>
<td>12H-4W(145-150)</td>
<td>107.45</td>
<td>-0.54</td>
<td>0.10</td>
<td>-0.25</td>
<td>0.08</td>
</tr>
<tr>
<td>18H-4W(145-150)</td>
<td>164.45</td>
<td>-0.39</td>
<td>0.04</td>
<td>-0.21</td>
<td>0.08</td>
</tr>
<tr>
<td>30H-5W(145-150)</td>
<td>279.95</td>
<td>-0.43</td>
<td>0.07</td>
<td>-0.20</td>
<td>0.05</td>
</tr>
<tr>
<td>33H-4W(145-150)</td>
<td>306.95</td>
<td>-0.32</td>
<td>0.03</td>
<td>-0.16</td>
<td>0.04</td>
</tr>
<tr>
<td>36X-4W(145-150)</td>
<td>335.65</td>
<td>-0.28</td>
<td>0.04</td>
<td>-0.14</td>
<td>0.04</td>
</tr>
<tr>
<td>48X-3W(140-150)</td>
<td>450.2</td>
<td>-0.30</td>
<td>0.03</td>
<td>-0.17</td>
<td>0.02</td>
</tr>
<tr>
<td>54X-5W(140-150)</td>
<td>509.3</td>
<td>-0.28</td>
<td>0.02</td>
<td>-0.16</td>
<td>0.01</td>
</tr>
<tr>
<td>60X-4W(00-007)</td>
<td>564.4</td>
<td>-0.20</td>
<td>0.04</td>
<td>-0.10</td>
<td>0.02</td>
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<tr>
<td>63X-4W(140-150)</td>
<td>594.9</td>
<td>-0.13</td>
<td>0.02</td>
<td>-0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>66X-4W(140-150)</td>
<td>623.8</td>
<td>-0.17</td>
<td>0.04</td>
<td>-0.10</td>
<td>0.01</td>
</tr>
<tr>
<td>72X-3W(140-150)</td>
<td>679.9</td>
<td>-0.17</td>
<td>0.01</td>
<td>-0.09</td>
<td>0.02</td>
</tr>
</tbody>
</table>

* As reported in the ODP Initial Report (Kroenke et al., 1991).
* Average values of 2-4 replicates of each sample measured on Neptune Plus MC-ICPMS at Penn State MIL.
Table 3.3. Strontium isotopic composition of bulk carbonates measured from ODP Hole 806B

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth mbsf a</th>
<th>Age Ma b</th>
<th>87Sr/86Sr c</th>
<th>2SE internal d</th>
<th>SD external d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg 130 Hole 806B-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H-1W-(111-113)</td>
<td>1.11</td>
<td>0.09</td>
<td>0.709182</td>
<td>0.000016</td>
<td></td>
</tr>
<tr>
<td>1H-1W-(111-113)</td>
<td>1.11</td>
<td>0.09</td>
<td>0.709150*</td>
<td>0.000008</td>
<td></td>
</tr>
<tr>
<td>1H-3W (34-36)</td>
<td>3.34</td>
<td>0.26</td>
<td>0.709166</td>
<td>0.000009</td>
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</tr>
<tr>
<td>1H-3W (34-36)</td>
<td>3.34</td>
<td>0.26</td>
<td>0.709151*</td>
<td>0.000006</td>
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</tr>
<tr>
<td>2H-5W (35-37)</td>
<td>12.85</td>
<td>0.64</td>
<td>0.709160</td>
<td>0.000006</td>
<td></td>
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<tr>
<td>3H-5W (34-36)</td>
<td>22.34</td>
<td>1.06</td>
<td>0.709136</td>
<td>0.000008</td>
<td></td>
</tr>
<tr>
<td>3H-5W (34-36)</td>
<td>22.34</td>
<td>1.06</td>
<td>0.709114*</td>
<td>0.000009</td>
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</tr>
<tr>
<td>4H-5W (34-36)</td>
<td>31.84</td>
<td>1.46</td>
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<tr>
<td>5H-6W (36-38)</td>
<td>42.86</td>
<td>2.049</td>
<td>0.709081</td>
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<tr>
<td>6H-6W (38-40)</td>
<td>52.38</td>
<td>2.34</td>
<td>0.709069</td>
<td>0.000005</td>
<td>0.000019</td>
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<tr>
<td>11H-7W (73-75)</td>
<td>101.73</td>
<td>4.01</td>
<td>0.709023</td>
<td>0.000005</td>
<td>0.000014</td>
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<tr>
<td>11H-7W (73-75)</td>
<td>101.73</td>
<td>4.01</td>
<td>0.709015*</td>
<td>0.000006</td>
<td>0.000014</td>
</tr>
<tr>
<td>17H-1W (109-111)</td>
<td>150.09</td>
<td>5.3</td>
<td>0.709012</td>
<td>0.000007</td>
<td>0.000009</td>
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<td>22H-3W (109-111)</td>
<td>200.59</td>
<td>6.53</td>
<td>0.708962</td>
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<td>0.000023</td>
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<td>27H-4W (104-106)</td>
<td>249.54</td>
<td>7.70</td>
<td>0.708948</td>
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<tr>
<td>32H-6W (110-112)</td>
<td>300.1</td>
<td>8.68</td>
<td>0.708912</td>
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<tr>
<td>49X-1W (9-11)</td>
<td>455.59</td>
<td>13.07</td>
<td>0.708817</td>
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<tr>
<td>54X-1W (4-6)</td>
<td>501.94</td>
<td>14.68</td>
<td>0.708773</td>
<td>0.000006</td>
<td></td>
</tr>
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</table>

a As reported in the ODP Initial Report (Kroenke et al., 1991)

b Based on age-depth model using magneto- and biostratigraphy (Kroenke et al., 1991).

c Measured on TIMS at University of California, Berkeley.

d Measured on Neptune Plus MC-ICPMS at Penn State MIL. NBS-987 = 0.710243 ± 0.000008 (long-term average).

d In cases where replicates (2 - 4) were analyzed, the external reproducibility (2 standard deviation) is reported. In cases where no replicates were analyzed, the internal reproducibility (2 standard error) is reported.

Table 3.4. Strontium isotopic composition of pore fluids measured from ODP Hole 806B

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth mbsf a</th>
<th>87Sr/86Sr c</th>
<th>2SE internal d</th>
<th>SD external d</th>
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<tr>
<td>Leg 130 Hole 806B</td>
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<td></td>
</tr>
<tr>
<td>1H-3W (145-150)</td>
<td>4.45</td>
<td>0.709129</td>
<td>0.000005</td>
<td></td>
</tr>
<tr>
<td>1H-3W (145-150)</td>
<td>4.45</td>
<td>0.709147*</td>
<td>0.000008</td>
<td></td>
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<tr>
<td>2H-4W (145-150)</td>
<td>12.45</td>
<td>0.709086</td>
<td>0.000005</td>
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<tr>
<td>3H-4W (145-150)</td>
<td>21.95</td>
<td>0.709058</td>
<td>0.000005</td>
<td></td>
</tr>
<tr>
<td>3H-4W (145-150)</td>
<td>21.95</td>
<td>0.709035*</td>
<td>0.000006</td>
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</tr>
<tr>
<td>4H-4W (145-150)</td>
<td>31.45</td>
<td>0.709040</td>
<td>0.000005</td>
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</tr>
<tr>
<td>4H-4W (145-150)</td>
<td>31.45</td>
<td>0.709022*</td>
<td>0.000005</td>
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</tr>
<tr>
<td>Sample</td>
<td>Depth mbsf (^a)</td>
<td>(^{87})Sr/(^{86})Sr (^c)</td>
<td>(2SE)(_{\text{internal}}) (^d)</td>
<td>(SD)(_{\text{external}}) (^d)</td>
</tr>
<tr>
<td>------------------------</td>
<td>---------------------</td>
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<td>Leg 130 Hole 806B</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5H-4W (145-150)</td>
<td>40.95</td>
<td>0.709035</td>
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<tr>
<td>6H-4W (145-150)</td>
<td>50.45</td>
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<td>6H-4W (145-150)</td>
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<td>0.708988*</td>
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<td>9H-4W (145-150)</td>
<td>78.95</td>
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<td>0.000006</td>
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</tr>
<tr>
<td>12H-4W (145-150)</td>
<td>107.45</td>
<td>0.708975</td>
<td>0.000006</td>
<td>0.0000019</td>
</tr>
<tr>
<td>12H-4W (145-150)</td>
<td>107.45</td>
<td>0.708957*</td>
<td>0.000007</td>
<td>0.0000010</td>
</tr>
<tr>
<td>15H-4W (145-150)</td>
<td>135.95</td>
<td>0.708960</td>
<td>0.000007</td>
<td>0.000014</td>
</tr>
<tr>
<td>18H-4W (145-150)</td>
<td>164.45</td>
<td>0.708933</td>
<td>0.000004</td>
<td>0.000009</td>
</tr>
<tr>
<td>18H-4W (145-150)</td>
<td>164.45</td>
<td>0.708917*</td>
<td>0.000006</td>
<td>0.000016</td>
</tr>
<tr>
<td>21H-4W (145-150)</td>
<td>192.95</td>
<td>0.708914</td>
<td>0.000007</td>
<td>0.000023</td>
</tr>
<tr>
<td>24H-4W (145-150)</td>
<td>221.45</td>
<td>0.708886</td>
<td>0.000005</td>
<td></td>
</tr>
<tr>
<td>27H-4W (145-150)</td>
<td>249.95</td>
<td>0.708870</td>
<td>0.000005</td>
<td></td>
</tr>
<tr>
<td>30H-5W (145-150)</td>
<td>279.95</td>
<td>0.708836</td>
<td>0.000005</td>
<td></td>
</tr>
<tr>
<td>33H-4W (145-150)</td>
<td>306.95</td>
<td>0.708809</td>
<td>0.000010</td>
<td></td>
</tr>
<tr>
<td>36X-4W (145-150)</td>
<td>335.65</td>
<td>0.708793</td>
<td>0.000010</td>
<td></td>
</tr>
<tr>
<td>54X-5W (145-150)</td>
<td>509.3</td>
<td>0.708510</td>
<td>0.000010</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) As reported in the ODP Initial Report (Kroenke et al., 1991)

\(^b\) Based on age-depth model using magneto- and biostratigraphy (Kroenke, et al., 1991).

\(^c\) Measured on TIMS at University of California, Berkley.

\(^*\) Measured on Neptune Plus MC-ICPMS at Penn State MIL. NBS-987 = 0.710243 ± 0.000008 (long-term average).

\(^d\) In cases where replicates (2 - 4) were analyzed, the external reproducibility (2·standard deviation) is reported. In cases where no replicates were analyzed, the internal reproducibility (2·standard error) is reported.
Table 3.5. Calcium isotopic composition of bulk carbonates measured from ODP Hole 806B

<table>
<thead>
<tr>
<th>Samples</th>
<th>Depth mbsf</th>
<th>Age Ma</th>
<th>$\delta^{44/40}$CaBE ‰</th>
<th>$\delta^{44/40}$CaSRM-915 ‰</th>
<th>2SD ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H-1W-(111-113)</td>
<td>1.11</td>
<td>0.08789</td>
<td>-0.52</td>
<td>0.49</td>
<td>0.1</td>
</tr>
<tr>
<td>1H-2W (34-36)</td>
<td>1.84</td>
<td>0.1457</td>
<td>-0.54</td>
<td>0.46</td>
<td>0.11</td>
</tr>
<tr>
<td>1H-3W (34-36)</td>
<td>3.34</td>
<td>0.26447</td>
<td>-0.61</td>
<td>0.39</td>
<td>0.1</td>
</tr>
<tr>
<td>2H-5W (35-37)</td>
<td>12.85</td>
<td>0.63773</td>
<td>-0.6</td>
<td>0.4</td>
<td>0.14</td>
</tr>
<tr>
<td>3H-5W (34-36)</td>
<td>22.34</td>
<td>1.06425</td>
<td>-0.56</td>
<td>0.44</td>
<td>0.12</td>
</tr>
<tr>
<td>4H-5W (34-36)</td>
<td>31.84</td>
<td>1.45664</td>
<td>-0.36</td>
<td>0.65</td>
<td>0.16</td>
</tr>
<tr>
<td>5H-6W (36-38)</td>
<td>42.86</td>
<td>2.04945</td>
<td>-0.5</td>
<td>0.5</td>
<td>0.26</td>
</tr>
<tr>
<td>6H-6W (38-40)</td>
<td>52.38</td>
<td>2.33715</td>
<td>-0.4</td>
<td>0.6</td>
<td>0.17</td>
</tr>
<tr>
<td>11H-7W (73-75)</td>
<td>101.73</td>
<td>4.00737</td>
<td>-0.47</td>
<td>0.53</td>
<td>0.17</td>
</tr>
<tr>
<td>17H-1W (109-111)</td>
<td>150.09</td>
<td>5.29641</td>
<td>-0.39</td>
<td>0.61</td>
<td>0.14</td>
</tr>
<tr>
<td>22H-3W (109-111)</td>
<td>200.59</td>
<td>6.52842</td>
<td>-0.41</td>
<td>0.59</td>
<td>0.06</td>
</tr>
<tr>
<td>3H-4W (145-150)</td>
<td>249.54</td>
<td>7.69654</td>
<td>-0.52</td>
<td>0.48</td>
<td>0.09</td>
</tr>
<tr>
<td>32H-6W (110-112)</td>
<td>300.1</td>
<td>8.67912</td>
<td>-0.58</td>
<td>0.42</td>
<td>0.14</td>
</tr>
<tr>
<td>49X-1W (9-11)</td>
<td>455.59</td>
<td>13.0728</td>
<td>-0.57</td>
<td>0.43</td>
<td>0.14</td>
</tr>
<tr>
<td>54X-1W (4-6)</td>
<td>501.94</td>
<td>14.6807</td>
<td>-0.56</td>
<td>0.44</td>
<td>0.06</td>
</tr>
</tbody>
</table>

* As reported in the ODP Initial Report (Kroenke et al., 1991)

b Based on age-depth model using magneto- and biostratigraphy (Kroenke et al., 1991)

c Measured on TIMS at University of California, Berkeley.

* Measured on Neptune Plus MC-ICPMS at Penn State MIL.

Table 3.6. Calcium isotopic composition of pore fluids measured from ODP Hole 806B

<table>
<thead>
<tr>
<th>Samples</th>
<th>Depth mbsf</th>
<th>$\delta^{44/40}$CaBE ‰</th>
<th>$\delta^{44/40}$CaSRM-915 ‰</th>
<th>2SD ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H-3W (145-150)</td>
<td>4.45</td>
<td>0.27</td>
<td>1.27</td>
<td>0.03</td>
</tr>
<tr>
<td>2H-4W (145-150)</td>
<td>12.45</td>
<td>-0.12</td>
<td>0.89</td>
<td>0.04</td>
</tr>
<tr>
<td>3H-4W (145-150)</td>
<td>21.95</td>
<td>-0.35</td>
<td>0.65</td>
<td>0.21</td>
</tr>
<tr>
<td>3H-4W (145-150)</td>
<td>21.95</td>
<td>-0.13</td>
<td>0.87*</td>
<td>0.02</td>
</tr>
<tr>
<td>4H-4W (145-150)</td>
<td>31.45</td>
<td>-0.42</td>
<td>0.59</td>
<td>0.01</td>
</tr>
<tr>
<td>5H-4W (145-150)</td>
<td>40.95</td>
<td>-0.47</td>
<td>0.53</td>
<td>0.01</td>
</tr>
<tr>
<td>6H-4W (145-150)</td>
<td>50.45</td>
<td>-0.61</td>
<td>0.39</td>
<td>0.05</td>
</tr>
<tr>
<td>6H-4W (145-150)</td>
<td>50.45</td>
<td>-0.59</td>
<td>0.41*</td>
<td>0.04</td>
</tr>
<tr>
<td>9H-4W (145-150)</td>
<td>78.95</td>
<td>-0.64</td>
<td>0.36</td>
<td>0.06</td>
</tr>
<tr>
<td>12H-4W (145-150)</td>
<td>107.45</td>
<td>-0.69</td>
<td>0.31</td>
<td>0.03</td>
</tr>
<tr>
<td>Samples</td>
<td>Depth mbsf</td>
<td>δ(^{44/40})Ca(^{BE}) b</td>
<td>δ(^{44/40})Ca(^{SRM-915a}) b</td>
<td>2SD</td>
</tr>
<tr>
<td>----------------</td>
<td>------------</td>
<td>------------------------------</td>
<td>------------------------------</td>
<td>-----</td>
</tr>
<tr>
<td>Core-section interval (cm)</td>
<td></td>
<td>%oo</td>
<td>%oo</td>
<td></td>
</tr>
<tr>
<td>15H-4W (145-150)</td>
<td>135.95</td>
<td>-0.46</td>
<td>0.54</td>
<td>0.11</td>
</tr>
<tr>
<td>18H-4W (145-150)</td>
<td>164.45</td>
<td>-0.37</td>
<td>0.63</td>
<td>0.11</td>
</tr>
<tr>
<td>18H-4W (145-150)</td>
<td>164.45</td>
<td>-0.36</td>
<td>0.64*</td>
<td>0.03</td>
</tr>
<tr>
<td>21H-4W (145-150)</td>
<td>192.95</td>
<td>-0.61</td>
<td>0.39</td>
<td>0.08</td>
</tr>
<tr>
<td>24H-4W (145-150)</td>
<td>221.45</td>
<td>-0.7</td>
<td>0.31</td>
<td>0.07</td>
</tr>
<tr>
<td>27H-4W (145-150)</td>
<td>249.95</td>
<td>-0.64</td>
<td>0.36</td>
<td>0.11</td>
</tr>
<tr>
<td>30H-5W (145-150)</td>
<td>279.95</td>
<td>-0.51</td>
<td>0.49</td>
<td>0.12</td>
</tr>
<tr>
<td>33H-4W (145-150)</td>
<td>306.95</td>
<td>-0.65</td>
<td>0.35</td>
<td>0.00</td>
</tr>
<tr>
<td>36X-4W (145-150)</td>
<td>335.65</td>
<td>-0.67</td>
<td>0.33</td>
<td>0.00</td>
</tr>
<tr>
<td>54X-5W (145-150)</td>
<td>509.3</td>
<td>-0.73</td>
<td>0.27</td>
<td>0.11</td>
</tr>
</tbody>
</table>

*a As reported in the ODP Initial Report (Kroenke et al., 1991).

b Measured on TIMS at University of California, Berkley.

* Measured on Neptune Plus MC-ICPMS at Penn State MIL.
Table 3.7. Elemental chemistry of bulk carbonates measured from ODP Hole 806B

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth</th>
<th>CaCO$_3$% measured</th>
<th>CaCO$_3$% calculated</th>
<th>$[\text{Sr}]$ ppm</th>
<th>Sr/Ca mmol/mol</th>
<th>$[\text{Mg}]$ ppm</th>
<th>Mg/Ca mmol/mol</th>
<th>$[\text{Na}]$ ppm</th>
<th>Na/Ca mmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg 130 Hole 806B-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H-1W (1H-1)</td>
<td>1.11</td>
<td>83.35</td>
<td>81.87</td>
<td>1523.89</td>
<td>1.74</td>
<td>629.36</td>
<td>2.59</td>
<td>931.04</td>
<td>4.06</td>
</tr>
<tr>
<td>1H-3W (111-111)</td>
<td>3.34</td>
<td>84.25</td>
<td>76.82</td>
<td>1384.38</td>
<td>1.58</td>
<td>592.05</td>
<td>2.44</td>
<td>995.56</td>
<td>4.34</td>
</tr>
<tr>
<td>3H-5W (34-36)</td>
<td>22.34</td>
<td>87.98</td>
<td>82.41</td>
<td>1514.50</td>
<td>1.73</td>
<td>386.37</td>
<td>1.59</td>
<td>528.54</td>
<td>2.30</td>
</tr>
<tr>
<td>5H-6W (36-38)</td>
<td>42.84</td>
<td>90.49</td>
<td>82.56</td>
<td>1461.31</td>
<td>1.67</td>
<td>637.59</td>
<td>2.63</td>
<td>571.88</td>
<td>2.49</td>
</tr>
<tr>
<td>1H-7W (73-75)</td>
<td>101.73</td>
<td>90.83</td>
<td>81.95</td>
<td>1406.36</td>
<td>1.61</td>
<td>633.30</td>
<td>2.61</td>
<td>655.51</td>
<td>2.86</td>
</tr>
<tr>
<td>17H-1W (109-111)</td>
<td>150.09</td>
<td>92.60</td>
<td>85.13</td>
<td>1272.35</td>
<td>1.49</td>
<td>714.85</td>
<td>3.01</td>
<td>799.46</td>
<td>3.56</td>
</tr>
<tr>
<td>22H-3W (109-111)</td>
<td>200.59</td>
<td>92.58</td>
<td>86.61</td>
<td>1391.84</td>
<td>1.63</td>
<td>658.09</td>
<td>2.78</td>
<td>635.44</td>
<td>2.84</td>
</tr>
<tr>
<td>32H-6W (110-112)</td>
<td>300.1</td>
<td>95.50</td>
<td>90.89</td>
<td>1023.85</td>
<td>1.18</td>
<td>860.32</td>
<td>3.57</td>
<td>680.56</td>
<td>2.99</td>
</tr>
<tr>
<td>49X-1W (9-11)</td>
<td>455.59</td>
<td>91.10</td>
<td>89.70</td>
<td>1127.66</td>
<td>1.29</td>
<td>809.30</td>
<td>3.34</td>
<td>578.10</td>
<td>2.52</td>
</tr>
<tr>
<td>54X-1W (14-16)</td>
<td>550.34</td>
<td>90.26</td>
<td>86.98</td>
<td>1128.37</td>
<td>1.30</td>
<td>746.97</td>
<td>3.11</td>
<td>669.25</td>
<td>2.95</td>
</tr>
<tr>
<td>64X-2W (48-50)</td>
<td>600.58</td>
<td>92.17</td>
<td>89.06</td>
<td>1024.46</td>
<td>1.22</td>
<td>772.44</td>
<td>3.30</td>
<td>581.06</td>
<td>2.63</td>
</tr>
<tr>
<td>74X-3W (105-107)</td>
<td>698.85</td>
<td>95.60</td>
<td>84.33</td>
<td>1024.23</td>
<td>1.20</td>
<td>626.36</td>
<td>2.65</td>
<td>533.79</td>
<td>2.39</td>
</tr>
</tbody>
</table>

$^a$ As reported in the ODP Initial Report (Kroenke et al., 1991).
$^b$ Calculated from Ca concentrations in the digested bulk carbonates.
$^c$ Estimated concentrations in the bulk calcite ($\mu$g/g CaCO$_3$).
### Table 3.8. Magnesium isotopic composition of pore fluids from ODP Holes 762A and B

<table>
<thead>
<tr>
<th>Sample</th>
<th>Core-section interval (cm)</th>
<th>Depth mbsf(^a)</th>
<th>(\delta^{26})Mg(_{DSM3}) (‰)</th>
<th>(2\sigma) (‰)</th>
<th>(\delta^{25})Mg(_{DSM3}) (‰)</th>
<th>(2\sigma) (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Leg 122 Hole 762A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H-2W (145-150)</td>
<td>2.9</td>
<td>-0.75</td>
<td>0.08</td>
<td>-0.40</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td><strong>Leg 122 Hole 762B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H-2W (145-150)</td>
<td>2.9</td>
<td>-0.77</td>
<td>0.03</td>
<td>-0.40</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>3H-4W (145-150)</td>
<td>19.23</td>
<td>-0.75</td>
<td>0.03</td>
<td>-0.39</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>6H-5W (145-150)</td>
<td>49.8</td>
<td>-0.60</td>
<td>0.05</td>
<td>-0.30</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>12H-1W(145-150)</td>
<td>99.4</td>
<td>-0.41</td>
<td>0.04</td>
<td>-0.22</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>12H-5W (145-150)</td>
<td>106.8</td>
<td>-0.39</td>
<td>0.06</td>
<td>-0.21</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>15H-5W (145-150)</td>
<td>135.3</td>
<td>-0.49</td>
<td>0.02</td>
<td>-0.26</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>18H-1W (145-150)</td>
<td>156.4</td>
<td>-0.35</td>
<td>0.02</td>
<td>-0.19</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>18H-5W (145-150)</td>
<td>163.8</td>
<td>-0.41</td>
<td>0.02</td>
<td>-0.22</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) As reported in the Initial report (Haq et al., 1990).

\(^b\) Average values of 2-4 replicates of each sample measured on Neptune Plus MC-ICPMS at Penn State MIL.

---

### Table 3.9. Magnesium isotopic composition of bulk carbonates measured from ODP Hole 762B

<table>
<thead>
<tr>
<th>Sample</th>
<th>Core-section interval (cm)</th>
<th>Depth mbsf(^a)</th>
<th>(\delta^{26})Mg(_{DSM3}) (‰)</th>
<th>(2\sigma) (‰)</th>
<th>(\delta^{25})Mg(_{DSM3}) (‰)</th>
<th>(2\sigma) (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Leg 122 Hole 762B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H-1W (104-106)</td>
<td>1.04</td>
<td>-4.45</td>
<td>0.12</td>
<td>-2.29</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>2H-2W (94-96)</td>
<td>6.84</td>
<td>-4.36</td>
<td>0.15</td>
<td>-2.23</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>3H-2W (96-98)</td>
<td>16.32</td>
<td>-4.22</td>
<td>0.1</td>
<td>-2.18</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>4H-2W (95-97)</td>
<td>25.89</td>
<td>-4.22</td>
<td>0.12</td>
<td>-2.19</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>5H-6W (91-93)</td>
<td>41.31</td>
<td>-4.71</td>
<td>0.15</td>
<td>-2.41</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>6H-6W (90-92)</td>
<td>50.8</td>
<td>-4.72</td>
<td>0.12</td>
<td>-2.43</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>9H-6W (87-89)</td>
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<td>-2.73</td>
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<td>10H-4W (90-92)</td>
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<tr>
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<td>13H-5W (64-66)</td>
<td>115.54</td>
<td>-4.49</td>
<td>0.12</td>
<td>-2.29</td>
<td>0.08</td>
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</tr>
<tr>
<td>14H-2W (83-89)</td>
<td>120.78</td>
<td>-4.01</td>
<td>0.13</td>
<td>-2.22</td>
<td>0.08</td>
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</tr>
<tr>
<td>15H-4W (57-59)</td>
<td>132.79</td>
<td>-4.48</td>
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<td>-2.32</td>
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</tr>
<tr>
<td>16H-1W (60-62)</td>
<td>138.0</td>
<td>-4.19</td>
<td>0.09</td>
<td>-2.17</td>
<td>0.02</td>
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<tr>
<td>16H-5W (70-74)</td>
<td>144.11</td>
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<tr>
<td>18H-3W (76-80)</td>
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<td>-4.74</td>
<td>0.12</td>
<td>-2.47</td>
<td>0.06</td>
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<tr>
<td>19H-1W (72-74)</td>
<td>166.62</td>
<td>-4.57</td>
<td>0.05</td>
<td>-2.31</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) As reported in the Initial report (Haq et al., 1990).

\(^b\) Average values of 2-4 replicates of each sample measured on Neptune Plus MC-ICPMS at Penn State MIL.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth mbsf&lt;sup&gt;a&lt;/sup&gt;</th>
<th>δ&lt;sup&gt;26&lt;/sup&gt;Mg&lt;sub&gt;DSM3&lt;/sub&gt;‰</th>
<th>2σ&lt;sup&gt;b&lt;/sup&gt;</th>
<th>δ&lt;sup&gt;25&lt;/sup&gt;Mg&lt;sub&gt;DSM3&lt;/sub&gt;‰</th>
<th>2σ&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg 122 Hole 762B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12H-4W (88-90)</td>
<td>104.78</td>
<td>0.27</td>
<td>0.08</td>
<td>0.15</td>
<td>0.05</td>
</tr>
<tr>
<td>13H-5W (64-66)</td>
<td>115.54</td>
<td>0.16</td>
<td>0.09</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>14H-2W (83-89)</td>
<td>120.78</td>
<td>-0.08</td>
<td>0.07</td>
<td>-0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>15H-4W (57-59)</td>
<td>132.79</td>
<td>0.08</td>
<td>0.01</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>16H-1W (60-62)</td>
<td>138.0</td>
<td>0.14</td>
<td>0.08</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>16H-5W (70-74)</td>
<td>144.11</td>
<td>-0.09</td>
<td>0.03</td>
<td>-0.04</td>
<td>0.03</td>
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<sup>a</sup> As reported in the Initial report (Haq et al., 1990).

<sup>b</sup> Average values of 2-4 replicates of each sample measured on Neptune Plus MC-ICPMS at Penn State MIL.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth mbsf&lt;sup&gt;a&lt;/sup&gt;</th>
<th>δ&lt;sup&gt;44/40&lt;/sup&gt;Ca&lt;sub&gt;BE&lt;/sub&gt;‰</th>
<th>2σ&lt;sup&gt;b&lt;/sup&gt;</th>
<th>δ&lt;sup&gt;44/40&lt;/sup&gt;Ca&lt;sub&gt;SRM-915a&lt;/sub&gt;‰</th>
<th>2σ&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg 122 Hole 762B</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1H-2W (145-150)</td>
<td>2.9</td>
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<td>1.75</td>
<td>0.50</td>
<td>0.07</td>
</tr>
<tr>
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<td>-0.08</td>
<td>0.92</td>
<td>0.70</td>
<td>0.06</td>
</tr>
<tr>
<td>6H-5W (145-150)</td>
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<td>0.72</td>
<td>0.65</td>
<td>0.03</td>
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<tr>
<td>12H-1W(145-150)</td>
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<td>0.79</td>
<td>0.64</td>
<td>0.04</td>
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<tr>
<td>12H-5W (145-150)</td>
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<td>-0.08</td>
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<td>0.06</td>
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<tr>
<td>15H-5W (145-150)</td>
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<td>0.43</td>
<td>0.05</td>
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<tr>
<td>18H-1W (145-150)</td>
<td>156.4</td>
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<td>0.63</td>
<td>0.57</td>
<td>0.04</td>
</tr>
<tr>
<td>18H-5W (145-150)</td>
<td>163.8</td>
<td>-0.57</td>
<td>0.43</td>
<td>0.57</td>
<td>0.03</td>
</tr>
</tbody>
</table>

<sup>a</sup> As reported in the Initial report (Haq et al., 1990).

<sup>b</sup> Average values of 2-4 replicates of each sample measured on Neptune Plus MC-ICPMS at Penn State MIL.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth mbsf&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Age Ma</th>
<th>δ&lt;sup&gt;44/40&lt;/sup&gt;Ca&lt;sub&gt;BE&lt;/sub&gt;‰</th>
<th>2σ&lt;sup&gt;b&lt;/sup&gt;</th>
<th>δ&lt;sup&gt;44/40&lt;/sup&gt;Ca&lt;sub&gt;SRM-915a&lt;/sub&gt;‰</th>
<th>2σ&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg 122 Hole 762B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H-1W (104-106)</td>
<td>1.04</td>
<td>0.04</td>
<td>-0.50</td>
<td>0.50</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>3H-2W (96-98)</td>
<td>16.32</td>
<td>1.04</td>
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<td>0.70</td>
<td>0.06</td>
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<tr>
<td>6H-6W (90-92)</td>
<td>50.8</td>
<td>2.83</td>
<td>-0.35</td>
<td>0.65</td>
<td>0.01</td>
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<tr>
<td>9H-6W (87-89)</td>
<td>79.27</td>
<td>3.92</td>
<td>-0.36</td>
<td>0.64</td>
<td>0.04</td>
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<td>11H-6W (88-90)</td>
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<td>4.63</td>
<td>-0.29</td>
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<td>0.06</td>
<td></td>
</tr>
<tr>
<td>19H-1W (72-74)</td>
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<td>32.70</td>
<td>-0.25</td>
<td>0.75</td>
<td>0.02</td>
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<sup>a</sup> As reported in the Initial report (Haq et al., 1990).

<sup>b</sup> Average values of 2-4 replicates of each sample measured on Neptune Plus MC-ICPMS at Penn State MIL.
<table>
<thead>
<tr>
<th>Sample Core-section interval (cm)</th>
<th>Depth mbsf</th>
<th>Age Ma</th>
<th>(^{87}\text{Sr}/^{86}\text{Sr} )</th>
<th>2SE(_{\text{internal}})</th>
<th>2SD(_{\text{external}})</th>
</tr>
</thead>
<tbody>
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<td><strong>Leg 122 Hole 762B</strong></td>
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<tr>
<td>1H-2W (145-150)</td>
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<td>0.1378</td>
<td>0.70913694</td>
<td>0.000006</td>
<td>8.93707E-06</td>
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<tr>
<td>3H-4W (145-150)</td>
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<td>1.51058E-05</td>
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<td>12H-1W(145-150)</td>
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<td>2.21461E-05</td>
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<td>0.000010</td>
<td>1.59722E-05</td>
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\( ^{87}\text{Sr}/^{86}\text{Sr} \) measured on Neptune Plus MC-ICP-MS at Penn State MIL. NBS-987 = 0.710243 ± 0.000008 (long-term average).

<table>
<thead>
<tr>
<th>Sample Core-section interval (cm)</th>
<th>Depth mbsf</th>
<th>Age Ma</th>
<th>(^{87}\text{Sr}/^{86}\text{Sr} )</th>
<th>2SE(_{\text{internal}})</th>
<th>2SD(_{\text{external}})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Leg 122 Hole 762B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H-1W (104-106)</td>
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<td>0.04</td>
<td>0.709152</td>
<td>0.000006</td>
<td>8.94E-06</td>
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<tr>
<td>3H-2W (96-98)</td>
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<td>0.709133</td>
<td>0.000003</td>
<td>1.51E-05</td>
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<tr>
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<td>2.83</td>
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<td>0.000007</td>
<td>2.17E-06</td>
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<tr>
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<td>4.63</td>
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<td>0.000007</td>
<td>8.92E-06</td>
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<tr>
<td>12H-4W (88-90)</td>
<td>104.78</td>
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<td>0.000006</td>
<td>1.86E-05</td>
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<tr>
<td>13H-5W (64-66)</td>
<td>115.54</td>
<td>8.74</td>
<td>0.708855</td>
<td>0.000008</td>
<td>8.40E-07</td>
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<tr>
<td>14H-2W (83-89)</td>
<td>120.73</td>
<td>9.85</td>
<td>0.708840</td>
<td>0.000006</td>
<td>2.89E-05</td>
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<tr>
<td>15H-4W (57-59)</td>
<td>132.97</td>
<td>15.17</td>
<td>0.708568</td>
<td>0.000006</td>
<td>2.77E-06</td>
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<tr>
<td>16H-1W (60-62)</td>
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<td>19.39</td>
<td>0.708452</td>
<td>0.000006</td>
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<tr>
<td>16H-5W (70-74)</td>
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<tr>
<td>19H-1W (72-74)</td>
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<td>32.70</td>
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<td>0.000007</td>
<td>1.16E-05</td>
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</table>

\( ^{87}\text{Sr}/^{86}\text{Sr} \) measured on Neptune Plus MC-ICP-MS at Penn State MIL. NBS-987 = 0.710243 ± 0.000008 (long-term average).
Table 3.15. Elemental chemistry of bulk carbonates measured from ODP Hole 762B

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth mbsf&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CaCO&lt;sub&gt;3&lt;/sub&gt;% measured</th>
<th>CaCO&lt;sub&gt;3&lt;/sub&gt;% calculated&lt;sup&gt;b&lt;/sup&gt;</th>
<th>[Sr] ppm&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Sr/Ca mmol/mol</th>
<th>[Mg] ppm&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Mg/Ca mmol/mol</th>
<th>[Na] ppm&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Na/Ca mmole/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H-1W (104-106)</td>
<td>1.04</td>
<td>86.33</td>
<td>81.87</td>
<td>1696.17</td>
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<td>715.83</td>
<td>2.95</td>
<td>945.14</td>
<td>4.11</td>
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<tr>
<td>2H-2W (94-96)</td>
<td>6.84</td>
<td>84.74</td>
<td>76.82</td>
<td>1446.90</td>
<td>1.65</td>
<td>749.85</td>
<td>3.09</td>
<td>781.91</td>
<td>3.40</td>
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<tr>
<td>3H-2W (96-98)</td>
<td>16.32</td>
<td>83.24</td>
<td>82.41</td>
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<td>1.96</td>
<td>578.62</td>
<td>2.38</td>
<td>641.73</td>
<td>2.79</td>
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<td>4H-2W (95-97)</td>
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<td>79.33</td>
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<td>1.78</td>
<td>698.92</td>
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<td>5H-6W (91-93)</td>
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<td>1.77</td>
<td>604.48</td>
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<td>543.69</td>
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<td>81.13</td>
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<td>2.00</td>
<td>617.97</td>
<td>2.54</td>
<td>590.06</td>
<td>2.57</td>
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<td>83.16</td>
<td>80.61</td>
<td>1711.06</td>
<td>1.95</td>
<td>606.34</td>
<td>2.49</td>
<td>497.64</td>
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<tr>
<td>10H-4W (90-92)</td>
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<td>83.08</td>
<td>83.89</td>
<td>1490.85</td>
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<td>381.55</td>
<td>1.57</td>
<td>278.52</td>
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<td>11H-6W (88-90)</td>
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<td>88.08</td>
<td>88.70</td>
<td>1687.01</td>
<td>1.93</td>
<td>562.65</td>
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<td>403.93</td>
<td>1.76</td>
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<td>86.98</td>
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<td>92.58</td>
<td>89.06</td>
<td>1154.57</td>
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<td>880.00</td>
<td>3.62</td>
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<td>87.16</td>
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<td>1267.57</td>
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<td>744.28</td>
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<td>877.03</td>
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<td>976.34</td>
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<td>16H-5W (70-74)</td>
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<td>87.33</td>
<td>85.11</td>
<td>1466.02</td>
<td>1.67</td>
<td>856.79</td>
<td>3.53</td>
<td>844.28</td>
<td>3.67</td>
</tr>
<tr>
<td>18H-3W (76-80)</td>
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<td>73.41</td>
<td>70.5</td>
<td>1057.74</td>
<td>1.21</td>
<td>943.25</td>
<td>3.88</td>
<td>394.30</td>
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<tr>
<td>19H-1W (72-74)</td>
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<td>79.16</td>
<td>80.01</td>
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<td>1.31</td>
<td>707.28</td>
<td>2.91</td>
<td>505.36</td>
<td>2.20</td>
</tr>
</tbody>
</table>

<sup>a</sup> As reported in the ODP Initial Report (Haq et al., 1990).  
<sup>b</sup> Calculated from Ca concentrations in the digested bulk carbonates.  
<sup>c</sup> Estimated concentrations in the bulk calcite (µg/g CaCO<sub>3</sub>).
Fig. 3.1. (a) Map showing the locations of ODP Holes 807A, 806B (Leg 130) and ODP Hole 762B. Data are adopted from Kroenke et al. (1991).

Fig. 3.2. Comparison between three ODP Holes (807A, 806B, and 762B) in terms of (a) pore fluid [Mg$^{2+}$] (b) pore fluid Mg/Ca, (c) pore fluid [Sr$^{2+}$], and (e) pore fluid Sr/Ca from ODP Holes 807A, 806B (Leg 130) and ODP Hole 762B. Data are adopted from Kroenke et al. (1991) and Haq et al. (1992).
Fig. 3.3. Comparison between Mg isotopic composition ($\delta^{26}\text{Mg}_{\text{DSM3}}$) of (a) pore fluids and (b) bulk carbonates from the ODP Holes 806B, 762B (this study), and from ODP Hole 807A (Higgins and Schrag, 2012). (c) The $\delta^{26}\text{Mg}$ vs. $\delta^{25}\text{Mg}$ plot showing that all measured data fall on the straight line with slope $\sim0.519 \pm 0.003$ which is identical to the slope of equilibrium mass dependent fractionation line (0.520).
Fig. 3.4. Magnesium isotopic composition ($\delta^{26}$Mg$_{DSM3}$) of (a) pore fluids and (b) bulk carbonates, and (c) bulk clays from the ODP Hole 762B measured in this study.
Fig. 3.5. (a) Comparison between the $^{87}$Sr/$^{86}$Sr ratios of bulk carbonates and pore fluids from the ODP Hole 806B and 762B (this study) with Hole 807A (Fantle and DePaolo, 2006) and global seawater $^{87}$Sr/$^{86}$Sr curve (McArthur and Howarth, 2004) as a function of age.

Fig. 3.6. Calcium isotopic composition ($\delta^{44/40}$Ca$_{\text{SRM 915a}}$) of pore fluids and bulk carbonates from ODP Holes (a) 806B and (b) 762B measured in this study.
Fig. 3.7. The measured trace elemental chemistry of two holes (806B and 762B) are compared with the chemistry of bulk carbonates from Hole 807A in terms of (a) Mg/Ca, (b) Sr/Ca (c) Na/Ca ratios and (e) Mg, (f) Sr, and (g) Na concentrations ($\mu$g/g of bulk carbonate).
Fig. 3.8. The correlations between trace elemental chemistry of three holes (762B, 806B and 807A) are presented. The Mg/Ca vs. Sr/Ca ratios of (a) sediments upper 200 mbsf and (b) sediments below 200 mbsf in Hole 807A, (c) Mg/Ca vs. Sr/Ca of sediments in Hole 806B (d) Mg/Ca vs. Na/Ca ratios of sediments from upper 200 mbsf in Hole 806B; the Mg/Ca vs. Sr/Ca from (e) sediments from upper 100 mbsf and below 144 mbsf in Hole 762B and (f) sediments from the interval between 100-144 mbsf in Hole 762B; Mg/Ca vs. Na/Ca from (g) sediments from upper 100 mbsf and below 144 mbsf in Hole 762B and (h) sediments from interval between 100-144 mbsf in Hole 762B.
Fig. 3.9. The model fits to the measured data of (a) pore fluid δ²⁶Mg, (b) bulk carbonate δ²⁶Mg, (c) pore fluid [Mg²⁺] and (d) bulk carbonate Mg concentration from Hole 807A. All model runs used 6900 m²/Ma as diffusion coefficient (D_Mg) with a closed lower boundary, i.e., no diffusive exchange between pore fluids and lower boundary is allowed. The upper boundary [Mg²⁺] and δ²⁶Mg are fixed to the modern seawater composition ([Mg²⁺] = 53.1 mmole/kg and δ²⁶Mg DSM3 = -0.84‰). The open and closed symbols represent measured pore fluids and carbonates, respectively. The solid green and black dotted lines represent the model result and the initial conditions, respectively using a reaction rate of ~2%/Ma (R=0.023e⁻³⁵×15.686) (Fantle and DePaolo, 2006), K_Mg value of 1.65 and the diagenetic fractionation factor for calcite recrystallization (α_{diag}^{s-f}) of 0.9947. Measured carbonate δ²⁶Mg values are obtained from the publication by Higgins and Schrag (2012).
The model fits to the measured data of (a) pore fluid $\delta^{26}\text{Mg}$, (b) bulk carbonate $\delta^{26}\text{Mg}$, (c) pore fluid $[\text{Mg}^{2+}]$ and (d) bulk carbonate Mg concentration from Site 806B. All model runs used 6900 m$^2$/Ma as diffusion coefficient ($D_{\text{Mg}}$) with a value of $[\text{Mg}^{2+}] = 20$ mM and $\delta^{26}\text{Mg} = -0.15$‰ at the lower boundary. The upper boundary $[\text{Mg}^{2+}]$ and $\delta^{26}\text{Mg}$ are fixed to the modern seawater composition ($[\text{Mg}^{2+}] = 53.1$ mmole/kg and $\delta^{26}\text{Mg}_{\text{DSM3}} = -0.84$‰). The open and closed symbols represent measured pore fluids and bulk carbonates, respectively. The solid red and black dotted lines represent the model result and the initial conditions, respectively using a reaction rate of $\sim$5%/Ma ($R = 0.05e^{-\text{age}/6}$) $K_{\text{Mg}}$ value of 2.5 and the diagenetic fractionation factor for calcite recrystallization ($\alpha_{\text{diag}}$) of 0.9950.
Fig. 3.11. The model fits to the measured data of (a) pore fluid $\delta^{26}$Mg, (b) bulk carbonate $\delta^{26}$Mg, (c) pore fluid $[\text{Mg}^{2+}]$ and (d) bulk carbonate Mg concentration from Hole 762B. All model runs used 6900 m$^2$/Ma as diffusion coefficient ($D_{\text{Mg}}$) with a value of $[\text{Mg}^{2+}] = 25$ mM and $\delta^{26}$Mg = -0.15 ‰ at the lower boundary. The upper boundary $[\text{Mg}^{2+}]$ and $\delta^{26}$Mg are fixed to the modern seawater composition ($[\text{Mg}^{2+}] = 53.1$ mmole/kg and $\delta^{26}$MgDSM3 = -0.84‰). The open and closed symbols represent measured pore fluids and bulk carbonates, respectively. The solid red and black dotted lines represent the model result and the initial conditions, respectively using a reaction rate of ~5%$/\text{Ma}$ ($R = 0.0055 + 0.045e^{-\text{age}/2.1}$) $K_{\text{Mg}}$ value of 2.5 and the diagenetic fractionation factor for calcite recrystallization ($\alpha_{s-f}^{\text{diag}}$) of 0.9940.
Fig. 3.12. Magnesium isotopic composition ($\delta^{26}\text{Mg}_{\text{DSM3}}$) of (a) pore fluids and (b) bulk carbonates and bulk clays from ODP Hole 762B are compared with (c) changes in CaCO$_3$ wt%, clay wt% and porosity with depth.
Fig. 3.13. (a) Model results from the CrunchTope simulations showing clay precipitation within carbonate-rich sedimentary column and (b) the Stella box model results showing effect of clay precipitation, calcite recrystallization, and diffusion on pore fluid $\delta^{26}$Mg.

Fig. 3.14. Comparison of the bulk carbonate $\delta^{26}$Mg record from ODP Holes 807A (Higgins and Schrag, 2012), 806B, and 762B with foraminiferal $\delta^{26}$Mg record from ODP Holes 1264A and 1263A (Pogge von Strandmann et al., 2014) plotted against age.
3.8. References


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Chapter 4

Experimental quantification of exchange rates of foraminiferal calcite using $^{45}$Ca tracer: Implication for diagenetic alteration of geochemical proxies

4.1. Abstract

Development of foraminiferal-based geochemical proxies often relies on core-top calibration. However, because foraminiferal tests are susceptible to mineral-fluid exchange it is critical to evaluate the extent of post-mortem calcite-fluid exchange on modern foraminiferal tests. Accordingly, this study experimentally quantifies the calcite-fluid exchange rates for both modern (Cariaco basin sediment traps) and fossil (Ocean Drilling Project Site 807) foraminiferal calcite using a $^{45}$Ca radiotracer technique over a three-month period. Foraminiferal tests are equilibrated with a $^{45}$Ca-spiked solution, saturated with respect to calcite, at a high solid/fluid Ca mass ratio in batch reactors; the solutions in a subset of reactors are amended with dissolved SiO$_2$.

A simple time-dependent box model that simulates mineral dissolution and reprecipitation is employed to quantify the exchange rate in each reactor. Modern foraminiferal tests exhibit faster exchange ($6.50 \cdot 10^{-4}$ to $0.30 \cdot 10^{-4}$ mol/m$^2$/d) than fossil foraminiferal tests ($2.50 \cdot 10^{-4}$ to $0.40 \cdot 10^{-5}$ mol/m$^2$/d) and the exchange rates generally are higher in the first nine days and decrease over the remaining eighty-eight days of the experiment. Furthermore, the presence of aqueous SiO$_2$ decelerates the exchange of modern foraminifera ($3.70 \cdot 10^{-4}$ to $0.13 \cdot 10^{-4}$ mol/m$^2$/d). Unlike foraminiferal calcite, the exchange rates for inorganic calcites are remarkably slow ($2.70 \cdot 10^{-9}$ to $1.9 \cdot 10^{-8}$ mol/m$^2$/d). In addition, parallel non-tracer reactors exhibit increase in
Multiple model simulations demonstrate that the main mechanism of the atom exchange in the reactors is partial dissolution-reprecipitation of calcite at a non-steady state influenced by intra-test chemical heterogeneity. Such short-term exchange, which is feasible in the seawater column and in core-tops near sediment-water interface, can readily overprint the trace elemental chemistry (e.g. Mg) of the foraminiferal tests. High-resolution SEM and micro-CT scans indicate no clear morphological changes in the tests during the experimental period suggesting that the physically “well-preserved” tests may not always produce reliable proxy data. Additionally, slower exchange rates of modern foraminifera in the presence of dissolved silica than the rates observed in the absence of silica suggest that in clay-rich environments foraminifera tend to be better preserved than in the carbonate-rich sediments without any clay. Ultimately, this study suggests that the effect of short-term exchange should be considered critically while calibrating geochemical proxies using modern foraminiferal tests from core-tops.

4.2. Introduction

Marine calcareous microfossils are extensively utilized as geochemical proxy archives. Foraminiferal $\delta^{18}$O and $\delta^{13}$C are traditionally used as geochemical tools to determine numerous paleoceanographic parameters, such as seawater temperature, ice volume, sea level, dissolved inorganic carbon (DIC) concentrations in seawater, productivity, and ocean circulation (e.g., Urey et al., 1951; Epstein et al., 1951; Boyle and Keigwin, 1985; Duplessy et al., 1988; Spero et al., 1997; Katz et al., 2008; Katz et al., 2010). However, the reconstruction of environmental parameters from traditional isotope proxies is not always straightforward. For instance, foraminiferal $\delta^{18}$O is related to both temperature and seawater $\delta^{18}$O, such that temperature can be
constrained if seawater $\delta^{18}O$ is known. Because seawater $\delta^{18}O$ depends on sea-ice volume, it is difficult to decouple the temperature signal from the foraminiferal $\delta^{18}O$ record without independent constraints on seawater $\delta^{18}O$. Hence, paleoceanographic reconstructions demand development of complimentary proxies that can be used in combination with traditional proxies to deconvolve multiple environmental signals.

In recent years, technological advancements in analytical geochemistry have offered a new suite of non-traditional geochemical proxies developed from trace elements (e.g., Sr/Ca, Mg/Ca, Ba/Ca, B/Ca) (Lea and Spero, 1992; Nürnberg et al., 1996; Rosenthal et al., 1997; Lea et al., 1999; Lear et al., 2000; Martin et al., 2002; Billups and Schrag, 2003; Honisch and Hemming, 2004; Foster, 2008) and isotopic compositions (e.g., $\delta^{11}B$, $\delta^{44/40}Ca$, and $\delta^{26}Mg$) in foraminiferal calcite (Burke, 1982; DePaolo and Ingram, 1985; Griffith et al., 2008; Fantle, 2010; Hodell et al., 2007; Higgins and Schrag, 2012; Fantle and Tipper, 2014; Pogge von Strandmanss et al., 2014) that are complementary to the traditional foraminifera-based proxies. These emerging metal isotopic proxies have the potential to reconstruct past variability in seawater chemistry and thereby contribute strongly to understanding long-term variations in the cycling of metals (e.g., Ca and Mg) that are directly linked to the global carbon cycle (Zhu and Macdougall, 1998; De La Rocha and DePaolo, 2000; Fantle and DePaolo, 2005; Hodell et al., 2007; Griffith et al., 2008; Higgins and Schrag, 2010; Higgins and Schrag, 2012, Fantle and Tipper, 2014; Pogge von Strandmanss et al., 2014). However, due to their low concentrations, the trace metals in carbonates (e.g., Mg, Sr, Ba, B) are also very sensitive to post-depositional alteration (Honisch and Hemming, 2004; Ni et al., 2007; Fantle et al., 2010; Fantle and Higgs, 2014; Fantle, 2015). Therefore, accurate interpretations of these developing proxies require critical constraints on the extent of post-formational alteration.

Post-formational alteration of proxy archives, such as marine carbonates, can involve two processes. One is partial dissolution in the water and/or sedimentary column; the other is...
dissolution-reprecipitation at chemical equilibrium, which mainly occurs in the sedimentary column. The effect of partial dissolution on foraminiferal tests (Berger, 1967; Berger, 1970; Parker et al., 1971; Berger, 1978; Honjo and Erez, 1978; Berger et al., 1982) and its impact on the foraminiferal trace elemental chemistry (e.g., Mg/Ca, Sr/Ca) have been fairly well documented (Savin and Dougles, 1973; Lohmann, 1995; Brown and Elderfield, 1996; Rosenthal and Lohmann, 2002; Dekens et al., 2002; Benway et al., 2003; Barker et al., 2005; Regenberg, 2006). Several qualitative and semi-quantitative methods have been developed to identify the effect and extent of dissolution on foraminiferal calcite. Fragmentation indices (Peterson and Prell, 1985; Le and Shackleton, 1992; Mekik et al., 2007), textural characteristics (“glassy” versus “frosty”) (Berger, 1970; Pearson et al., 2001; Pearson et al., 2007), and relative mass loss (Berger et al., 1982; Conan et al., 2002, de Villiers, 2005) are usually utilized to quantify the effect of partial dissolution. Alternatively, the extent to which foraminiferal tests are influenced by the exchange at near equilibrium conditions is still not well constrained.

There is strong geochemical evidence for long-term (i.e., hundreds of thousands to millions of years) exchange between bulk carbonates and pore fluids in the sedimentary column, and the impact of this process on trace elemental (e.g., Sr/Ca, Mg/Ca) and isotopic compositions (e.g., $^{87}\text{Sr}/^{86}\text{Sr}$) has been inferred to be significant (Richter and DePaolo, 1988; Richter and Liang, 1993; Fantle and DePaolo, 2006; Fantle and DePaolo, 2007; Fantle et al., 2010; Fantle, 2015). Additionally, mineral-fluid exchange has been documented to occur in various minerals (e.g., calcite, barite, gypsum) over short, experimental timescales under equilibrium conditions (Carlsson and Alto, 1996; Curti et al., 2005; Curti et al., 2010; Lestini et al., 2013; Avrahamov et al., 2013). Thus, there is strong evidence that minerals react with coexisting fluids over a range of time scales. While bulk sediments have been the main focus of the long time scale work, little work has been done to constrain the effects of exchange at the test level.
Understanding test-specific alteration is important given that foraminiferal archives are the primary source of high quality paleo-environmental reconstructions. In addition, there are multiple opportunities for tests to alter after formation. For instance, planktonic foraminiferal tests experience temperature, pressure, and saturation state conditions that differ markedly from the surface ocean as they settle through the water column and reside at the seafloor. The exposure time of foraminiferal tests to seawater can vary between several weeks to several years (Be et al. 1977; Be et al., 1981; Nigam et al., 2003). If alteration occurs during settling and prior to burial, foraminiferal archives may be biased.

Further, foraminiferal proxy reconstructions rely on calibrations using modern foraminiferal tests collected from either the water column (e.g., sediment traps) or the seafloor (e.g., core-top sediments) (Dekens et al., 2002; Lear et al., 2002; McConnell and Thunell, 2005; Brown et al., 2011). In both cases, foraminiferal tests are exposed to conditions that differ from the surface ocean; if the mineral-fluid exchange takes place under such conditions, then the proxy calibration can be biased and the proxy interpretation impacted. Therefore, it is necessary to evaluate the extent to which modern foraminiferal tests are susceptible to diagenetic exchange for accurate calibration of the foraminifera-based proxies.

Accordingly, in this investigation we examine the susceptibility of modern foraminiferal tests to mineral-fluid exchange over experimental timescales. The primary motivating questions are as follow: (1) Is there any evidence for test-fluid exchange at near-equilibrium conditions? (2) If so, at what rate does exchange occur? (3) Is this consistent with is observed in natural systems over longer time scales? The exchange is quantified using a $^{45}$Ca radiotracer technique, and the influence of solution chemistry (e.g., presence of aqueous Si) and age (i.e., modern vs. fossil) on the extent of mineral-fluid exchange specifically explored. Ultimately, this study has important implications for the fidelity of foraminiferal proxy archives and allows for initial constraints to be placed on the alteration that may occur in the natural environment.
4.3. Materials and Methods

4.3.1. Samples and locations

The exchange experiments are performed using three different types of calcite samples: (1) foraminiferal tests from sediment trap samples (250-500 µm), (2) foraminiferal tests from sediments cores (250-500 µm) and (3) inorganic calcite (Iceland spar) (250-500 µm).

The sediment trap samples are collected from the Cariaco Basin, situated on the northern continental shelf of Venezuela (Fig. 4.1a) by the researchers in the Marine Sediments Research Laboratory, University of South Carolina. The Cariaco basin is one of world’s largest anoxic basin with a maximum water depth of ~1400 m. The sediment trap samples collected from the uppermost depth interval (~230 m) are used in this study. The collection cups in the sediment trap are deployed with a buffered 4% formalin solution to preserve the samples. Upon recovery, the sediment trap samples are split using a precision rotary splitter and are stored in buffered sodium borate solution in a refrigerator at 4°C in the repository of the Marine Sediments Research Laboratory, University of South Carolina. After obtaining the sediment trap samples from University of South Carolina, they are washed repeatedly with ammonia buffered deionized water (pH ~8.5) to concentrate the foraminiferal tests of 250-500 µm size fractions using wet sieving techniques (500 and 250 µm size sieves) at Penn State. During the washing steps, the foraminiferal tests are examined under microscopes to verify complete removal of any organic matter and clays from the test surface. Two selective species (Orbulina universa and Globigerinoides ruber) that are most abundant are identified under reflected light microscope and hand picked from the concentrated sample of 250-500 µm size fractions. The physical preservation of the tests is determined using high-resolution SEM and micro-CT images (Appendix Fig. C.1 and C.2).
The sediment core samples are obtained the Ocean Drilling Project Site 807 (3°36.420 N, 156°37.490 E) located on the northeastern margin of Ontong Java Plateau (water depth of 2804 m) in the Pacific Ocean basin. The foraminiferal tests of 250-500 µm size of three species (Orbulina universa, Globigerinoides sacculifer, and Globigerina bulloides) are picked from the pre-washed size-sorted fractions of the bulk sediments and rinsed with the ammonia buffered deionized water to remove any clay, nannofossils or cement material from the test surface until they looked clean under microscope (Appendix Fig. C.1).

The inorganic calcite grains (250-500 µm) are obtained by breaking the Iceland spar calcite rhomb with controlled stroke of a metal blade followed by dry sieving of the finer particle using 500 and 250 µm sieves.

### 4.3.2. Preparation of equilibration solutions

Two different types of equilibration solutions are prepared for the batch exchange experiments. The first solution is prepared by dissolving 14.50 mg of high purity CaCl₂ salt and 10.86 mg of high purity Na₂CO₃ salt to 928.58 g deionized MilliQ water. The solution contains 1.407 \( \cdot 10^{-4} \) M Ca²⁺ and 2.205 \( \cdot 10^{-4} \) M Na⁺ with a pH of 9.94. The second solution is prepared in the similar way except with an addition of dissolved SiO₂ from single element ICP Si-standard (High Purity) to make the Si concentration as 9.42 ppm and the pH of this solution is 8.9. The saturation states of both of the equilibrium solutions are estimated with the geochemical modeling package PHREEQC (3.1.3-8914; phreeqc database; Parkhurst et al., 1999) to ensure that the solutions are at saturation with respect to calcite. The elemental concentrations are analyzed using a Quadrupole ICP-MS and the analytical methods are described in Appendix section C.4.
4.3.3. Experimental design

A total 148 reactors are designed to conduct 7 parallel sets of batch exchange experiments with $^{45}$Ca radiotracer over three months where each set consists of 15-20 reactors. The $^{45}$Ca radiotracer spike solution of $301.6 \pm 5$ nM concentration is prepared gravimetrically by adding $\sim 13.48 \mu g$ of $^{45}$CaCl$_2$ Perkin Elmer NEZ013 solution ($23.9 \mu M$ $^{45}$Ca; initial activity = 1 mCi on December 11$^{th}$ 2015; $t_{1/2} = 163$ day) to $\sim 1.07$ g of deionized MilliQ water. The experiments are conducted in acid-cleaned plastic micro-centrifuge tube with 0.6 ml of reservoir volume and 0.2 ml of headspace. Three sets of 6-8 standards are prepared gravimetrically from the same $^{45}$Ca tracer solution using both types of equilibration solution (i.e., with and without Si) and 0.1N HCl solution to calibrate the activity of the spike solution. The range of activity of the standards varies from $\sim 445$ to $\sim 1317,000$ cpm.

The experiments are conducted in acid cleaned plastic microcentrifuge tubes with 0.6 ml reservoir volume and 0.2 ml headspace. Prior to the experiment, individual foraminiferal tests are weighed using a microbalance and 9-10 tests, that weighed $\sim 550-700 \mu g$, are added to each reactor. The modern foraminiferal tests from sediment trap samples are added to 40 reactors and another 60 reactors are set up with the fossilized foraminiferal tests obtained from three different depth intervals (0-100 mbsf, 100-200 mbsf, and 200-300 mbsf) in ODP Hole 807A where each depth interval is represented by 20 reactors. Another 20 reactors are prepared by adding 9-10 the inorganic Iceland spar calcite grains ($\sim 600 - 700 \mu g$). Then $\sim 0.77$ g of the equilibrium solution without SiO$_2$ is added to 20 reactors with modern sediment trap samples, 60 reactors with fossilized sediment core samples, and 15 reactors with inorganic calcite samples. In the remaining 20 reactors containing modern foraminiferal tests $\sim 0.77$ g of the equilibration solution with SiO$_2$ is added followed by the addition of $\sim 2 \mu l$ of the same $^{45}$Ca tracer spike solution. A set of 15 empty reactors is also set up with $\sim 0.77$ g of equilibrium solution without dissolved SiO$_2$ as a
control experiment. At the beginning of the experiment, ~2 µl of the $^{45}$Ca tracer spike solution containing $\sim 7.5 \cdot 10^{-13}$ moles of $^{45}$Ca (estimated later from the calibration curve) is added to each reactor which then is sealed and placed on a VWR rocking platform shaker with a rocking motion of 19° angle and a speed of 80 rpm at room temperature. The weight of individual reactor is recorded before and after addition of the foraminiferal tests, the respective equilibration solution, and $^{45}$Ca spike.

Another 18 reactors are set up for non-tracer experiments where the effect of partial dissolution or net precipitation of calcite is monitored. Among those reactors, 15 are designed with the equilibrium solution without silica where the first 10 reactors contain ~600-800 µg of foraminiferal calcite from sediment traps and the rests contain a similar mass of foraminiferal calcite from the sediment cores (ODP Hole 807A, 0-100 mbsf depth interval). The remaining 3 reactors are prepared with ~600-800 µg of sediment trap foraminiferal tests and the equilibration solution with dissolved SiO$_2$. Instead of adding any radiotracer, ~2 µl of deionized water is added to each reactor.

Five time intervals are chosen over the three-month period where 3-4 reactors per each set of experiments are sampled. During the first month of experiment, the sampling is done more frequently (day 1, day 9, and day 32) followed by two long-term sampling intervals at the end of the second and the third month. Before sampling, the reactors are weighed and the solid particles are separated from the solution using 0.5 ml microcentrifuge filtration units (UltraceI -10K, Amicon) at 14000 rpm for 30 minutes. The detailed sampling method is described in the Appendix (section C3). Ultimately, the activity (in counts per minute) of $^{45}$Ca in each sample vial is measured using the liquid scintillation counter (LSC; Beckman Coulter Model LS6500 Liquid Scintillation Counter, Penn State).
4.3.4. Calculation of the moles of $^{45}$Ca exchanged between the solid and fluid

The total moles of $^{45}$Ca in each measured component (solid, fluid, and rinse) are calculated using the calibration curves derived from the set of standards prepared for each type of sample matrices. The blank subtracted counts for each set of standards are used to calculate the counting efficiency (C.E.) of the instrument for each type of matrix. The blank subtracted measured counts for each sample is then corrected for C.E. for the respective matrix type and decay of $^{45}$Ca ($t_{1/2} = 163$ day) followed by calculation of total moles of $^{45}$Ca present in each phase using the following set equations (1 to 5):

Counting efficiency (C.E.) = $\frac{A_{\text{std.meas}}}{A_{\text{std.expct}}}$ ---- (4.1)

where the terms $A_{\text{std.meas}}$ and $A_{\text{std.expct}}$ represent the expected and measured activity of known standard solutions respectively.

$A_{\text{Corr.C.E}} = \frac{A_{\text{meas}}}{C.E.}$ ---- (4.2)

where the terms $A_{\text{meas}}$ and $A_{\text{Corr.C.E}}$ stand for the measured and C.E. corrected activity of unknown samples respectively.

$A_{\text{Corr.decay}} = A_{\text{Corr.C.E}} \cdot e^{\lambda \cdot t}$ ---- (4.3)

Here $A_{\text{Corr.decay}}$ represents the decay corrected activity of samples and the terms $\lambda$ and $t$ stand for the decay constant ($4.93179 \cdot 10^{-08}$ per sec) and elapsed time since the beginning of the experiment.

$\text{moles}_{\text{meas}} = A_{\text{Corr.decay}} \cdot \text{slope} \cdot \text{intercept}$ ---- (4.4)
The term \( m_{\text{meas}} \) represents the moles of \(^{45}\text{Ca}\) present in the aliquot of sample measured. The slope and intercept are derived from the standard calibration curves.

\[
\text{moles}_{\text{actual}} = \frac{\text{moles}_{\text{meas}} \cdot \text{mass}_{\text{component}}}{\text{mass}_{\text{component aliquot}}} \quad ---- (4.5)
\]

Here the total mass of \(^{45}\text{Ca}\) (in moles) present in each component (solid, fluid, or rinse) is represented by the term \( \text{moles}_{\text{actual}} \). The terms \( \text{mass}_{\text{component}} \) and \( \text{mass}_{\text{component aliquot}} \) defined by the total mass of each component and the aliquot of each component measured.

A mass balance calculation is done by adding the moles of \(^{45}\text{Ca}\) from all three components of the system, i.e. solid, fluid and rinse and comparing the resultant moles of \(^{45}\text{Ca}\) to the initial moles of \(^{45}\text{Ca}\) added to the reactor at the beginning of the experiment using the following equation (6) to ensure the conservation of mass.

\[
\text{moles}_{\text{total}} = \text{moles}_{\text{fluid}} + \text{moles}_{\text{solid}} + \text{moles}_{\text{rinse}} \quad ---- (4.6)
\]

In this equation, the total moles of \(^{45}\text{Ca}\) in the reactor is represented by the term \( \text{moles}_{\text{total}} \) and the actual moles of \(^{45}\text{Ca}\) present in each component (solid, fluid, and rinse) are represented by the three terms \( \text{moles}_{\text{fluid}}, \text{moles}_{\text{solid}}, \) and \( \text{moles}_{\text{rinse}} \).

The exchange % is calculated in terms of % \(^{45}\text{Ca}\) incorporated in the solid relative to the total moles of \(^{45}\text{Ca}\) in the reactor using the following equation:

\[
\% ^{45}\text{Ca} \text{ incorp. solid} = 100 \cdot \frac{\text{moles}_{\text{solid}}}{\text{moles}_{\text{total}}} \quad ---- (4.7)
\]

where the term \( \frac{\text{moles}_{\text{solid}}}{\text{moles}_{\text{total}}} \) is the fraction of \(^{45}\text{Ca}\) incorporated into the solid phase relative to the total moles of \(^{45}\text{Ca}\) added to each reactor.
Additionally, the % exchange of Ca in solid relative to total Ca in solid is expressed by the following equation (8) assuming a homogeneous exchange (e.g., Reddy and Nancollas, 1970; Severin, 2012; Tetre et al., 2012; Lestini et al. 2013), where the fraction of total moles of Ca exchanged in the solid relative to the total moles of Ca in the fluid \((\frac{\text{Ca}_{\text{solid}}}{\text{Ca}_{\text{fluid}}})\) is considered to be equivalent to the mole fraction of \(^{45}\text{Ca}\) incorporated in the solid relative to remaining the moles of \(^{45}\text{Ca}\) in the fluid.

\[
\% \text{Ca}_{\text{exch}} = 100 \cdot \left( \frac{\frac{\text{Ca}_{\text{solid}} \cdot \text{Ca}_{\text{fluid}}}{\text{Ca}_{\text{fluid}}}}{\text{Ca}_{\text{solid}}} \right) 
\]

\[\text{---- (4.8)}\]

The total moles of Ca in solid and fluid are calculated from the mass of total solid present in each reactor (assuming the solid phase is entirely composed of calcite; formula weight of calcite = 100.09 g/mole) and the concentration of Ca in the solution and the mass of total solution in each reactor. The error in the analysis is computed from the 1\(\cdot\) standard deviation of the weights recorded for each reactor and the % error from the LSC counting.

4.4. Results

4.4.1. Exchange of \(^{45}\text{Ca}\) tracer by modern foraminiferal tests from sediment traps

In the experiments with reactors containing modern foraminiferal tests from Cariaco basin sediment traps and equilibration solution spiked with \(^{45}\text{Ca}\) radiotracer, the solid exhibit a distinct signal of incorporation of \(^{45}\text{Ca}\) tracer from the beginning of the experiment. In the first 9 days of experiment, the reactors containing equilibration solution without silica, the percent incorporation of \(^{45}\text{Ca}\) in the solid phase (% \(^{45}\text{Ca}_{\text{incorp.solid}}\) relative to the total \(^{45}\text{Ca}\) tracer in the reactor increases rapidly from 8.5 ± 1.0 % (day 1) to 20.6 ± 2.3% (day 9). However, the % \(^{45}\text{Ca}_{\text{incorp.solid}}\) decreases slightly to 12.5 ± 1.4% on day 32 followed by almost no change in next 30
days (12.3 ± 1.7% on the day 62) and an increase to 17.4 ± 2.1% (day 97) at the end of the three-month experiment. The % of $^{45}\text{Ca}$ remain in fluid samples (% $^{45}\text{Ca}_{\text{remain, fluid}}$) from the same reactors also decreases from 91.4 ± 1.0% (day 1) to 79.4 ± 2.3% (day 9) followed by a subsequent increase over next 15 days (87.1 ± 1.4% on day 32). In the second month of the experiment, the fluid samples show almost no change (87.7 ± 1.8% on the day 62) followed by a slight decrease (82.5 ± 2.1% on the day 97) at the end of the experiment (Fig. 4.2).

In experiments with modern sediment trap foraminiferal tests in the presence of dissolved silica and a similar amount of $^{45}$Ca spike, the solids exhibit similar temporal trend in the evolution of % $^{45}\text{Ca}_{ \text{incorp, solid}}$ as observed in the experiments without any Si in the solution. However, the magnitude of uptake of $^{45}$Ca by the solid in presence of Si over 3 months appears to be smaller relative to the solids from reactors without the presence of Si. In the first month of the experiment, the % $^{45}\text{Ca}_{ \text{incorp, solid}}$ increases sharply from 7.0 ± 1.1% (day 1) to 13.3 ± 2.2% (day 9) followed by a very little change in the following two months (13.1 ± 0.7% on the day 32, 12.6 ± 0.3% on the day 62, and 13.1 ± 3.7% on the day 97). The evolution of the moles of $^{45}$Ca in the fluid also shows a parallel trend, which is complementary to the trend in solids (Fig. 4.3).

4.4.2. Exchange of $^{45}$Ca tracer by fossil foraminiferal tests from sediment cores

The fossil foraminiferal tests from ODP Hole 807A from the Pacific Ocean basin exchange to a smaller extent relative to the modern foraminiferal calcite from the sediment trap samples. Moreover, among the core samples from different depth intervals the samples from shallower depths (0-100 mbsf) exhibit higher incorporation of $^{45}$Ca tracer as compared to the samples from deeper cores (200-300 mbsf).

The solid samples from the depth interval of 0-100 mbsf show a % $^{45}\text{Ca}_{ \text{incorp, solid}}$ of 2.3 ± 0.5% (day 1) within 24 hours of exchange followed by a sharp increase to 8.2 ± 2.6% in next 9
days and a decrease to 3.3 ± 0.3 % at the end 32 days. However, in the period of next two months, the solids from the same depth interval increase the uptake of $^{45}$Ca tracer, i.e., 5.6 ± 1.1 % on the day 62 and 6.2 ± 0.8 % on the day 97 (Fig. 4.4).

In the reactors with foraminiferal tests from the sediment core of 100-200 mbsf from ODP Hole 807A exhibit a smaller magnitude of exchange relative to the core samples from 0-100 mbsf. The % incorporation of $^{45}$Ca tracer in solids sampled within first 9 days of the experiment increases from 0.7 ± 0.05 % (day 1) to 5.5 ± 2.4 % (day 9). The solids from the reactors sampled on the day 32 and the day 62 of the experiment show a slightly smaller magnitude of % incorporation of $^{45}$Ca tracer (3.8 ± 2.7 % and 4.0 ± 1.0 % respectively) as compared to the previous days. The % incorporation of $^{45}$Ca tracer exhibited by the reactors sampled at the end of the third month is greater (6.7 ± 2.6 %, on the day 97) than that showed by the solids sampled in the previous two months (Fig. 4.5).

Finally, the fossil foraminiferal tests from the deepest core samples (200-300 mbsf) display almost similar magnitude of exchange compared to the core samples from 100-200 mbsf depths. The % incorporation of $^{45}$Ca tracer in the solids sampled within first 10 days of the experiment increase from 0.5 ± 0.09 % (day 1) to 3.8 ± 1.5 % (day 9). The solids from the reactors sampled over the next two months of the experiment show a similar % incorporation of $^{45}$Ca tracer (3.5 ± 0.4 %), followed by a slight increase in % incorporation of $^{45}$Ca tracer at the end of the 3rd month (6.1 ± 2.7 %, on the day 97) (Fig. 4.6). The coevolution of the mass of $^{45}$Ca tracer in the fluids from all 60 reactors reveals parallel trends complementary to the trend in the solids over the period of three month.
4.4.3. Exchange of $^{45}$Ca tracer by inorganic calcite grains

Unlike the experiments conducted with the biogenic calcite from both modern sediment traps and millions of years old marine core sediments, the inorganic calcites (Iceland spar crystals) show a significantly low incorporation of $^{45}$Ca tracer (0.05-0.2% incorporation of $^{45}$Ca) over the course of three months. In the reactors sampled three times (day 1, day 9, and day 32) during the first month of the experiment the measured activity of $^{45}$Ca in the solid phase is almost negligible (117- 800 cpm) as compared to the procedural blank measured (300 cpm) on the LSC. This indicates that % incorporation of $^{45}$Ca in the solid is insignificant during this stage. However, in the long-term sampling intervals (day 62 and 97), the inorganic calcite exhibits a relatively higher incorporation of $^{45}$Ca (0.2 ± 0.04 %) over 97 days (Fig. 4.7).

4.4.4. Temporal change in the solution chemistry in the non-tracer reactors

The non-tracer reactors set up to document the effect of partial dissolution on the trace metal concentrations in the fluid are also sampled during the same time intervals as the $^{45}$Ca-tracer reactors. On the first day of sampling (day1), in the reactor with equilibrium solution that does not contain dissolved SiO$_2$ the concentration of Ca in the fluids remain the same (5.65± 0.02 ppm) as compared to the initial composition of the equilibrium solution (5.64 ± 0.05 ppm). However, in the reactors sampled on the day 9, 32, 62, and 97 Ca concentration in the fluid increases up to ~34 ± 3 ppm. Similar to Ca, the concentration of Mg and Sr also show systematic increase over the entire three-month period of the experiment up to 0.72 ± 0.1 ppm and 0.12 ± 0.05 ppm respectively, given that the initial solutions contain neither of these two elements (Fig. 4.8).
The three reactors with equilibrium solution containing aqueous SiO$_2$ that are sampled on the day 9, day 32, and day 62 also show distinct increase in Ca concentration up to 15± 0.1 ppm, Mg up to 0.4± 0.05 ppm and Sr concentration up to 0.1± 0.01 ppm. The silica concentration in these three reactors decreases a little (9.42 ± 0.1 to 8.9 ± 0.05 ppm) over the experimental period (Fig. 4.8d).

4.4.5. Exchange rates of natural biogenic calcite versus inorganic calcite using $^{45}$Ca tracer

The exchange rates of Ca in the samples are calculated from the % Ca exchanged using moles of Ca in the solid and the fluid phase and the $^{45}$Ca present in both phases (Eq. 4.8). The exchange rates are normalized by the average surface area of the solids present in the reactors. The specific surface area for foraminiferal tests are estimated using micro-CT scans and the SEM images obtained for different types of particles used in this study (Appendix C: section C4, Fig. C2, and C3). Estimations from micro-CT scans show an average value of 0.12 ± 0.05 m$^2$/g for surface area of foraminiferal tests with a size of 250-500µm (Table 4.4 to 4.6).

The modern foraminiferal tests, in absence of aqueous SiO$_2$, exhibit an exchange rate of $\sim$1.1$\cdot$10$^{-4}$ to 1.4$\cdot$10$^{-4}$ mol/m$^2$/d in the beginning of the experiment (day1) followed by a sharp decrease to $\sim$3.2$\cdot$10$^{-5}$ – 4.0$\cdot$10$^{-5}$ mol/m$^2$/d (day 9). In the following month, the rate of decrease in exchange rate is relatively slower, i.e., from $\sim$ 6.4$\cdot$10$^{-6}$ – 7.4$\cdot$10$^{-6}$ mol/m$^2$/d (day 32) to 2.5$\cdot$10$^{-6}$ – 3.2$\cdot$10$^{-6}$ mol/m$^2$/d (day 97) (Fig. 4.2 and Table 4.1).

Modern foraminiferal tests in the presence of dissolved SiO$_2$ exchange at a slower rate compared to those reacted in the absence of SiO$_2$. The rates from the SiO$_2$-experiments are estimated to be 7.8$\cdot$10$^{-5}$ to 1.5$\cdot$10$^{-4}$ mol/m$^2$/d mol/m$^2$/d in the beginning (day1). After $\sim$9 days, the solids show a rapid decrease in rates of exchange ($\sim$2.4$\cdot$10$^{-5}$ – 3.0$\cdot$10$^{-5}$ mol/m$^2$/d on day 9).
solids from the reactors exchange slowly over the next 88 days ($5.5 \cdot 10^{-6} – 7.2 \cdot 10^{-6} \text{ mol/m}^2/\text{d}$ on the day 32 followed by $1.3 \cdot 10^{-6} – 2.4 \cdot 10^{-6} \text{ mol/m}^2/\text{d}$) (Fig. 4.3 and Table 4.2).

The fossilized foraminiferal tests recovered from the sediment core exhibit exchange rates considerably lower than the rates estimated from the modern foraminiferal tests. In the reactor containing fossil foraminiferal tests from 0-100 m depth interval, the initial rates estimated from the first 9 days of exchange are significantly smaller ($2.5 \cdot 10^{-5} – 4.0 \cdot 10^{-5} \text{ mol/m}^2/\text{d}$ on day 1 to $7.0 \cdot 10^{-6} – 1.5 \cdot 10^{-5} \text{ mol/m}^2/\text{d}$ on day 9) than the rates of exchange observed in modern foraminiferal tests over the same time interval. In the first day of sampling, the foraminiferal tests from deeper sediments show a slower exchange ($8.5 \cdot 10^{-6} – 1.7 \cdot 10^{-5} \text{ mol/m}^2/\text{d}$ from 100-200 mbsf interval and $5.3 \cdot 10^{-6} – 7.1 \cdot 10^{-6} \text{ mol/m}^2/\text{d}$ from 200-300 mbsf interval) than the samples from shallow sediments. The exchange rates in the both sets of experiments display similar temporal evolution over three months where the rates exponentially decrease to the similar values $\sim 9.5 \cdot 10^{-7} \pm 3.0 \cdot 10^{-7} \text{ mol/m}^2/\text{d}$ on the day 97 (Fig. 4.4 to Fig. 4.6 and Table 4.3 to Table 4.5).

The inorganic calcites, on the other hand, exhibit nearly no exchange in the first 60 days of the experimental period. However, only after three months, there is a slight increase in the activity of $^{45}\text{Ca}$ in the solid, which is used here to estimate the exchange rates. The estimated rates from the reactors sampled on the day 97 are $8.9 \cdot 10^{-9} \text{ to } 1.2 \cdot 10^{-8} \text{ mol/m}^2/\text{d}$. The surface area for the calcite crystals are estimated to be $\sim 0.2\text{-}0.3 \text{ m}^2/\text{g}$ using the geometric shape of the crystals and also from the BET surface area reported in previous studies (Curti et al., 2005; Avrahamov et al., 2013) (Fig. 4.7 and Table 4.6).
4.5. Discussion

The primary purpose of this section is to demonstrate that the observations from exchange experiments provide answers to the initial research questions regarding the susceptibility of foraminiferal tests to mineral-fluid exchange that motivated this study. The general experimental observation that the $^{45}$Ca tracer is being incorporated to the foraminiferal tests suggests that the calcite tests interact with the equilibration solution near calcite saturation. However, the incorporation of the radiotracer to the inorganic calcites is significantly lower than that in foraminiferal tests. The observed increase in $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, and $[\text{Sr}^{2+}]$ in the solutions from the non-tracer reactors confirms the occurrence of partial dissolution. Besides, the change in solution chemistry coupled with change in $^{45}$Ca tracer activity in the solid suggests that the $^{45}$Ca is incorporated into foraminiferal calcite via a short-term mineral-fluid exchange instead of a net precipitation of secondary calcite. The comparison between the temporal evolution of $^{45}$Ca uptake in the solids from different reactors over 97 days also suggest that the modern foraminiferal tests exchange more extensively with the surrounding solutions as compared to the fossilized foraminiferal tests from deep marine sediments. Moreover, fossilized samples from the shallower depth (0-100 mbsf) exhibit a greater amount of exchange relative to the samples from deeper sections (200-300 mbsf). The presence of aqueous SiO$_2$ in the reactors also influences the extent of the exchange between the foraminiferal tests and the equilibration solution by reducing the incorporation of $^{45}$Ca tracer into modern foraminiferal tests.

In the following sections we quantify the exchange rates and explore the mechanism of exchange between the biogenic calcite and the fluid near calcite saturation using a simple box model and demonstrate the implication of short-termed exchange on the foraminifera-based geochemical proxies. We also discuss the importance of short-term near-saturation calcite-fluid
exchange in foraminifera-based proxy calibration along with the role of morphology, age and solution chemistry in the mineral-fluid exchange.

4.5.1. Mechanism of exchange in natural biogenic calcite

In the literature many different terminologies have been used to describe post-formational alterations of minerals in the presence of aqueous solution, such as, recrystallization, isotope exchange, and atom exchange. This article is mainly focused on describing the mineral alteration without any distinct mineralogical transformation (i.e. calcite remains calcite) via mineral-fluid interaction that involves exchange of both trace elements as well as the isotopes between two components within the system. Such phenomenon can be described using the term “atom exchange” that refers to both trace elemental and isotopic substitution in the solid phase via solid-fluid interaction.

In a low temperature (T<100˚C) aqueous system, dissolution-reprecipitation is considered to be the primary mechanism that drives the atom exchange process (Cole and Chakraborty, 2001; Putnis, 2009; Putnis, 2014). Another viable process that can alter the chemistry and isotopic composition of the foraminiferal tests is solid-state diffusion (Davis et al., 1987; Watson, 2004) as biologically precipitated calcites tend to have numerous defects due to their fast growth rates. However, at low temperature the solid-state diffusion is considered to be too slow to operate in an experimental framework (Urey, 1948; Fisler and Cygan, 1999; Cole and Chakraborty, 2001).

The systematic increase in [Ca$^{2+}$], [Mg$^{2+}$], and [Sr$^{2+}$] of the solution (Fig. 4.8) along with the % weight loss (~7-8%) of the solids (Fig. 4.9) in each reactor of the non-tracer experiment confirm partial dissolution of the foraminiferal tests as the dominant mechanism to drive the solid-fluid exchange. The extensive incorporation of $^{45}$Ca observed over three months suggests
that the partial dissolution is coupled with reprecipitation to incorporate the radiotracer into the solid.

The overall exchange rates observed from all of the reactors suggest a two-stage exchange where the solid initially exchange rapidly with fluid in the first nine days followed a slower exchange. One plausible explanation for the observed two-stage exchange rates is that the process is not occurring quite at equilibrium, which can be possible if all parts of the same test are not at saturation with the solution. Growth-related intra-test heterogeneity in the distribution of Mg has been reported from a few species of planktonic foraminifera (e.g. *Orbulina universa*, *Globigerinoides ruber*, *Globigerinoides sacculifer*) (Eggins et al., 2003; Eggins et al., 2004). Because the incorporation of Mg$^{2+}$ in the calcite lattice increases the solubility of the calcite (Davis et al., 2000), such heterogeneous distribution of Mg across the test wall is likely to result in variable dissolution susceptibility of calcite within the single test (e.g., Lohmann, 1995; Brown and Elderfield, 1996; Nurnberg et al., 1996; Rosenthal and Lohmann, 2002). Therefore, the equilibration solution, which is saturated with respect to pure calcite, is possibly undersaturated relative to the more soluble Mg-rich parts of the foraminiferal test. Thus the calcite-fluid exchange, observed in the experiment might not occur in equilibrium. Instead, a rapid partial dissolution of Mg-rich parts of the test at the beginning of the experiment drives the exchange resulting rapid uptake of $^{45}$Ca tracer. Later, upon removal of Mg-rich parts the residual tests (low-Mg calcite) approach towards equilibrium with the solution via slow dissolution coupled with the incorporation of $^{45}$Ca tracer via precipitation of secondary calcite. At this stage, because of the high initial solid/fluid Ca molar ratio in the reactor, partial dissolution of calcite reduces the ratio between $^{45}$Ca and total Ca (i.e., $^{45}$Ca/Ca) ratio in the solution significantly. The uptake of $^{45}$Ca into the solid phase is a function of solution $^{45}$Ca/Ca ratio. Thus, dilution of solution $^{45}$Ca/Ca ratio reduces the incorporation of $^{45}$Ca into the solid phase resulting a deceleration of the exchange rates after the first nine days of the experiment. The temporal evolution of the relative changes in
Mg/Ca and Sr/Ca ratio in the solutions also indicate that initially the dissolving solids have higher Mg/Ca and Sr/Ca ratio during the first nine days of exchange as compared to the solids dissolving later (Fig. 4.8e and f). This observation supports the hypothesis that heterogeneity in the initial solid trace elemental chemistry results variable partial dissolution of the tests causing the two-stage exchange between foraminiferal tests and equilibration solutions.

Although the exchange rates from each set of experiments exhibit a two-stage process, in the temporal evolution of incorporation of $^{45}$Ca tracer to the solids show three distinct steps. The initial sharp increase in the $^{45}$Ca tracer uptake is followed by a decrease and a subsequent gradual increase in all reactors containing foraminiferal tests. The nature of incorporation of the $^{45}$Ca tracer and the increase of Ca, Mg, and Sr in the non-tracer reactors suggest that the initial rapid uptake of $^{45}$Ca is partially controlled by the exchange at the test surface, which then begins to re-equilibrate with the solution. Such phenomenon, termed as “back-reaction” can have a significant influence in the experiments as the reactors had high solid/ fluid Ca molar ratios, which gives the solid Ca a strong potential to alter the Ca in the solution. Therefore, the observed decrease in the activity of $^{45}$Ca in the solid and an increase in the activity of $^{45}$Ca in fluid after 30 days of exchange is considered to be the result of back-reaction.

Despite of the chemical evidence indicating partial dissolution in the reactors no overall morphological changes in the foraminiferal tests are observed in the full surface view of foraminiferal tests imaged using high-resolution SEM and micro-CT images (Fig. 4.12). However, some microstructural changes (e.g., change in pore shape and size) are observed when individual test is scanned at higher resolution using SEM and micro-CT techniques and such features indicate the effect of partial dissolution (Fig. 4.10).
4.5.2. **Determination of the rate of calcite-fluid exchange using a time-dependent box model**

The primary purpose of the model is to validate the proposed mechanism responsible for the mineral-fluid exchange in each reactor, quantify the rate of exchange and evaluate the impact of short-term exchange on geochemical proxies. Foraminiferal calcite is the foundation of many proxy-based reconstruction. Hence, understanding the mechanism of exchange and determination of rate of mineral-fluid exchange in foraminiferal calcite is critical for accurate estimation of the extent of post-formational alterations on carbonate-based proxies.

The reaction rates estimated in most of the atom exchange experiments are under the basic assumption of homogeneous exchange at equilibrium (illustrated in the Appendix C, section C1) (e.g., Moller and Sastri, 1973; Binsma and Kolar, 1984; Curti et al., 2010; Severin, 2012; Tetre et al., 2012; Lestini et al. 2013). However, in case of the biogenic calcites with intra-test chemical heterogeneity (Eggins et al., 2003; Eggins et al., 2004), such assumption may not always be applicable as the variable distribution of trace metals in the test can result intra-test variation in dissolution susceptibility. In this case, preferential dissolution and reprecipitation may not take place at equilibrium as some parts of the test (e.g. Mg and Sr-rich) become more soluble than the rests resulting a heterogeneous distribution of the $^{45}\text{Ca}$ tracer within the solid. In this article, we utilized a simple box model (described in Appendix section C.1, Fig. C.3), that accounts for the heterogeneous trace metal chemistry (i.e., Mg and Sr) of the initial solid. In this model the exchange takes place by partial dissolution of the solid by the preferential removal of more soluble Mg and Sr-rich calcite and incorporation of $^{45}\text{Ca}$ by secondary calcite precipitation at a non-steady state. All the reactors are treated as individual experiment to account for initial variability in their solid composition, solid/fluid Ca ratio and variable amount of $^{45}\text{Ca}$ tracer. In this modeling exercise, each reactor is modeled based on the initial mass of Ca in the fluid in each
reactor, its solid/fluid Ca ratio and moles of $^{45}$Ca added initially to the reactor at the onset of the experiment. All the model assumptions and variables are enlisted in the Appendix Table C1.

The box model is simulated under non-steady state condition, where the total dissolution flux to the fluid reservoir is greater than the precipitation flux from the fluid. Here the precipitation flux from the fluid is only balanced by the dissolution fluxes from the exchanged solid reservoir and from the un-exchanged solids with low-Mg-Sr calcite. The model results are able to reproduce the observed increase in the $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, and $[\text{Sr}^{2+}]$ in the solution and incorporation of $^{45}$Ca in the solids (Fig. 4.11). A comparison between the model-fits using both the steady state and non-steady state simulation is done to justify the importance of flux imbalance in the model in reproducing the observed solution chemistry (Appendix C. Fig.C4a and b). The sensitivity of the rate of exchange to the back reaction is also tested in the model. The results indicate that the exchange rate required to reproduce the observed $^{45}$Ca data is higher if the exchanged solid is allowed entirely to re-equilibrate with the fluid (i.e., 100% back-reaction) as compared to the case when back-reaction is not allowed at all (Appendix. Fig. C.4c and d).

Utilizing the model the mass of $^{45}$Ca in the solid and in the fluid is reproduced empirically by minimizing the Chi-squared value calculated between the observed and the model derived $^{45}$Ca values in both solid and fluid. The fraction of the Ca exchanged between the solid and the fluid is determined from the model derive uptake of $^{45}$Ca in the solid, which is then used to calculate the rate of exchange. The rates normalized to the surface area estimated using the micro-CT scans are listed in Table 4.2 to Table 4.6. The overall exchange rates obtained from the model simulation of a non-steady state condition are higher that the rates estimated from the $^{45}$Ca incorporation assuming a steady state exchange.

The rates of atom exchange for both modern and fossil foraminiferal tests exhibit a two-step exchange where the initial rapid exchange rates observed within the first nine days are followed by significantly slower exchange rates during the rest of the experiment (88 days). The
model-derived exchange rates for modern foraminiferal tests decreases sharply from $6.5 \cdot 10^{-4}$ to $1.2 \cdot 10^{-4}$ mol/m$^2$/d over the first nine days of experiment followed by a more gradual and slow decrease from $1.0 \cdot 10^{-4}$ to $3.0 \cdot 10^{-5}$ mol/m$^2$/d between the day 32 and the day 97 of the experiments (Fig. 4.2). The experiments conducted in presence of dissolved SiO$_2$ display a similar temporal change in exchange rates, although the magnitude of exchange rate is relatively smaller than that observed without aqueous SiO$_2$. The model-estimated exchange rates for sediment trap samples, in presence of Si, also decreases sharply from $3.7 \cdot 10^{-4}$ to $1.1 \cdot 10^{-4}$ mol/m$^2$/d in the first nine days of experiment and then exhibit a gradual decrease from $9.7 \cdot 10^{-6}$ to $2.04 \cdot 10^{-6}$ mol/m$^2$/d between 32 and 97 days of the experiment (Fig. 4.3). The rates estimated from the model for the fossilized foraminifera from sediment cores suggest that the deeper sediment core samples (200-300 mbsf) exchanged at even at slower rates ($1.5 \cdot 10^{-4}$ to $5.0 \cdot 10^{-5}$ mol/m$^2$/d) relatively to the rates obtained for foraminifera from shallower core (0-100 mbsf) from the same marine site ($2.5 \cdot 10^{-4}$ to $6.7 \cdot 10^{-5}$ mol/m$^2$/d) (Fig. 4.4 to 4.6).

4.5.3. Role of morphology and age on calcite-fluid exchange

Investigating the role of morphology on the near-equilibrium calcite-fluid exchange is one of the key objectives of this study. Here, the influence of surface structure and morphology of the solid is tested via comparing the exchange rates between foraminiferal calcite and inorganic Iceland spar calcite crystals. This study estimated the exchange rates for the Iceland spar calcite to be $\sim 8.9 \cdot 10^{-9}–1.7 \cdot 10^{-8}$ mol/m$^2$/d which is nearly 10 times smaller in magnitude as compared to the formerly determined exchange rates for inorganic calcites ($1 \cdot 10^{-4}$ to $1 \cdot 10^{-6}$ mol/m$^2$/y) (Carlsson and Alto, 1996; Curti et al., 2005; Avrahamov et al., 2013). Moreover, the exchange rates estimated for foraminiferal calcite in this study appear to be in the range of $6.5 \cdot 10^{-4}$ to 4.0
\[10^5 \text{ mol/m}^2/\text{d},\] which is significantly higher than the rates estimated for inorganic calcite in this study.

The morphology of foraminiferal tests differs significantly from the inorganic calcite crystals of the same size fraction. The surface of foraminiferal tests has several microscopic pores and delicate microstructures while the inorganic calcite grains have non-porous smooth surfaces. Besides, the foraminiferal tests are formed during fast biological calcification in the surface ocean and such processes tend to incorporate more defects into the lattice than the slowly grown inorganic calcites. Therefore, higher exchange rates observed in the foraminiferal tests compared to inorganic island spar calcite are reasonable.

Another primary research question that steered this investigation is whether the age of foraminiferal tests influences the rate of calcite-fluid exchange. Comparison of the rate of exchange between modern and fossil foraminiferal tests suggests that the modern foraminifera exchanges at a significantly faster rate than fossil foraminifera. The planktonic foraminifera are known to calcify at far from equilibrium with ambient seawater (e.g., Shackleton et al., 1973; Kahn, 1979; Kohfeld et al., 1996; Volkmann and Mensch, 2001). Therefore, when these tests are subjected to different solution chemistry, they are expected to react rapidly to attain equilibrium with respect to the surrounding solution composition. The sediment trap foraminiferal tests from the anoxic Cariaco basin are considered to retain well-preserved pores and microstructures, which potentially increase the reactive surface area resulting rapid exchange.

On the other hand, the bulk carbonates from ODP Hole 807A are already substantially recrystallized (Fantle and DePaolo, 2006; Fantle and DePaolo, 2007). The calcite recrystallization rates constrained by the Sr and Ca isotope geochemistry suggest a higher reaction rate (30-40% /Ma) for younger bulk carbonates (<1 Ma) (Fantle and DePaolo, 2007) and a slower rate (\(\leq 2\% /\text{Ma}\)) for older bulk carbonates (>1 Ma) where the reaction rate decreases with age (Fantle and DePaolo, 2006). The bulk carbonates being comprised of 20-50 % of foraminiferal tests, it is
likely that the foraminiferal tests from sediment cores (ODP Hole 807A) have already been reacted with the coexisting pore fluids near calcite saturation for many million years and have achieved the local chemical and isotopic equilibrium (Fantle and DePaolo, 2007). Our observation of a lesser incorporation of $^{45}$Ca tracer in the fossil foraminiferal tests from the sediment cores as compared to the modern foraminifera supports the hypothesis that age of the tests influences the rate of exchange. Additionally, the fossil foraminifera from deeper and older sediments (200-300 m ~10Ma) indicate a lesser reactivity than the fossil foraminifera from the shallower and younger sediments (0-100 mbsf, ~5Ma) suggesting that the exchange rates decreases with the age of the sediment. This observation is in agreement with the age-dependent reaction rate expression, which is used to model the effect of calcite recrystallization on the geochemistry of bulk carbonates and pore fluids from deep marine sediments (Richter and Liang, 1993; Fantle and DePaolo, 2006; Fantle et al., 2010; Fantle, 2015). Therefore, higher the exchange rates observed in modern foraminifera from the Cariaco basin as compared to the fossil foraminifera from ODP Hole 807A confirms the influence of age on the exchange rates.

4.5.4. Effect of dissolved SiO$_2$ on the atom exchange exhibited by foraminiferal calcite

Presence of dissolved SiO$_2$ in the bottom water near the seafloor and in the pore fluids from marine carbonate-rich sedimentary column is common in the marine system. In many sedimentary sections foraminiferal tests are found to exhibit better preservation within clay-rich layers as compared to carbonate-rich layers (e.g., Pearson et al., 2001; Sexton et al, 2006). Therefore, it is critical to constrain the impact of dissolved SiO$_2$ on the extent of short-term exchange between modern foraminiferal tests and the fluid near calcite saturation to ensure the proxy calibration using modern foraminiferal tests. In the experiments conducted in the presence of dissolved SiO$_2$ in alkaline pH (pH~ 8.9), modern foraminiferal tests exhibit a smaller
magnitude of exchange as compared to the tests in experiments performed without aqueous SiO$_2$. Additionally, the concentration of dissolved SiO$_2$ in the reactors decreases slightly (from 9.42 ppm to 8.84 ppm over 63 days) suggesting a loss of silica due to the incorporation into the foraminiferal tests.

In previous experiments the uptake of SiO$_2$ in calcite is considered to be mostly by adsorption at lower pH (~6) and near calcite saturation condition (Kastner et al., 1977; Klein and Walter, 1995; Karaseva et al., 2009). On the other hand, in an alkaline solution (pH >8), supersaturated with respect to calcite, silica is incorporated into calcite via co-precipitation (Kitano et al., 1979; Klein and Walter, 1995). From the scope of our experiments it is difficult to ascertain the mechanism of silica uptake into the foraminiferal tests, given a solution with high pH (~8.9) and nearly saturated with respect to calcite it is possible that the incorporation of SiO$_2$ into the foraminiferal calcite occurs by co-precipitation of amorphous silica onto the calcite surface.

At alkaline pH (~8.5 to 10.5) and 25°C, in a solution supersaturated with respect to calcite (log $\Omega$=1.02 to 1.10) and undersaturated with respect to amorphous silica, different degree of polymerization of aqueous SiO$_2$ is observed depending on the concentration of SiO$_2$. The presence of silica monomers (H$_2$SiO$_4$) and oligomers (H$_2$SiO$_{4-2}$) at low concentration (~9-11 ppm) may exhibit an inhibition effect on calcite growth (Pina et al., 2009). In these experiments we observe a smaller increase in [Ca$^{2+}$], [Mg$^{2+}$], and [Sr$^{2+}$] in the solution and lesser amount of incorporation of $^{45}$Ca into the solids in the reactors containing ~9.42 ppm of SiO$_2$ at alkaline pH as compared to the solids in the reactors without SiO$_2$. These observations suggest that the incorporation of polymerized silica onto the foraminiferal tests possibly reduces the exchange resulting a slow partial dissolution and a small uptake of $^{45}$Ca tracer.
4.5.5. Comparison between laboratory-derived exchange rates of foraminiferal calcite and exchange rates in natural sediments

A comparison between the exchange rates obtained from this study and previously estimated exchange rates from laboratory experiments and from natural sediments is done using the reaction rate vs. age plot previously proposed by Maher et al. (2004). Such comparison revealed that the exchanged rates constrained for foraminiferal calcite in this study, assuming 100% solid is reacting with the fluid, are consistent with the previous data (Carlsson and Aalto, 1996; Curti et al., 2005; Avrahamov et al., 2013). However, instead of falling right on the rate-age ($R_d = 0.1 \text{Age}^{-1}$, Maher et al., 2004; Fig. 4.12) line, our data falls slightly below the line with a linear trend that intersects the rate-age line. The rates estimated over the short duration (~10 days) falls farther from the line while the long-term rates (~100 days) fall closer the line.

Clustering below the rate-age line is considered to be the case when mineral and the fluid are not in equilibrium and the reaction is slow to reach the equilibrium (Maher et al., 2004; Reeves and Rothman, 2013). As the experimental observation suggests the predominance of partial dissolution during the atom exchange involving foraminiferal calcite, i.e., the exchange is not occurring at equilibrium, plotting of the foraminiferal exchange rates below the line is reasonable. The preferential dissolution of Mg and Sr-rich parts of foraminiferal tests evident in our experiments indicates intra-test trace elemental heterogeneity which can be the reason for variable chemical disequilibrium between different parts of the solid and the fluid resulting a long time to attain equilibrium.

4.5.6. Implication of short-term exchange on the fidelity of geochemical proxy

As short-term mineral-fluid exchange could be a viable process responsible for significant alteration of proxy archives in marine settings quantifying the rate exchange and
evaluating its extent on the geochemical proxies is critical. One of the prerequisites for foraminifera-based proxy reconstruction is calibrating the sensitivity of the proxy against the physical, chemical, and biological factors using modern foraminiferal tests. Such calibrations are performed either using cultured foraminifera in controlled laboratory conditions or using modern foraminifera collected from sediment traps within the seawater column and from the core-top sediments at sediment-water interface. In marine settings three main regions where modern foraminiferal tests can be exposed to short-term mineral-fluid exchange are: 1) surface ocean, 2) deep ocean, and 3) seafloor/sediment-water interface.

In the surface ocean, the residence time for foraminiferal tests near photic zone can be considered as few weeks as the average life span of foraminifera varies between 1-4 weeks (Be et al., 1977; Be et al., 1981; Nigam et al., 2003). Within the seawater column below photic zone the foraminiferal tests can be in contact with seawater for ~1-2 weeks (for test > 150 µm) depending on the test size and weight, and the average post-mortem settling velocity (Berger and Piper, 1972; Takahashi and Be, 1984). Finally, after settling on the seafloor, the foraminiferal tests can reside near-sediment water interface for many months to several years before burial (Dekens et al., 2002, Regenberg et al., 2007). Therefore, it is obvious that foraminiferal tests can be exposed to the seawater for a considerable amount of time when short-term mineral-fluid exchange is feasible.

Previous studies have documented that partial dissolution can significantly bias the temperature calibration of foraminiferal Mg/Ca ratio from core-top samples (Brown and Elderfield, 1996; Dekens et al., 2002; Rosenthal and Lohmann, 2002; Regenberg et al., 2007). For instance, species-specific the core-top calibration using G. ruber from multiple cores at different water depths from the Pacific and the Atlantic Ocean showed a significant scatter in the Mg/Ca ratios of samples calcified at same temperature where the decrease in Mg/Ca ratio correlates well with increasing water depth (Fig. 4.13). This observation suggests that samples
from core-topes at different water depth can undergo different extent of partial dissolution, which
can alter the chemistry of foraminiferal tests. Such alterations are often potential to bias the
proxy-calibration even during a short-term exposure to seawater. In this regard, short-term
laboratory exchange experiments over few months are relevant.

In this study, we observed that within three months foraminiferal tests could experience
significant chemical alteration via atom exchange (dissolution-reprecipitation) with coexisting
solution even in a near-equilibrium condition. Such exchange could have a sizeable impact on the
trace metal and its isotopic compositions, although the effect of partial dissolution-reprecipitation
on the test morphology is not readily discernible even in high-resolution images. For, example,
element like Mg in foraminiferal tests, which is routinely used for paleo-temperature
reconstruction, is greatly influenced by atom exchange even in a short duration. Using the
exchange rate estimated for modern foraminiferal calcite the Mg/Ca ratio of the solid is found to
be lowered by ~6-8 % over 97 days (Fig. 4.14). Alteration of Mg/Ca of the foraminiferal test to
such extent can result a significant bias in the temperature estimation that uses the following
equation (e.g., Nurnberg et al., 1996; Rosenthal et al., 1997a; Lea et al., 1999; Elderfield and
Ganssen, 2000; Lear et al., 2000; Martin et al., 2002; Billups and Schrag, 2003):

\[
\text{Mg/Ca (mmole/mole)} = B e^{A + T}
\]

where \(A\) and \(B\) are constants for exponential data fit that depend on the different species and \(T\) is
the calcification temperature in K. According to this equation, ~6-8% difference in Mg/Ca ratio
can result at least 0.5-1°C differences in temperature estimation.

In many cases the proxy calibration utilizes core-top materials that are considered to be
least affected by burial diagenesis. Traditionally, the preservation state of the handpicked
foraminifera is usually ascertained based on the overall test morphology using microscope images
or in some cases using SEM scans. Our study shows that such assumption about “well-preserved”
tests can lead to a potential underestimation of sea surface temperature derived from core-top foraminiferal tests that have actually re-equilibrated with the cold bottom water for several years. Such example demonstrates that the proxy records developed from material with apparent good physical preservation may actually be chemically altered without any overt morphological changes. However, in a clay-rich environment, presence of dissolved silica can influence the extent of alteration of foraminiferal tests by inhibiting the exchange as observed in this experiment. Therefore, clay-rich marine sections are more favorable for generating high-fidelity foraminifera-based proxy records.

4.6. Conclusions

The experimental data on foraminiferal calcite-fluid exchange using $^{45}$Ca tracer suggest that the exchange rate is strongly dependent on the age of the material. The modern foraminiferal tests obtained from sediment trap samples exhibit faster exchange rates as compared to the fossilized foraminifera recovered from the deep marine sediments. The extent of exchange in the foraminiferal tests also varies within the sediment core. The fossil foraminiferal tests from the deeper sediments exchange more than the tests recovered from the shallower section of the same sedimentary column. Parallel partial dissolution experiments suggest that at least 7-8% of the foraminiferal test have undergone net partial dissolution, which indicates that the mechanism of atom exchange is dissolution-reprecipitation. The evidence of net dissolution also indicates that growth-related chemical heterogeneity can be responsible for such preferential dissolution of Mg-rich part of the foraminiferal tests. Therefore, the exchange might not occur at equilibrium in this experiment.

No significant change in the overall preservation of the foraminifera tests is observed before and after the exchange experiment suggesting that the recrystallization occurred without
any obvious physical or morphological alteration. Although, detailed observation in the high-resolution SEM and micro-CT scans reveal some distortion of the pore shape and size that may be considered as a “dissolution feature”. Therefore, this investigation indicates that the geochemical proxy records developed from handpicked “well-preserved” fossil foraminiferal tests may not actually reflect its true state of chemical preservation. As the modern foraminifera exhibit significant susceptibility to exchange within a short experimental period, proxy-calibration using modern test collected from various water depths has a fair chance to be biased by such exchange. Additionally, presence of aqueous Si in the reactor appears to decelerate the exchange rate in the modern foraminifera. Hence, in the nature a system with dissolved silica may have a better chance of preserving the foraminiferal proxy archives resulting higher fidelity proxy records.

4.7. Acknowledgments

We acknowledge a research assistantship support from NSF Grant EAR-OCE-1154839 to Dr. Matthew S. Fantle and invaluable support from Dr. Christopher Gorski, Rosie Oakes, Prachi Joshi, Sarah Cronk, Jeffrey Leavey, Greg Herman, Scott Hynek, Matt Gonzalez, and Julie Anderson (Penn State).

Data Tables

Table 4.1. Experimental and model derived exchange rates for modern foraminiferal calcite from the Cariaco basin

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (days)</th>
<th>Surface Area m²/g</th>
<th>% Ca exchanged</th>
<th>Rate of exchange (mol/m²/d)</th>
<th>Model derived Rate of exchange (mol/m²/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>0.90</td>
<td>0.12±0.05</td>
<td>0.19</td>
<td>1.75·10⁻⁴</td>
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<td>A-2</td>
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<td>0.14</td>
<td>0.14</td>
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<td>0.16</td>
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<td>4.87·10⁻⁴</td>
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<td>A-4</td>
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<td>0.17</td>
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<td>5.07·10⁻⁴</td>
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<tr>
<td>A-5</td>
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<td>0.42</td>
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<td>1.15·10⁻⁴</td>
</tr>
<tr>
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<td>0.30</td>
<td>7.92·10⁻⁶</td>
<td>1.01·10⁻⁴</td>
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</table>
### Table 4.2. Experimental and model derived exchange rates for modern foraminiferal calcite from the Cariaco basin

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (days)</th>
<th>Surface Area m²/gᵃ</th>
<th>% Ca exchangedᵇ</th>
<th>Rate of exchange (mol/m²/d)ᶜ</th>
<th>Model derived Rate of exchange (mol/m²/d)ᵈ</th>
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<tbody>
<tr>
<td>Modern foraminiferal calcite (Sediment Trap)</td>
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<td></td>
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<tr>
<td>A-10</td>
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<td>7.06·10⁻⁶</td>
<td>1.00·10⁴</td>
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<td>A-11</td>
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<td>1.11·10⁴</td>
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<td>3.46·10⁻⁶</td>
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<td>A-18</td>
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<td>A-20</td>
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<td>3.26·10⁻⁶</td>
<td>2.97·10⁵</td>
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*ᵃ Surface area calculated from micro-CT scans of individual foraminiferal tests
ᵇ % Ca exchanged between the solid and fluid, calculated from moles of ⁴⁰Ca and Ca present in solid and fluid.
ᶜ Rates calculated from the moles of Ca exchanged from the experimental data
ᵈ Rates derived from the box model.
Table 4.3. Experimental and model derived exchange rates for fossil foraminiferal calcite from the Ontong Java Plateau cores

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (days)</th>
<th>Surface Area m²/g</th>
<th>% Ca exchanged b</th>
<th>Rate of exchange (mol/m²/d) c</th>
<th>Model derived Rate of exchange (mol/m²/d) d</th>
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<tr>
<td>C-1</td>
<td>0.90</td>
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<td>1.64×10⁻⁴</td>
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<td>7.66×10⁻⁵</td>
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<tr>
<td>C-13</td>
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<td>0.15</td>
<td>1.99×10⁻⁶</td>
<td>7.17×10⁻⁵</td>
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<tr>
<td>C-14</td>
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<td>1.21×10⁻⁶</td>
<td>5.60×10⁻⁵</td>
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<td>C-15</td>
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<td>C-16</td>
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<td>1.33×10⁻⁶</td>
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<td>C-17</td>
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a Surface area calculated from micro-CT scans of individual foraminiferal tests

b % Ca exchanged between the solid and fluid, calculated from moles of ⁴⁰Ca and Ca present in solid and fluid.

c Rates calculated from the moles of Ca exchanged from the experimental data

d Rates derived from the box model.

Table 4.4. Experimental and model derived exchange rates for fossil foraminiferal calcite from the Ontong Java Plateau cores

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (days)</th>
<th>Surface Area m²/g</th>
<th>% Ca exchanged b</th>
<th>Rate of exchange (mol/m²/d) c</th>
<th>Model derived Rate of exchange (mol/m²/d) d</th>
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<tr>
<td>D-1</td>
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<td>0.0127</td>
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<td>1.32×10⁻⁴</td>
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<tr>
<td>D-3</td>
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<td>0.0132</td>
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<td>0.08±0.02</td>
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<td>6.36×10⁻⁵</td>
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</tr>
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</table>
Table 4.5: Experimental and model derived exchange rates for fossil foraminiferal calcite from the Ontong Java Plateau cores

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (days)</th>
<th>Surface Area $m^2/g$</th>
<th>% Ca exchanged $^b$</th>
<th>Rate of exchange (mol/m²/d) $^c$</th>
<th>Model derived Rate of exchange (mol/m²/d) $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil foraminiferal calcite (807A 200-300 mbsf)</td>
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<td>E-2 0.90</td>
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<td>1.66·10⁻⁵</td>
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<tr>
<td>E-3 0.90</td>
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<td>9.96·10⁻⁶</td>
<td>1.74·10⁻⁵</td>
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<td>5.16·10⁻⁵</td>
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<tr>
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<td>E-9 31.79</td>
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<tr>
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<tr>
<td>E-17 97.79</td>
<td>0.059</td>
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<td>5.30·10⁻⁷</td>
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<tr>
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<tr>
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<td>4.01·10⁻⁷</td>
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<tr>
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<td>2.50·10⁻⁷</td>
<td>5.03·10⁻⁷</td>
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$^a$ Surface area calculated from micro-CT scans of individual foraminiferal tests
$^b$ % Ca exchanged between the solid and fluid, calculated from moles of $^{45}Ca$ and Ca present in solid and fluid.
$^c$ Rates calculated from the moles of Ca exchanged from the experimental data
$^d$ Rates derived from the box model.

Table 4.6: Experimental and model derived exchange rates for inorganic Iceland spar calcite grains

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (days)</th>
<th>Surface Area $m^2/g$ $^a$</th>
<th>% Ca exchanged $^b$</th>
<th>Rate of exchange (mol/m²/d) $^c$</th>
<th>Model derived Rate of exchange (mol/m²/d) $^d$</th>
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</thead>
<tbody>
<tr>
<td>Inorganic calcite (Iceland spar)</td>
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<tr>
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<td>0.2±0.02</td>
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<td>n.d</td>
<td>n.d</td>
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</tr>
<tr>
<td>F-3 0.90</td>
<td>0.000</td>
<td>n.d</td>
<td>n.d</td>
<td>n.d</td>
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</tr>
<tr>
<td>Experiment</td>
<td>Time (days)</td>
<td>Surface Area m²/g</td>
<td>% Ca exchanged</td>
<td>Rate of exchange (mol/m²/d)</td>
<td>Model derived Rate of exchange (mol/m²/d)</td>
</tr>
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<tr>
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<td>63.58</td>
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<tr>
<td>F-20</td>
<td>97.79</td>
<td>0.003</td>
<td>1.21 x 10⁻⁸</td>
<td>1.76 x 10⁻⁸</td>
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</tr>
</tbody>
</table>

*Surface area calculated from micro-CT scans of individual foraminiferal tests

b % Ca exchanged between the solid and fluid, calculated from moles of ⁴⁴Ca and Ca present in solid and fluid.

Rates calculated from the moles of Ca exchanged from the experimental data

Rates derived from the box model.

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Fig. 4.1. Locations of the sampling sites for foraminiferal tests.
Fig. 4.2. Results from experiment A with modern foraminiferal tests. (a) % incorporation of $^{45}$Ca in solids and (b) % $^{45}$Ca remained in the fluid relative to the total $^{45}$Ca added to the reactors; model fit to the measured moles of $^{45}$Ca in (c) solid and (d) fluid, (e) % Ca exchanged relative to the total Ca in the solid, and (f) surface area normalized rate of exchange (mol/m$^2$/d) are plotted against the sampling time (days).
Fig. 4.3. Results of experiment B with modern foraminiferal tests and equilibration solution with dissolved silica. (a) % incorporation of $^{45}$Ca in solids and (b) % $^{45}$Ca remained in the fluid relative to the total $^{45}$Ca added to the reactors; model fit to the measured moles of $^{45}$Ca in (c) solid and (d) fluid, (e) % Ca exchanged relative to the total Ca in the solid, and (f) surface area normalized rate of exchange (mol/m$^2$/d) are plotted against the sampling time (days).
Fig. 4.4. Results from exchange experiment C with fossil foraminiferal tests from ODP 807A sediment core (0-100 mbsf depth). (a) % incorporation of $^{45}$Ca in solids and (b) % $^{45}$Ca remained in the fluid relative to the total $^{45}$Ca added to the reactors; model fit to the measured moles of $^{45}$Ca in (c) solid and (d) fluid, (e) % Ca exchanged relative to the total Ca in the solid, and (f) surface area normalized rate of exchange (mol/m$^2$/d) are plotted against the sampling time (days).
Fig. 4.5. Results from exchange experiment D with fossil foraminiferal tests from ODP 807A sediment core (100-200 mbsf depth). (a) % incorporation of $^{45}$Ca in solids and (b) % $^{45}$Ca remained in the fluid relative to the total $^{45}$Ca added to the reactors; model fit to the moles of $^{45}$Ca in (c) solid and (d) fluid, (e) % Ca exchanged relative to the total Ca in the solid, and (f) surface area normalized rate of exchange (mol/m²/d) are plotted against the sampling time (days).
Fig. 4.6. Results from exchange experiment E with fossil foraminiferal tests from ODP 807A sediment core (200-300 mbsf depth). (a) % incorporation of $^{45}$Ca in solids and (b) % $^{45}$Ca remained in the fluid relative to the total $^{45}$Ca added to the reactors; model fit to the moles of $^{45}$Ca in (c) solid and (d) fluid, (e) % Ca exchanged relative to the total Ca in the solid, and (f) surface area normalized rate of exchange (mol/m$^2$/d) are plotted against the sampling time (days).
Fig. 4.7. Results from exchange experiment F with inorganic calcite (a) % incorporation of $^{45}\text{Ca}$ in solids and (b) % $^{45}\text{Ca}$ remained in the fluid relative to the total $^{45}\text{Ca}$ added to the reactors; model fit to the moles of $^{45}\text{Ca}$ in (c) solid and (d) fluid, (e) % Ca exchanged relative to the total Ca in the solid, and (f) surface area normalized rate of exchange (mol/m$^2$/d) are plotted against the sampling time (days).
Fig. 4.8. Results from partial dissolution experiments with foraminiferal tests. (a) Change in solution [Ca$^{2+}$], (b) [Mg$^{2+}$], (c) [Sr$^{2+}$], and (d) dissolved silica, (e) change in Sr/Ca ratio and (f) Mg/Ca ratio of the fluids are plotted against sampling time. The red and blue symbols represent experiment using modern and fossil foraminiferal tests respectively. The green symbols stand for the experiment with modern foraminifera and solution with dissolved silica.
Fig. 4.9. Percent loss in weights of foraminiferal tests from each reactor after exchange plotted against the sampling time (days). The red and blue symbols stand for experiment using modern and fossil foraminiferal tests respectively. The green symbols represent the experiment with modern foraminifera and Si-spiked solution.
Fig. 4.10. SEM images for the foraminiferal tests before partial dissolution experiment: (a) Full surface view and (b) micro-structures and pores of *Orbulina universa* from the Cariaco basin sediment trap before experiment; (d) full surface view and (e) micro-structures and pores and of *Orbulina universa* and from the Cariaco basin sediment trap after 97 days of partial dissolution. Micro-CT scans of *Orbulina universa* (c) full surface view before experiment and (f) full surface view after experiment. The red box on image “e” indicates “dissolution features”.


Fig. 4.11. Results from partial dissolution experiments involving foraminiferal tests and the model fits. (a) Changes in solution $[\text{Ca}^{2+}]$, (b) change in solution $[\text{Mg}^{2+}]$ and (c) change in $[\text{Sr}^{2+}]$ and are plotted against sampling time. The red and blue symbols represent experiment using modern and fossil foraminiferal tests respectively. The green symbols stands for the experiment with modern foraminifera and Si-spiked solution. The open and closed symbols represents measured data and model fits respectively.
Fig. 4.12 (a) the log-log plot of exchange rates (per year) against time (year) obtained from various laboratory-based experiments and diagenetic rates constrained for the deep-sea sediments using a box model. (b) The data from this study for all experiments involving modern and fossil foraminifera and inorganic calcites represented by cross symbols of different colors.
Fig. 4.13 (a) Core-top calibration of Mg/Ca ratios of *Globigerinoides ruber* against sea surface temperature (SST °C) (Dekens et al., 2002) from various Pacific (blue triangles) and Atlantic (red circles) cores from different water depths and (b) the spread of Mg/Ca ratio indicating change in Mg/Ca of *Globigerinoides ruber* with the water depth due to partial dissolution.

Fig. 4.14. Implication of atom exchange on Mg/Ca ratio of foraminifera plotted against % Ca exchanged: (a) dissolution %, percent change in Mg/Ca ratios for (b) Diss%= 3*t^{-1.385}, (c) Diss%= 2*t^{-1.181} and (d) Diss%= 0.5*t^{-1.138}. The solid lines represent 100% back reaction and the dotted line represent no back reaction.
4.8. References


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Severin A. (2012); Radionuclide microscopic diagnostics of the translational mobility of atoms and of the crystal defectiveness, with the crystallization of CaSO4·2H2O from supersaturated aqueous solution as example. *Radiochemistry* 54 568-572.


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Chapter 5
Conclusions and future directions

The primary motivation of the dissertation is to gain a comprehensive understanding of carbonate diagenesis and its implication on carbonate-based metal isotope proxies. The impact of diagenesis on geochemical proxies has been recognized since the onset of utilizing proxies in reconstructing the Earth’s history (Urey et al., 1951; Epstein et al., 1951). Since the sensitivity of elements in carbonates to diagenetic alteration depends largely on the relative abundance of the particular element in the carbonates and in coexisting pore fluids, it is critical to quantify the effect of diagenetic reactions on the individual element and its isotopes. For example, trace metals like Mg in carbonates exhibit a strong sensitivity to diagenetic exchange due to a very low concentration of Mg in carbonates as compared to the coexisting pore fluids. As marine biogenic carbonates, especially, foraminiferal δ²⁶Mg has great potential to record variability in seawater δ²⁶Mg and consequently can be utilized to understand the long-term changes in Mg geochemical cycle, quantifying the effect of diagenetic exchange on the δ²⁶Mg of marine carbonates is extremely critical. The quantification of diagenetic recrystallization requires a thorough investigation of various factors that influence the recrystallization rates in marine carbonates, especially, the impact of active transport processes (e.g. advection) and lithological variability within the carbonate-rich sedimentary column. In this dissertation, these aspects are addressed using a multi-site approach across various oceanographic settings showing a range of sediment thickness, lithological variation and influence of transport processes (e.g. diffusion and advection).

In the chapter 2, the impact of calcite recrystallization on carbonate δ²⁶Mg is quantified in an open marine site (ODP Site 1171) influenced by active advection. As active advection helps to
maintain the chemical and isotopic disequilibrium between the pore fluids and carbonates in a sedimentary column for a long period, the extent of diagenetic exchange is enhanced. In a previous study, the impact of such amplified diagenetic exchange on the Ca and Sr isotopic compositions of the carbonates and pore fluids has already been documented (Fantle, 2015), which made the Site 1171 a potential candidate for investigating the diagenetic effect on the $\delta^{26}$Mg of marine carbonates. In this study, the $\delta^{26}$Mg of bulk carbonates and pore fluids are measured along with the trace elemental chemistry (Mg/Ca and Sr/Ca) and $^{87}$Sr/$^{86}$Sr ratios of carbonates. The $\delta^{26}$Mg of bulk carbonates show a significant decrease by $\sim$ -2.0‰ over $\sim$170 m depth while the pore fluids exhibit a gradual down-depth increase from -0.80‰ to -0.39‰. Such variability in bulk carbonate $\delta^{26}$Mg also correlate well with increase in Mg/Ca ratio, decrease in Sr/Ca and Na/Ca ratios over the same depth along with the offset of bulk carbonate $^{87}$Sr/$^{86}$Sr ratios relative to the global seawater $^{87}$Sr/$^{86}$Sr curve (McArthur and Howard, 2004). As the deviation of $^{87}$Sr/$^{86}$Sr ratios from the global seawater curve is a characteristic signal for diagenetic alteration, the observed variability in bulk carbonate $\delta^{26}$Mg from the Site 1171 is interpreted as diagenetic signal. A mass balance calculation using the smear slide abundances of foraminiferal and coccolith tests and the end member Mg/Ca and $\delta^{26}$Mg values rules out the possibility that the observed $\delta^{26}$Mg variability in carbonates is a reflection of initial compositional variability (i.e. abundance and species composition of foraminiferal and coccolith tests) in the sediment. Application of reactive transport model demonstrates that in an advection-dominated sedimentary column the extent of calcite recrystallization is very pronounced on trace elements like Mg and its isotopes carbonate and as a result of calcite recrystallization $\delta^{26}$Mg of carbonates decreases the by a substantial amount ($\sim$ -0.8.0 to -2.0‰). This study also highlights the utility of bulk carbonates $\delta^{26}$Mg in fingerprinting the overall diagenetic effect in a sedimentary column, which can be a potential tool in evaluating the chemical fidelity of finer proxy archives (e.g. hand picked foraminiferal tests) developed from marine sediments.
In the third chapter, the impact of calcite recrystallization on carbonate-based geochemical proxies is evaluated from a different oceanographic set up where the thick (~1000 m) carbonate-rich sedimentary columns (ODP Holes 807A, 806B, and 762B) are not influenced by active advection. In such sedimentary sections, which can be considered as “closed system”, the reactive length scale of Mg is larger relative to Ca and Sr (Fantle and DePaolo, 2006; Fantle and DePaolo, 2007; Fantle et al., 2010; Fantle, 2015). Hence, the spatial extent of diagenetic alteration on Mg and its isotopes in the carbonate are greater than Sr and Ca. Therefore, Mg isotopes have a higher chance in exhibiting diagenetic alterations even in the deeper part of the sedimentary column.

In order to estimate the diagenetic impact in a closed carbonate-rich system the pore fluids and bulk carbonates are analyzed for Ca, Mg and Sr isotopic compositions. The two adjacent Holes 807A and 806B on the Ontong Java Plateau are selected as they exhibit significant variability in pore fluid [Ca$^{2+}$], [Sr$^{2+}$], and [Mg$^{2+}$] despite having a similar depositional history. Therefore, the main focus of this investigation is to find out if the diagenetic recrystallization rates are different in these two adjacent sites and the potential factor causing such difference in diagenesis. The carbonate $\delta^{26}$Mg from both Site 807A and 806B exhibit a sharp decrease by $\sim$ -0.50‰ in upper ~50 mbsf followed by a gentle gradual decrease by $\sim$ -0.80‰. However, the pore fluid $\delta^{26}$Mg shows a sizeable difference between Holes 807A and 806B.

Reactive transport modeling of the pore fluid and bulk carbonate Sr chemistry (Sr/Ca and $^{87}$Sr/$^{86}$Sr) suggested that the recrystallization rates of carbonates older than 1 Ma at Hole 806B is higher (~5%/Ma) that the rates estimated for Hole 807A carbonates (~2%/Ma; Fantle and DePaolo, 2006; Fantle and DePaolo, 2007). Modeling of pore fluid chemistry indicated that the pore fluids at Hole 806B have diffusive communication with the lower boundary. On the contrary, pore fluids at Hole 807A do not interact with the lower boundary, which is likely to be due to the presence of an impermeable chert layer below ~1000 mbsf depth. The continuous
diffusive communication of pore fluids with lower boundary alters the pore fluid chemistry and thus helps to maintain the chemical and isotopic mismatch between the pore fluids and coexisting carbonates. Hence, the extent of diagenetic alteration is greater in the Hole 806B than the adjacent Hole 807A with closed lower boundary. Therefore, this study highlights the influence of lower boundary conditions on calcite recrystallization and indicates that the geochemical proxies would have a better chance of preservation in a site where diffusive interaction between pore fluids and lower boundary is physically interrupted.

Although the modeling could reasonably generate the increasing trends in pore fluid $\delta^{26}$Mg and decreasing trends in bulk carbonate $\delta^{26}$Mg, a -0.2 to -0.3‰ difference below 200-300 mbsf could not be reproduced by the integrated effect of calcite recrystallization and diffusion in the sedimentary column. Due to the evidence of trace amount of clay in the section of the Hole 807A such we hypothesized that the observed difference in pore fluid $\delta^{26}$Mg below ~200 mbsf is a result of diagenetic reactions involving Mg-clay minerals as clay sequester heavier Mg isotopes from the pore fluids. However, as the amount of clay present in the bulk sediment is too little to be analyzed for Mg isotopes, we investigated the effect of clay precipitation on carbonate diagenesis in a separate Hole (ODP 762B) where lithological and mineralogical variation within the carbonate-rich section is pronounced and adequate amount of clay is present in the bulk sediments for isotope analysis.

The $\delta^{26}$Mg of pore fluids and bulk carbonates from Hole 762B exhibit a similar overall down-depth variability as observed in other sites. However, pore fluids from the clay-bearing (smectite and illite) depth interval (120-140 mbsf) display a -0.15‰ shift in the $\delta^{26}$Mg depth profile, i.e. the pore fluid $\delta^{26}$Mg from that depth interval are relatively depleted in heavier Mg isotopes compared to the pore fluids from depths above and below. Analysis of bulk clay fraction from this depth interval reveals that the clays are indeed enriched in heavier Mg isotopes relative to the pore fluids, which validates our hypothesis that the decrease in pore fluid $\delta^{26}$Mg in a certain
depth interval within carbonate-rich sediments can be related to authigenic clay precipitation. Additionally, a combination of the Stella box model and the CrunchTope geochemical model is employed to confirm that the Mg-clay precipitation is a feasible process in a carbonate-rich sedimentary column and only a small amount of clay precipitation is required to simulate the -0.15‰ decrease in pore fluid $\delta^{26}Mg$.

In addition, in the same depth interval, a $\sim$0.6‰ increase in bulk carbonate $\delta^{26}Mg$ is observed along with higher values of Sr/Ca, Na/Ca and Mg/Ca ratios relative to the overlying and underlying carbonates. The Sr/Ca, Na/Ca and Mg/Ca correlate well above and below the clay-bearing interval. However, the lack of correlation between these geochemical parameters within the clay-bearing layer indicates that they are not of diagenetic origin and hence the carbonates within the clay-bearing interval are better preserved than the overlying and underlying layers. The calcite recrystallization rates ($\sim$5%/Ma for sediment $>1$Ma) estimated by the reactive transport model shows that the increase in bulk carbonate $\delta^{26}Mg$ within the clay-rich depth interval (120-140 mbsf) cannot be simulated using the recrystallization model. Therefore, a lesser extent of calcite recrystallization within the clay-rich interval is the cause of the observed increase in carbonate $\delta^{26}Mg$. Such observation suggests that the presence of silicates in a carbonate-rich sedimentary column actually increases the chance of preservation of proxy material resulting higher fidelity in the proxy record. Hence, this study highlights the influence of lithological variability on carbonates diagenesis and evaluates its implication on geochemical proxies.

The final study outlined in the fourth chapter involves quantification of the rates of recrystallization in foraminiferal calcite using a radiotracer ($^{45}$Ca) exchange experiments over the periods of three months. The main motivation of this study is to evaluate the susceptibility of foraminiferal calcite to mineral-fluid exchange over experimental periods. Biogenic calcification incorporates various trace metals in the calcite structure as impurities and the amount of trace metal incorporation often reflects various physico-chemical conditions. As a result, trace metals
and their isotopes in biogenic calcites are widely used as proxies to determine past climatic and oceanographic conditions. However, marine biogenic calcites are known to exchange with the surrounding fluid over many million-year time scale, which can complicate the carbonate-based proxy records. Therefore, it is critical to quantify the exchange rates between the carbonates and coexisting pore fluids and evaluate its implication on the elemental and isotopic chemistry of biogenic carbonates.

In this study, we conducted a series of near-equilibrium batch exchange experiments using $^{45}$Ca tracer with both modern and fossilized foraminiferal tests from marine sediments. Some experiments are conducted in the presence of dissolved silica in the reactor. The modern foraminiferal tests (250-500 µm size) are obtained from the Cariaco basin sediment trap samples collected from ~230 m water depth. The fossilized foraminiferal tests are obtained from 250-500 µm size fractions of deep-sea sediment cores from different depth intervals at Hole 807A. Another set of batch reactors are set up with inorganic calcites. A set of parallel non-tracer batch reactors is monitored for the effect of partial dissolution. Interestingly, all of the reactors with foraminiferal calcites exhibit atom exchange to some degree via incorporation of $^{45}$Ca tracer from the onset of the experiment while the inorganic calcites exhibit almost no exchange. Among biogenic carbonates, modern foraminiferal tests exchange more rapidly than the sediment core samples. Beside, fossilized foraminiferal tests from the deepest sediment cores (200-300 mbsf) show the least amount of exchange compared to tests from the shallower (0-100 mbsf) sediments. The difference in the exchange rates between the modern and fossil foraminiferal calcite suggest that the modern foraminifera are more susceptible to diagenetic exchange compared to partially recrystallized fossil foraminiferal tests. These findings confirm the potential of calcite-fluid exchange to alter the foraminiferal test chemistry even over a short experimental period. Such susceptibility to diagenetic exchange poses the biggest challenge in interpreting foraminiferal proxy records.
The parallel non-radiotracer experiments suggest that partial dissolution and re-precipitation were the key processes responsible for observed atom exchange. However, partial dissolution was the dominating process as strong signal of net increase in [Ca$^{2+}$], [Mg$^{2+}$], and [Sr$^{2+}$] in the solution are observed over three months. Besides, the Mg/Ca and Sr/Ca ratios of the solutions sampled over three months decrease over time. This indicates that at the onset of the experiment the solids in the reactors were preferentially dissolving the parts of the calcite tests with high Mg/Ca and Sr/Ca followed by dissolution of the part that were relatively less enriched in Mg and Sr in the later phase of experiment.

Surprisingly, the experiment with modern foraminiferal tests with Si-spiked equilibration solution exhibits lesser extent of diagenetic exchange relative to the experiments in absence of aqueous Si. Such observation implies that presence of Si decelerates the rate of diagenetic exchange possibly by reducing the availability of reactive surfaces via co-precipitation of polymerized silica onto the calcite surfaces and thus minimizes the impact of recrystallization on geochemical proxies. Hence, the outcome of the experiment also corroborates our inference about the higher preservation of carbonates in the clay-bearing sediments from Hole 762B indicated by the increase in bulk carbonate $\delta^{26}$Mg, Sr/Ca, are Na/Ca ratios.

The rates estimated from the tracer incorporation in the solid imply that the partial dissolution was also accompanied by re-precipitation of calcite. Interestingly, the evidence of any morphological or structural change of the tests related to this exchange are hardly discernible under regular optical microscopy and imaging techniques, unless high resolution ESEM or micro-CT scans are used to image individual tests more rigorously. Thus, the experimental results highlights the significance of early non-structural diagenetic alterations of the foraminiferal tests that are potential to partially overprint the primary chemistry of the tests without any overt changes in the test morphology. Since most of the carbonate-based geochemical proxy records (e.g., $\delta^{26}$Mg, $\delta^{44/40}$Ca, Mg/Ca, and Sr/Ca) are developed from hand picked foraminiferal or
nannofossil tests from the bulk sediments constraining exchange rates involving these finer archives provides valuable insights in evaluating the fidelity of proxy material recovered from geologic records and quantifying the extent to which the diagenetic exchange modifies the proxy data. Besides, in many cases foraminiferal proxy development relies on the core-top calibration techniques that assume foraminiferal tests from core-topes are least altered and can retain their primary signal. In this context, this experimental approach suggests that the foraminiferal tests can get chemically altered via short-term mineral-fluid exchange while settling through the water column or residing on the seafloor. Therefore, short-term exchange has potential to mask their original chemistry and thus can lead to biased proxy interpretation.

Ultimately, the research presented in this dissertation are all inter-related in terms of the general theme, i.e. evaluating the role of diagenesis in altering carbonate-based geochemical proxies, especially the $\delta^{26}$Mg. Marine diagenesis being one of the primary challenges in developing and interpreting the geochemical proxies is always a concern to the geochemists. However, such challenge can be overcome by taking a multi-site and multi-proxy approach. As different elements in carbonates exhibit different degree of sensitivity to diagenetic alteration, comparing multiple proxy records from various sites, especially from bulk sediments can give us valuable insights into the overall diagenetic history of the sediments. Such information is useful in qualitative assessment of the fidelity of finer proxy archives. The Mg isotopes in marine carbonates, when considered with Sr and Ca isotopes from the bulk carbonates can provide valuable insight regarding the deep diagenetic reactions in the sedimentary column and the extent to which such diagenetic reactions can influence the preservation of biogenic carbonates in the section. As in many cases, proxy-based reconstruction require site selection, Mg isotopes, together with Sr and Ca in bulk sediments can be utilized as a tool to identify the sedimentary section potential to generate high-fidelity proxy records. Besides, in the older geologic records
where development of finer proxy (e.g. hand picked foraminifera) archives is not feasible, metal isotopes like Mg in bulk carbonates shows great potential in estimating the effect of diagenesis.

5.1. References


Appendix A

Additional information for Chapter 2

A.1. Model sensitivity

In the simplest version of the model, the role of diffusion on the pore fluid chemistry is tested using a range of diffusion coefficients for Mg (6400 to 8000 m²/Ma). The values of $D_{\text{Mg}}$ are chosen from the calculated values of $D_{\text{Mg}}$ in a sedimentary column with porosity varying from 66% to 56% and temperature ranging from 2°C (at $z = 0$ mbsf) to 18°C (at $z = 273$ mbsf) down-hole (equation 12-14 and Table A.5). Since the isotopic fractionation of Mg during diffusion is negligible (Richter et al., 2006) in this model the $D_{\text{Mg}}$ for all three stable nuclides of Mg are considered to be equal. The diffusion-only models suggests that the elemental and isotopic composition of pore fluids in the sedimentary column of Site 1171 cannot be fully explained by simple diffusive communication of the pore fluids with the bottom boundary (Fig. A.6).

The influence of advection on pore fluid Mg profiles from Site 1171 is also illustrated using a range of advection velocities (80-250 m/Ma) and varying the elemental and isotopic compositions of advecting fluid (Fig. A.7). The model simulations demonstrates that an increase in advection velocity at a constant $D_{\text{Mg}}$ results shortening of the diffusive boundary layer of $[\text{Mg}^{2+}]$ and $\delta^{26}\text{Mg}$ in the pore fluids (Fig. A7a). The model iterations also suggest that apart from the advection velocity, the composition of the advecting fluid has great impact on the shape of the observed profiles of pore fluid Mg at Site 1171 site (Fig. A.7c).

The effects of constant versus variable initial pore fluid $[\text{Mg}^{2+}]$ at a constant advection velocity and $D_{\text{Mg}}$ (Fig. A.7b) as well as at different $D_{\text{Mg}}$ values (Fig. A.7d) are also illustrated using this model. Ultimately, the model simulations suggest that (1) diffusion even with a significant upward advection (250 m/Ma) still cannot fully replicate the observed trends in pore
fluid elemental (e.g., [Mg$^{2+}$]) and isotopic (e.g. $\delta^{26}$Mg) compositions, and (2) the chemistry of the advecting fluid required to generate reasonable fit to the observed pore fluid [Mg$^{2+}$] and $\delta^{26}$Mg profiles is different from the modern seawater composition.

The sensitivity of the pore fluid and carbonate $\delta^{26}$Mg profiles to various reaction rates is tested in this study via iterative model runs using a range of recrystallization rates from 2-7 %/Ma without any advection in the column (Fig. A.8). Comparison between these model results with the outcome of model simulations using advection velocity of 250 m/Ma and the reaction rates of ~7%/Ma (Fig. A9) suggests that higher recrystallization rates in combination with the high advection velocity are required to explain the features in the pore fluid and bulk carbonate Mg profiles. Moreover, application of various lower boundary and advecting fluid compositions in the model simulations illustrated the sensitivity of the pore fluid profiles to these factors (Fig. A10).

The experimentally derived partition coefficient ($K_{\text{calcite}}^{\text{calcite}}$) of Mg during calcite precipitation obtained under temperatures ranging between 10-50 °C and at a pressure below 1 atmosphere varies from 0.012 to 0.040 (Mucci and Morse, 1983; Oomori et al., 1987; Huang and Fairchild, 2001). Unfortunately, none of these experiments were conducted at a temperature lower than 2°C and at a higher pressure (>1 atmosphere), which are comparable to the conditions in the deep marine sediments. However, the laboratory derived $K_{\text{Mg}}$ values are observed to decrease with decreasing temperature (Mucci and Morse, 1983; Oomori et al., 1987; Huang and Fairchild, 2001) suggesting a reference $K_{\text{Mg}}$ value to be much lower than experimentally obtained data for the section at 1171. In this study the model was tested using a range of $K_{\text{Mg}}$ between 1.0 and 2.0 that is equivalent to 0.0012 to 0.0032 ($in K_{\text{Mg}/Ca}^{\text{calcite}}$ scale) to reproduce the observed depth profiles of [Mg$^{2+}$] and $\delta^{26}$Mg of pore fluids and carbonates (Fig. A.11). Although these values are much smaller than the experimentally derived values, they are comparable to the range of $K_{\text{Mg}}$
used to model the Mg profiles in the ODP Hole 807A (Fantle and DePaolo, 2006; Higgins and Schrag, 2012).

The diagenetic fractionation factor ($\alpha^{\text{Diag}}_{s-f}$) is another free parameter to be constrained to model the pore fluid and bulk carbonate $\delta^{26}\text{Mg}$ profiles. The experiments and field observations of abiogenic calcite precipitation suggest a fractionation factor of Mg isotopes between 0.9975 to 0.9982 between the calcite and the parent solution (Galy et al., 2002; Buhl et al., 2007; Kisakurek et al., 2009, Immenhauser et al., 2010), which is similar to the fractionation factor report for the high-Mg calcites, such as read algae and Echinoides (0.9976 – 0.9988), but smaller than the fractionation factors estimated for the low-Mg foraminiferal calcite (0.9950- 0.9961) (Chang et al., 2004; Pogge von Strandmann, 2008; Hippler et al., 2009; Wombacher et al., 2011; Pogge von Strandmann et al., 2014). However, the theoretical calculations using density functional electronic structures have reported an equilibrium fractionation factor of Mg ~0.9950 (Rustad et al., 2010). Based on these pre-existing data a range of fractionation factors between 0.9945 and 0.9960 are chosen to test the sensitivity of the pore fluid and bulk carbonate $\delta^{26}\text{Mg}$ (Fig. A12). The model outcomes justify our estimation of $\alpha^{\text{Diag}}_{s-f}$ to be 0.9955 to reasonably explain the observed Mg data.

In the model, the value of initial pore fluid $\delta^{26}\text{Mg}$ is assumed to be constant and equal to the modern seawater value (-0.84‰). However, the sensitivity of the model output to variable initial pore fluid $\delta^{26}\text{Mg}$ is also tested to justify our preliminary assumption (Fig. A13). The effect of constant versus variable initial bulk carbonate $\delta^{26}\text{Mg}$ is also tested. These model outcomes suggest that although the variability in the initial seawater $\delta^{26}\text{Mg}$ does not get preserved in the pore fluid, the variation in initial bulk carbonate $\delta^{26}\text{Mg}$ can still be partially retained in the observed bulk carbonate $\delta^{26}\text{Mg}$ profile despite of being significantly altered.
### Appendix Tables

**Table A.1.** Trace elemental ratios in the digested bulk carbonates from ODP Site 1171A

<table>
<thead>
<tr>
<th>Sample Core-section interval (cm)</th>
<th>Depth mbsf(^a)</th>
<th>Al/Ca mmole/mole (^b)</th>
<th>Mn/Ca mmol/mol (^b)</th>
<th>Fe/Ca mmol/mol (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Leg 189 Hole 1171A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1H-1W(73-74)</td>
<td>0.735</td>
<td>0.038</td>
<td>0.04</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>1H-3W(73-74)</td>
<td>3.73</td>
<td>0.01</td>
<td>0.07</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>3H-4W(3-4)</td>
<td>21.145</td>
<td>&lt;0.01</td>
<td>0.04</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>4H-4W(3-4)</td>
<td>30.635</td>
<td>&lt;0.01</td>
<td>0.10</td>
<td>0.012</td>
</tr>
<tr>
<td>5H-4W(3-4)</td>
<td>40.135</td>
<td>&lt;0.01</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>6H-4W(3-4)</td>
<td>49.635</td>
<td>&lt;0.01</td>
<td>0.03</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>8H-4W(3-4)</td>
<td>67.275</td>
<td>&lt;0.01</td>
<td>0.04</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>10H-4W(3-4)</td>
<td>87.635</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>11H-4W(3-4)</td>
<td>97.135</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>14X-4W(73-74)</td>
<td>115.53</td>
<td>&lt;0.01</td>
<td>0.10</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

\(^a\) As reported in Exon et al. (2001).
\(^b\) Measured on a Perkin-Elmer Optima 5300 UV ICP-AES (Penn State MIL).

**Table A.2.** Instrument operating condition during Mg and Sr isotope analyses using Neptune Plus MC-ICP-MS (Penn State MIL)

<table>
<thead>
<tr>
<th>Instrument Parameter</th>
<th>Mg isotope analysis</th>
<th>(^{87})Sr/(^{86})Sr isotope analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample introduction</td>
<td>Apex IR, dry plasma</td>
<td>Quartz spray chamber Wet Plasma,</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>100 µl/min desolvating nebulizer</td>
<td>33 µl/min ESI PFA micro-flow nebulizer</td>
</tr>
<tr>
<td>Sample cone</td>
<td>Spectron Jet cone</td>
<td>Spectron regular cone</td>
</tr>
<tr>
<td>Skimmer cone</td>
<td>Spectron H-cone</td>
<td>Spectron H-cone</td>
</tr>
<tr>
<td>RF power</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>Cooling gas (Ar)</td>
<td>15.12</td>
<td>15.12</td>
</tr>
<tr>
<td>Auxiliary gas (Ar)</td>
<td>0.70</td>
<td>0.70</td>
</tr>
<tr>
<td>Sample gas (Ar)</td>
<td>0.850 - 0.870</td>
<td>0.98 – 1.050</td>
</tr>
<tr>
<td>Additional Gas (Ar)</td>
<td>0.15 - 0.09</td>
<td>0.0</td>
</tr>
<tr>
<td>(N_2)</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Mass Resolution</td>
<td>Medium</td>
<td>Low</td>
</tr>
</tbody>
</table>

**Table A.3.** Variables used in mass balance calculation for initial bulk carbonate \(\delta^{26}\)Mg

<table>
<thead>
<tr>
<th></th>
<th>(\delta^{26})Mg(_{DSM3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planktonic foraminiferal (\delta^{26})Mg(_{DSM3})</td>
<td>(-4.7 \pm 0.5 %)</td>
</tr>
<tr>
<td>Planktonic Foraminiferal Mg/Ca ratio</td>
<td>1.5 to 2.0 mmole/mole</td>
</tr>
<tr>
<td>Benthic foraminiferal (\delta^{26})Mg(_{DSM3})</td>
<td>(-2.90 \pm 0.5 %)</td>
</tr>
<tr>
<td>Benthic Mg/Ca ratio</td>
<td>1.5 to 2.0 mmole/mole</td>
</tr>
<tr>
<td>Nannofossil (\delta^{26})Mg(_{DSM3})</td>
<td>(-1.1 \pm 0.3 %)</td>
</tr>
<tr>
<td>Nannofossils Mg/Ca ratio</td>
<td>0.8 \pm 0.5 mmole/mole</td>
</tr>
</tbody>
</table>
Fig. A.1. Age-depth curves of the sediments for (a) 0-35 Ma and (b) 0-35 Ma from Site 1171 constructed from magneto- and biostratigraphic data (Exon et al., 2001; Stickley et al., 2004).

Fig. A.2. The elution curves from (a) and (b) Bio-Rad AG-50W-X8 resin, (c) Eichrom TODGA resin and (d) Eichrom Sr-spec resin.
Fig. A.3. Smear-slide images of the bulk sediments from ODP Site 1171A showing the variability in nannofossil assemblages with depth. Image details: FOV= 100X objective (1.8 mm), scale bar = 10µm
Fig. A.4. Downcore variability of (a) percent abundance of nannofossils and $\delta^{26}\text{Mg}$, (b) percent abundance of nannofossils and depth-detrended $\delta^{26}\text{Mg}$, (c) percent abundance of foraminifera and $\delta^{26}\text{Mg}$, and (d) percent abundance of foraminifera and depth-detrended $\delta^{26}\text{Mg}$ of bulk carbonates from ODP Hole1171A (Exon et al., 2001; Stickley et al., 2004).
Fig. A.5. Histograms showing distribution of $\delta^{26}$Mg for (a) planktonic, (b) benthic foraminifera, and (c) nannofossil tests from culture experiments and natural sediments (d) Sensitivity of the calculated bulk carbonate $\delta^{26}$Mg to different fractions of planktonic foraminifera in total foraminiferal abundance. (e) The range of $\delta^{26}$Mg for planktonic, benthic foraminiferal calcite and nannofossil test observed in culture experiments as well as natural sediments (Galy et al., 2002; Chang et al., 2003; Chang et al., 2004; Ra et al., 2010 (a, b); Wombacher et al., 2011; Pogge von Strandmann, 2008; Pogge von Strandmann et al., 2014)
Fig. A.6. Model results showing the sensitivity of the pore fluid (a) $[\text{Mg}^{2+}]$ and (b) $\delta^{26}\text{Mg}$ to various diffusion coefficients (6400 to 8000) m$^2$/Ma with no advection and recrystallization. The modern seawater composition ($[\text{Mg}^{2+}] = 53.1$ mmole/kg and $\delta^{26}\text{Mg}_{\text{DSM3}} = -0.84$ ‰) is set as upper boundary and the lower boundary (LB) is set at ($[\text{Mg}^{2+}] = 35$ mmole/kg and $\delta^{26}\text{Mg}_{\text{DSM3}} = -0.23$ ‰). The open circles represent the measured values of pore fluid $[\text{Mg}^{2+}]$ and $\delta^{26}\text{Mg}$ and the colored lines are model results.
Fig. A.7. Model results showing sensitivity of pore fluid (i) \([\text{Mg}^{2+}]\) and (ii) \(\delta^{26}\text{Mg}\) to different advection velocities (80-250 m/Ma), chemistry of the advecting fluid and diffusion coefficients \((D_{\text{Mg}} = 6500-8000 \text{ m}^2/\text{Ma})\) with no recrystallization; (a) \(v = 125\) and 80 m/Ma, \(D_{\text{Mg}} = 6500 \text{ m}^2/\text{Ma}\), (b) a range of initial pore fluid \([\text{Mg}^{2+}]\) with \(v = 125\) m/Ma, \(D_{\text{Mg}} = 7600 \text{ m}^2/\text{Ma}\), (c) \([\text{Mg}^{2+}]\) of advecting fluid between 36.7 and 45 mmole/kg with \(v = 250\) m/Ma and \(D_{\text{Mg}} = 7600 \text{ m}^2/\text{Ma}\), and (d) \(v = 125\) m/Ma, \(D_{\text{Mg}} = 6500 - 8000 \text{ m}^2/\text{Ma}\).
Fig. A.8. Model results showing pore fluid profiles of (a) $[\text{Mg}^{2+}]$ and (b) $\delta^{26}\text{Mg}$ and bulk carbonate profiles of (c) Mg concentration and (d) $\delta^{26}\text{Mg}$ using two different reaction rates ($\leq 2.3\%$/Ma and $\leq 7\%$/Ma) with a range of lower boundary $[\text{Mg}^{2+}]$ (36.7 to 40 mmole/kg) and $\delta^{26}\text{Mg}$ (-0.4 and -0.5‰) and advection velocities. The upper boundary is set to the modern seawater ($[\text{Mg}^{2+}] = 53.1$ mmole/kg and $\delta^{26}\text{Mg}_{\text{DSM3}} = -0.84$‰). The open and closed symbols represent measured pore fluids and bulk carbonates, respectively. The grey and colored lines represent initial conditions of and final model results, respectively.
Fig. A.9. The model results showing the effect of different upward advection velocities on the (a) pore fluid $[\text{Mg}^{2+}]$, (b) pore fluid $\delta^{26}\text{Mg}$, (c) bulk carbonate Mg concentration, and (d) bulk carbonate $\delta^{26}\text{Mg}$ using reaction rates $\leq 7\%$/Ma. The modern seawater composition ($[\text{Mg}^{2+}] = 53.1$ mmole/kg and $\delta^{26}\text{Mg}_{\text{DSM3}} = -0.84\%$) is chosen to be the upper boundary condition with the lower boundary (LB) at $[\text{Mg}^{2+}] = 40$ to 43 mmole/kg and $\delta^{26}\text{Mg} = -0.4\%$. The open and closed symbols represent measured data of pore fluids and bulk carbonates, respectively. The grey lines and different colored lines represent initial conditions and final results of the model simulation, respectively.
Fig. A.10. The model results showing the effect of different [Mg$^{2+}$] and $\delta^{26}$Mg of the upward advecting fluid on (a) pore fluid [Mg$^{2+}$], (b) pore fluid $\delta^{26}$Mg, (c) bulk carbonate Mg concentration, and (d) bulk carbonate $\delta^{26}$Mg using reaction rates $\leq 7\%$/Ma. The upper boundary is fixed at the modern seawater composition ([Mg$^{2+}$] = 53.1 mmole/kg and $\delta^{26}$Mg$_{DSM3}$ = -0.84‰). The lower boundary is same as the advection fluid composition. The open and closed symbols represent measured data of pore fluids and bulk carbonates, respectively. The grey and colored lines represent initial conditions and final model results, respectively. The abbreviation “adv” stands for advection.
Fig. A.11. The model results showing the sensitivity of the (a) pore fluid $[\text{Mg}^{2+}]$, (b) pore fluid $\delta^{26}\text{Mg}$, (c) bulk carbonate Mg concentration, and (d) bulk carbonate $\delta^{26}\text{Mg}$ values to a range of partition coefficient ($K_{\text{Mg}}$: 1.0 to 2.0) using reaction rates $\leq 7\%$/Ma. The modern seawater composition ($[\text{Mg}^{2+}] = 53.1$ mmole/kg and $\delta^{26}\text{Mg}_{\text{DSM3}} = -0.84\%$) is chosen to be the upper boundary condition. The open and closed symbols represent measured pore fluids and bulk carbonates, respectively. The grey and colored lines represent initial conditions and final model results, respectively. The abbreviations “LB” and “adv” stand for lower boundary and advection, respectively.
Fig. A.12. The model results showing the effect of a range of diagenetic fractionation factor ($\alpha_{Diag}^D$: 0.9945 to 0.9960) on (a) pore fluid and (b) bulk carbonates $\delta^{26}\text{Mg}$ using a reaction rate of $\leq 7\%$/Ma. The upper boundary is set to the modern seawater composition ([Mg$^{2+}$] = 53.1 mmole/kg and $\delta^{26}\text{Mg}_{DSM3} = -0.84\%$). The open and closed symbols represent measured data of pore fluids and bulk carbonates respectively. The initial conditions and final model results are represented by grey and solid colored lines, respectively. The abbreviations “LB” and “adv” stand for lower boundary and advection, respectively.
Fig. A.13. The model results showing the effect of constant versus variable initial composition of the $\delta^{26}$Mg of (a) pore fluids and (b) bulk carbonates using the reaction rate $\leq 7\%$/Ma and upward advection velocity ($v$) = 250 m/Ma. The upper boundary is set to the modern seawater composition ([Mg$^{2+}$] = 53.1 mmole/kg and $\delta^{26}$Mg$_{DSM3}$ = -0.84‰). The model run # represents three different scenario where (i) both pore fluid and bulk carbonate $\delta^{26}$Mg are constant, (ii) only bulk carbonate $\delta^{26}$Mg is variable and (iii) both pore fluid and bulk carbonate $\delta^{26}$Mg are variable. The open and closed symbols represent measured data of pore fluids and bulk carbonates, respectively. The dotted and solid lines represent initial conditions and final model results, respectively. The abbreviations “LB” and “adv” stand for lower boundary and advection, respectively.
Fig. A.14. The model results showing the effect of reaction rates, advection velocities and lower boundary conditions on $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of (a) pore fluids and (b) bulk carbonates. The depth-detrended values of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are plotted. The open and closed symbols represent measured data of pore fluids and bulk carbonates, respectively. The grey lines and the colored lines represent initial conditions and final model results, respectively. The abbreviations “LB” and “adv” stand for lower boundary and advection, respectively.
Appendix B

Additional information for Chapter 3

Section B.1.1. Digestion of pore fluids and bulk carbonates

The pore fluids samples were processed were filtered using 0.1 µm PVDF syringe filter membrane and processed with an oxidizing mixture of of 25% hydrogen peroxide (H₂O₂) and 6N HNO₃ at 80°C for 40 minutes (3 to 5 times) to remove the organic matter. Digested aliquotes were then dried down and reserved for chemical and isotopic analyses.

Bulk sediments of ~30 mg were gently homogenized using a clean agate mortar and pestle, weighed, and transferred to acid-cleaned pre-weighed polypropylene centrifuge tubes. About ~10 ml of a reducing solution, (25 g of NH₂OH·HCl (hydroxylamine hydrochloride) dissolved into 200 ml of concentrated NH₄OH and 300 ml of deionized water) was then added to each tube gravimetrically and shaken at room temperature for 12 hr in a circular shaker. Later, the sediment-solution slurry was centrifuged at 4500 rpm for 20 minutes to remove the supernatants. The reductive cleaning step was then repeated to ensure removal of any Fe-Mn oxide coatings from the carbonates.

Afterward, the sediment samples were shaken again with 10 ml of 1 N NH₄OH solution for 4 hr at room temperature followed by centrifuging at 4500 rpm for 20 minutes, removing the supernatants. Ultimately, the carbonate fractions were preferentially dissolved using 10 ml of a 0.1 M ammonium acetate-acetic acid buffer (pH ~ 4.7) by shaking for 5 hr. When the carbonate fractions are dissolved the mixture was centrifuged at 4500 rpm for 45 minutes and supernatants were removed and filtered using 0.1 µm PVDF syringe filter membrane. An aliquot of the supernatant was then, weighed, and stored in acid cleaned and pre-weighed teflon vials for later analysis. A Perkin-Elmer Optima 5300 UV ICP-AES was utilized to analyze elemental concentration of the digested samples prior to ion exchange chromatography.
Section B.1.2. Digestion procedure for silicate rocks (Penn State Metal Isotope Laboratory)

After selective digestion of the carbonate fractions, the silicate residue of bulk sediments are weighed in acid clean teflon vials and then heated at 90 °C with 1 ml of concentrated HNO₃ (full strength) and 3 ml of HF (full strength) acids with caps tightly sealed for 24 hours. Later, 1 ml of HClO₄ (full strength) acid is added to the vials and the samples evaporated the HF and HNO₃ at 120 °C. When 1mL left (HClO₄), closed the vials tight and place then back to the hotplate at 150 °C for overnight. After that the vials are cooled down and a mixture of 3mL of HNO₃ (full strength), 1mL of HCl (full strength) and 1mL of HF (full strength) is added to each vial and the vials are kept open until the reaction subsides for ~30 min. Once the reaction stops the vials are tightly capped and placed on the hotplate at 150 °C for 12 hours. After the digestion, the vials are uncapped and the mixture of HCl, HNO₃, and the HF is evaporated at 120 °C followed by drying down the 1 ml of the HClO₄ acid at 150 °C. After complete dry down 2 ml of full strength HNO₃ acid is added to the vials followed by heating the samples in the tightly capped vials at 90 °C for 5 hours. In the following step, 4 ml of deionized MilliQ H₂O is added to each vial and the samples are heated again at 90 °C until the solution gets clear (generally overnight), and then dry down completely. At the final stage, the samples are treated with a few drops of 4M HNO₃ and H₂O₂ 2-3 times to remove the organic matter.

Section B.1.3. Ion Chromatographic Purification of Mg, Ca, and Sr

Aliquots of the digested pore fluids and carbonates were purified for Ca using acid-cleaned Bio-Rad polypropylene columns filled with 1.5 ml Eichrom’s TODGA resin (Horwitz et al., 2005; Pourmand and Dauphas, 2010, Harouaka et al., 2016). Samples containing ~200 ug of Ca in 4N nitric acid were loaded in each column. After rinsing the column with 24 ml of 4N nitric acid followed by 15 ml of 0.25N nitric acid to elute all other elements except Ca, the Ca cuts are
collected in next 15 ml of 0.1N HCl acid. The average yield of the Ca, measured using an ICP-AES, was 98.5± 0.5% which confirms near quantitative purification of Ca.

The quantitative separation of Mg from the digested pore fluids and carbonates was performed using a combination of Bio-Rad’s AG-50W-X8 resin (Wombacher et al., 2009; Wombacher et al., 2011) and Eichrom’s TODGA resin (Horwitz et al., 2005; Pourmand and Dauphas, 2010, Harouaka et al., 2016). For pore fluids, aliquots containing ~20 µg of Mg were loaded to 1.9 ml of Bio-Rad’s AG-50W-X8 resin columns in 0.4 N HCl acid. The Na and K fractions were eluted in first 50 ml of 0.4 N HCl and 4 ml of 1 N HCl followed by the collection of Mg cuts in 15 ml of 1 N HCl. For bulk carbonates, samples containing 1-2 µg of Mg were initially passed through the Bio-Rad polypropylene columns filled with 1.5 ml TODGA resin to collect the Ca-free cuts in 24 ml of 4N HNO₃, which were then dried down, resuspended in 0.1 ml 0.4 N HCl, and loaded onto 1.9 ml AG-50WX-8 columns. Ultimately, the Mg from the bulk carbonate samples were purified using the elution technique illustrated in the Appendix Fig B2. The average yield of Mg separation was 99.5 ± 0.5%. The concentration of Al, Mn, and Fe were found very low in the digested carbonates. Additionally no positive correlation between Mg/Ca and Al/Ca, Fe/Ca or Mn/Ca rules out any influence of silicate-derived Mg in our measured Mg isotopic compositions. The yields were calculated from elemental concentration of Mg in sample load and collected elution cuts measured by an ICP-AES. Use of high purity reagents, milliQ deionized water and thoroughly acid-cleaned containers helped to minimize the procedural blank (<10 ng per ~1-2 µg of Mg). In the procedural blank the Mg concentration was determined from the intensity of the measured ²⁴Mg⁺ ion beam in Neptune Plus ICP-MS using a calibration curve developed from a set of single-element (Mg) ICP standards prepared gravimetrically.

The separation method of Sr from bulk carbonates and pore fluids were developed using the Eichrom’s Sr Spec resin following the technique described by Fantle and DePaolo (2006). Acid cleaned transfer pipettes of 300 – 500 µl column volume and polypropylene frit of 1/16”
thickness were used to make the column. The resin beds of ~ 500 µl volume were prepared by pouring the Sr-Spec resin pre-cleaned with 6N HCl and deionized water to the columns followed by rinsing the resin bed six times alternately with 1 ml of 4N HCl and deionized water and conditioning with 1 ml of 3N HNO₃. The pore fluid and digested carbonate samples were dried down, redissolved using 3N HNO₃ acid and centrifuged. Aliquots of the supernatants containing 1-2 µg of Sr were loaded to each column. The Sr was eluted in milliQ deionized following the column recipe illustrated in the Appendix Fig. B2 with an average yields of 98.3±0.5% and procedural blank of 0.2 to 0.5 ng.

Section.B.1.4. Offline interference and mass bias correction for Sr isotope data

The instrumental mass bias and Kr interference corrections were performed off-line by calculating the fractionation of Kr from its expected values (1.008) using an exponential law:

\[
\frac{I'_X}{I'_X}_{\text{meas}} = \frac{I'_X}{I'_X}_{\text{actual}} \times \left( \frac{m}{m_i} \right)^p
\]  ---- (Eq. B.1)

In this expression, the mass of a specific nuclide is represented by \( i_X \) and \( i'_X \) and \( m \) is the atomic mass of nuclide \( i \). The \(^{84}\text{Kr}\) and \(^{86}\text{Kr}\) ion beam intensities are not resolvable from the \(^{84}\text{Sr}\) and \(^{86}\text{Sr}\) ion beams on the Neptune. Hence the intensities for \(^{84}\text{Kr}\) and \(^{86}\text{Kr}\) were calculated from the measured intensities on mass 84 and 86 using the \( p \)-value derived from the above equation. After correcting for instrumental fractionation, the intensities of \(^{84}\text{Kr}\) and \(^{86}\text{Kr}\) were then subtracted from the measured intensities on mass 84 and 86 to determine the \(^{84}\text{Sr}^+\) and \(^{86}\text{Sr}^+\) intensities. The exponential law used to correct the Sr isotope ratios assumes the \(^{86}\text{Sr}/^{88}\text{Sr}\) of 0.1194 and the derived \( p \)-value is used to correct the mass bias on the \(^{87}\text{Sr}/^{86}\text{Sr}\). The corrections for Kr interference were less than 0.000010 on the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio. Another possible isobaric
interference comes from Rb at mass 87. Hence $^{85}\text{Rb}^+$ was routinely monitored at mass 85 in all runs. As the intensities on mass 85 were always <0.00005 V the $^{87}\text{Rb}^+$ interference at mass 87 was considered to be insignificant in all analyses. Multiple measurements of the standard SRM-987 over two years produce an average $^{87}\text{Sr}/^{86}\text{Sr}$ value of $0.710223 \pm 0.000038$ (2σ) (NIST certified value: 0.71034± 0.00026). Besides, several measurements of Sr purified from seawater samples yield an average $^{87}\text{Sr}/^{86}\text{Sr}$ of $0.709110 \pm 0.000042$ (comparable to the reported modern seawater value: 0.709175± 0.00002) within the analytical uncertainty. In this contribution, the $^{87}\text{Sr}/^{86}\text{Sr}$ values are linearly de-trended with respect to depth to help in comparison for relatively small-scale variability in the depth profile.

Section.B.1.5. Partition coefficient and fractionation factor in calcite recrystallization model

The equilibrium partition coefficient ($K_i$) of the element between the solid and coexisting pore fluids is defined by the following expression where $C_f$ and $C_s$ are the concentrations of that element in the fluid solid:

$$K_i = \frac{C_f}{C_s} \quad \text{----- (Eq.B.2)}$$

The mass dependent isotopic fractionation is defined between two stable nuclides $j$ and $k$ of element $i$ as:

$$\alpha_{\text{diag}} = \frac{K_{ij}}{K_{ik}} \quad \text{----- (Eq.B.3)}$$

Here, the model uses, $K_{M_B}$ which is formulated as described in Fantle et al. (2006):

$$K_{\text{calcite}}^{\text{Mg/Ca}} = \frac{(\text{Mg/Ca})_{\text{calcite}}}{(\text{Mg/Ca})_{\text{fluid}}} = \frac{(m_{\text{Mg}})_{\text{calcite}}}{(m_{\text{Mg}})_{\text{fluid}}} \cdot \frac{(m_{\text{Ca}})_{\text{fluid}}}{(m_{\text{Ca}})_{\text{calcite}}} \quad \text{----- (Eq.B.4)}$$

$$K_{\text{calcite}}^{\text{Mg/Ca}} = \frac{(\text{Mg/Ca})_{\text{calcite}}}{(\text{Mg/Ca})_{\text{fluid}}} = K_{\text{Mg}} \cdot \frac{(m_{\text{Ca}})_{\text{fluid}}}{(m_{\text{Ca}})_{\text{calcite}}} \quad \text{----- (Eq.B.5)}$$

This equation (10) can be rephrased as:
The $m$ and $n$ represent two different depths. The terms $(m_i)_\text{calcite}$ and $(m_i)_\text{fluid}$ stand for the mass of any element $i$ in calcite and pore fluid respectively. The expression $K_{Mg}$ uses the $[Ca^{2+}]$ in pore fluids from various depths and a reference $K_{Mg}^{\text{calcite}}$ (depth-independent value) to calculate the $K_{Mg}$ at each spatial grid point in the model.

In modeling Sr geochemistry, one has to assume a value for the equilibrium Sr partition coefficient ($K_{Sr}$) that is associated with calcite recrystallization. Experimentally derived $K_{Sr}$ values at low temperatures vary between 15 and 50 (Katz et al., 1972; Lorens, 1981). In previous studies of marine carbonates, the $K_{Sr}$ values estimated from the concentrations of Sr in pore fluids and coexisting bulk carbonates at depth below the diffusive boundary layer vary within the range of $\sim 18.5$ to 20.5. At ODP 807A the $K_{Sr}$ value used to model the pore fluid chemistry is $\sim 18.5$, which is estimated assuming that Sr in pore fluids and carbonates have attained equilibrium below the diffusive boundary layer (order 200 m).

However, at Sites 806B and 762B, the pore fluid Sr concentration profiles below the diffusive boundary layer indicate that the equilibrium between the carbonates and pore fluids has not been achieved in the deeper part of the sedimentary columns. Hence, the equilibrium partition coefficient ($K_{Sr}$) cannot be estimated from data at these two sites. We used a $K_{Sr}$ value of 18.5, which is the same as the value used at 807A (Fantle and DePaolo, 2006), at 806B and 762B, assuming that the equilibrium partition coefficient should be similar. This assumption is somewhat justified by the success of similar assumptions at other marine sites (e.g., ODP 1170 and 1171; Fantle, 2015).

The experimentally derived $K_{Mg/Ca}$ for calcite precipitation is in the range of 0.012 to 0.040 (Mucci and Morse, 1983; Oomori et al., 1987; Huang and Fairchild, 2001), equivalent to $\sim 10^{-36}$ in $K_{Mg}$ scale, is much higher that our estimates of $K_{Mg}$ to model the pore fluid Mg data at
As the partition coefficient of Mg in calcite depends on temperature, it is imperative that the $K_{\text{Mg}}$ associated with calcite recrystallization within deep marine sedimentary column (e.g. 2-12°C at 807A) will be much lower than that derived experimentally at $\geq25\degree C$. Additionally, the $K_{\text{Mg}}$ values used to model the effect of carbonate diagenesis on Mg profiles in various marine sedimentary sections are in the range of 0.84 to 2.5 (Fantle and DePaolo, 2006; Higgins and Schrag, 2012; Fantle and Higgins, 2014). These values are more comparable to our estimate of $K_{\text{Mg}}$ for Site 807A and thus justify our choice of $K_{\text{Mg}}$ for site 807A.

The choice of $\alpha_{S-f}^{\text{diag}}$ (0.9947) to generate reasonable fits to pore fluid $\delta^{26}\text{Mg}$ is almost identical to the theoretically calculated equilibrium fractionation factor ($\alpha_{S-f}^{\text{diag}} = 0.9950$; Rustad et al., 2010) and is also consistent with the range of fractionation factors (0.9945 to 0.9963) used to model the effect of diagenesis on Mg isotopes in marine carbonates (Higgins and Schrag, 2012; Fantle and Higgins, 2014).

The tortuosity corrected diffusion coefficient of element $i (D_i)$ is described by:

$$D_{\text{Mg}} = \frac{D_i^o}{\theta^2}$$

--- (Eq.B.7)

The $D_i^o$ is the diffusion coefficient of the element in infinite dilution. The tortuosity is defined by:

$$\theta^2 = 1 - \ln(\phi^2)$$

--- (Eq.B.8)

Temperature correction on diffusion coefficient is applied using the following equation:

$$D^o = M_1 + M_2 \times T$$

--- (Eq.B.9)

Here the coefficients of linear regression for $D_i^o$ of an ionic species against temperature are represented by two constants, $M_1$ and $M_2$ (T,°C; Boudreau, 1997).

**Section.B.1.6. Description of multi-component reactive transport model (CrunchTope)**

CrunchTope (Steefel et al., 2014) is a recently revised version of CrunchFlow, which is a software package for simulating multicomponent reactive transport processes that are applicable
to various problems in the earth and environmental sciences. The governing partial differential
equation used in CrunchFlow for conservation of solute mass combines the solute transport
(diffusion), flow (advection) and multicomponent equilibrium and kinetic reactions in a fluid or
porous medium is:

\[ R_i = \frac{\partial}{\partial t} (\Phi \rho_f M_W C_i) + \nabla \cdot (-D \nabla (\rho_f M_W C_i) + u \rho_f M_W C_i) \]  

(Eq.B.10)

In this equation the total reaction rate of the species ‘i’ in the solution is given by \( R_i \)
(moles per unit volume of rock per time). The reaction rate is a function of \( C_i \), the concentration
of the aqueous species (moles /L). In this expression, \( \rho_f \) is the density of the fluid, \( M_W \) is the
mass fraction of water in the system, \( u \) is the Darcian flow and \( D \) is the combined tensor for
diffusion and dispersion in the system.

The reaction term involves dissolution –precipitation reaction, aqueous reactions and
adsorption. The CrunchTope reads a user-provided input file on startup that provides the
necessary physical and chemical parameters (e.g. pH, temperature, initial concentration of the
primary species, porosity, initial mineral assemblage present in the medium) needed for a run and
it also considers the thermodynamic and kinetic properties of all the aqueous species and mineral
phases involved via EQ3/6 thermodynamic database which makes it useful not only to interpret
the outcome of a certain geochemical reaction but also provides information regarding the
feasibility of that reaction in the provided geochemical condition. Therefore, use of CrunchTope
gives us freedom to involve multiple mineral phases as well as the chemistry of the medium to
model a certain geochemical process in a more realistic way.

The main purpose of utilizing this model in this study is to evaluate the effect of diffusion
and co-precipitation of calcite and clay in a sedimentary column on the pore fluid chemistry. In
this study the CrunchTope simulation is performed for 1D sedimentary column of 170 m
thickness with 1 m grid spacing. The rate law for calcite and clay precipitation for the current
study is chosen to be the TST law, which has a dependence on the saturation state of the fluid with respect to the minerals involved. This rate law is formulated based on the Transition State Theory, which operates under the basic assumption of the miniscule reversibility associated with the dissolution and precipitation rates in a quasi-equilibrium system (Aagaard and Helgeson, 1982; Lasaga, 1984; DePaolo, 2011). The mathematical rate expression is as follows:

\[
R = A_m k_m \exp\left[-\frac{E_a}{RT}\right] \prod a_i^n [1 - \exp(m_2 g^{m_3})]^{m_1} \tag{Eq.B.11}
\]

\[
g = \frac{\Delta G}{RT} = \ln \left[\frac{Q}{K_{eq}}\right] \tag{Eq.B.12}
\]

where \(A_m\) and \(k_m\) stand for surface area of the mineral and intrinsic rate constant \((\text{mol/m}^2/\text{s})\). The activation energy is represented by \(E_a\) \((\text{kcal/mole})\). The term \(Q\) is the ion activity product in the reaction and \(K_{eq}\) is the equilibrium constant. The term \(\prod a_i^n\) stands for the product representing the effect of other ions present in the solution resulting inhibition or catalysis of the reaction raised to the power \(n\). The geochemical conditions used to simulate the models are tabulated in the Appendix (Table B4).

**Section.B.1.7. Box model for calcite recrystallization and clay precipitation**

A simple box model is developed to explore the effect of calcite dissolution-precipitation reaction and simultaneous clay precipitation reaction on the pore fluid chemistry. This model consists of two primary components; 1) a mass model that tracks the effect of calcite dissolution and precipitation and simultaneous clay precipitation on the mass of element in the solution reservoir and 2) an isotope model which is linked to the mass model. Using this model a three-layered sedimentary column is also developed where each layer contains both mass and isotope components and all the layers are connected to each other by diffusive flux.

In the mass model there are three reservoirs, fluid, calcite and clay. To simulate the calcite recrystallization effect, the dissolution flux from calcite to fluid is balanced by the
precipitation flux from the fluid to calcite. In the similar way, the clay reservoir is also connected with the fluid reservoir via dissolution and precipitation flux. There are also diffusion and advection fluxes going in and out of the fluid reservoir to simulate the reactive transport process.

In the isotope model the fluxes connected to each solid (calcite and clay) and fluid reservoir are linked to the mass flux in the mass model and fractionation factors are assigned to each of the fluxes to simulate the effect of isotopic fractionation during clay precipitation and calcite recrystallization.

Box model construct

**Known parameters**

Volume of the total sediment box= \( V_{\text{Tot}} \) [unit: cubic cm]

Porosity (\( \Phi \)) [fraction of total volume of sediment; unit less]

Weight fraction of carbonate in the bulk solid = \( f \) [unit less]

Density of carbonate= \( \rho_{\text{carb}} \) [unit: g/cc]

Density of silicate= \( \rho_{\text{sil}} \) [unit: g/cc]

Density of pore fluid= \( \rho_{\text{pf}} \) [unit: g/cc]

Rate of recrystallization = \( R_r \) [unit: %/Myr]

Rate of calcite dissolution= \( R_{\text{calcite-diss}} = (R_r/100) \times V_{\text{tot}} \times (1 - \frac{\Phi}{100}) \times \rho_{\text{carb}} \times f \)

\( k_1 \) = multiplication factor for rate of calcite precipitation

\( k_2 \) = multiplication factor for rate of clay precipitation

\( k_3 \) = multiplication factor for rate of clay dissolution

\( C_{\text{Mg.pf}} \) = concentration of Mg in pore fluids [unit: mmole/kg]

Partition coefficient of Mg for calcite precipitation = \( K_{\text{Mg.cal}} = \frac{\text{conc in calcite (mmole/kg)}}{\text{conc in pf (mmole/kg)}} \times \frac{C_{\text{Mg.cal}}}{C_{\text{Mg.pf}}} \)
Partition coefficient of Mg for clay precipitation = $K_{Mg,\text{clay}} = \frac{\text{conc in clay (mmole/kg)}}{\text{conc in pf (mmole/kg)}} = \frac{c_{Mg,\text{clay}}}{c_{Mg,\text{pf}}}$

**Derived parameter**

Volume of pore fluid = $V_{pf} = \Phi \times V_{tot}$ [unit: cubic cm]

Weight of bulk solid = $W_{BS}$

Volume of the bulk solid = $V_{BS} = (1 - \Phi) \times V_{tot}$ [unit: cubic cm]

$$= [W_{BS} \times \frac{f}{\rho_{\text{carb}}} + [W_{BS} \times (1-f)/\rho_{\text{sil}}]$$

$$= W_{BS} \times [(\rho_{\text{carb}} + f(\rho_{\text{sil}} - \rho_{\text{carb}})) / (\rho_{\text{sil}} \times \rho_{\text{carb}})]$$

Therefore, $W_{BS} = (V_{BS} \times \rho_{\text{sil}} \times \rho_{\text{carb}}) / ([\rho_{\text{carb}} + f(\rho_{\text{sil}} - \rho_{\text{carb}})]$

Weight of silicate = $W_{sil}$

Volume of silicate = $V_{sil} = W_{sil} / \rho_{sil} = (1-f)W_{BS} = (1-f) \times \rho_{\text{carb}} / (\rho_{\text{carb}} + f(\rho_{\text{sil}} - \rho_{\text{carb}})]$

Weight of carbonate = $W_{calcite} = V_{carb} \times \rho_{\text{carb}}$ [unit: g]

$W_{calcite} = (V_{BS} - V_{sil}) \times \rho_{\text{calcite}} = \rho_{\text{calcite}} \times V_{BS} [1 - (\rho_{calcite} / (\rho_{\text{calcite}} + f(\rho_{\text{sil}} - \rho_{\text{carb}}))]$

$$= \rho_{calcite} *(1 - \Phi) \times V_{tot}*\frac{1 - (\rho_{\text{calcite}} / (\rho_{\text{calcite}} + f(\rho_{\text{sil}} - \rho_{\text{carb}})))]}$$

Rate of dissolution of calcite = $R_{diss,\text{calcite}} = R_r \frac{W_{\text{carb}}}{100}$ [unit: g/Myr] [unit: g/Myr]

Rate of precipitation of calcite = $R_{prep,\text{calcite}} = k1 \times R_{diss,\text{calcite}}$ [unit: g/Myr; $k1$ is a multiplication factor]

Rate of precipitation of clay = $R_{prep,\text{clay}} = k2 \times R_{diss,\text{calcite}}$ [unit: g/Myr; $k2$ is a multiplication factor]

Rate of dissolution of clay = $R_{diss,\text{clay}} = k3 \times R_{prep,\text{clay}}$ [unit: g/Myr; $k3$ is a multiplication factor]

**Mass model**

Mass balance for total Mg in the pore fluid of a certain volume of sediment composed of mostly calcite and very less silicates:

$$\frac{dN_{Mg}^{pf}}{dt} = F_{\text{calcite diss}} + F_{\text{clay diss}} + F_{\text{adv.in}} - F_{\text{adv.out}} - F_{\text{prep.clay}} - F_{\text{prep.clay}} + F_{\text{diff.in}} - F_{\text{diff.out}} \quad \text{---- (Eq.B.13)}$$
All masses are represented in mmole, fluxes are in mmole/Ma unit. The subscripts “diss”, “prep”, “adv”, and “diff” stand for dissolution, precipitation, advection, and diffusion, respectively. The mass fluxes in to the pore fluid reservoir are:

\[ F_{\text{calcite diss}} = R_{\text{diss.calcite}} \times C_{\text{Mg_calcite-diss}} \]

\[ F_{\text{calcite diss}} = k_1 \times R_{\text{prep.calcite}} \times C_{\text{Mg_calcite-diss}} \]

\[ F_{\text{prep.clay}} = R_{\text{prep.clay}} \times C_{\text{Mg.clay}} = k_2 \times R_{\text{diss.calcite}} \]

\[ F_{\text{clay_diss}} = R_{\text{diss.clay}} \times C_{\text{Mg_clay-diss}} = k_3 \times R_{\text{prep.clay}} \]

\[ F_{\text{adv.IN}} = R_{\text{adv.IN}} \times C_{\text{Mg.adv.IN}} \]

\[ F_{\text{adv.OUT}} = R_{\text{adv.OUT}} \times C_{\text{Mg.adv.OUT}} \]

Now, diffusive flux between pore fluid in layer 1 and 2 = \( F_{\text{diff.IN}}(1\rightarrow 2) = D_{\text{Mg}} \times \left( \frac{(N_{26}^{24} - N_{24}^{24})}{dN_{24}^{24}} \right) \)

This flux is multiplied by the mass of pore fluid in each layer to convert into mass flux.

Similarly, the mass balance for the calcite and clay reservoirs are describe by:

\[ \frac{dN_{\text{calcite}}^{Mg}}{dt} = - F_{\text{calcite diss}} + F_{\text{prep.calcite}} \]

\[ \frac{dN_{\text{clay}}^{Mg}}{dt} = - F_{\text{clay_diss}} + F_{\text{prep.clay}} \]

**Isotope model**

Ratio of two nuclides = \( r = \frac{N_{26}^{24}}{N_{24}^{24}} \)

\[ \frac{dr}{dt} = \frac{dN_{26}^{24}}{dN_{24}^{24}} = \frac{N_{26}^{24}}{(N_{24}^{24})^2} \times \frac{dN_{26}^{24}}{dt} - \frac{N_{26}^{24}}{(N_{24}^{24})^2} \times \frac{dN_{24}^{24}}{dt} \]

\[ \frac{dr}{dt} = \frac{1}{N_{24}^{24}} \times \left( \frac{dN_{26}^{24}}{dt} - \frac{N_{26}^{24}}{N_{24}^{24}} \times \frac{dN_{24}^{24}}{dt} \right) \]

\[ \frac{dN_{24}^{24}}{dt} = \frac{dN_{26}^{24}}{dt} \times \frac{N_{26}^{24}}{N_{24}^{24}} \times \frac{dN_{24}^{24}}{dt} \]

\[ \frac{dN_{26}^{24}}{dt} = N_{24}^{24} \times \frac{dr}{dt} + r \times \frac{dN_{24}^{24}}{dt} \]  

\[ \text{----(Eq.B.14)} \]

\[ \text{----(Eq.B.15)} \]
Evolution of the pore fluid reservoir

\[ \frac{dN_{24}^{24}}{dt} = 24F_{\text{calcite diss}} + 24F_{\text{clay diss}} + 24F_{\text{adv IN}} + 24F_{\text{diff IN}} - 24F_{\text{prep calc}} - 24F_{\text{prep clay}} - 24F_{\text{adv OUT}} - 24F_{\text{diff OUT}} \]

-----(Eq.B.16)

\[ \frac{dN_{26}^{26}}{dt} = 26F_{\text{calcite diss}} + 26F_{\text{clay diss}} + 26F_{\text{adv IN}} + 26F_{\text{diff IN}} - 26F_{\text{prep calc}} - 26F_{\text{prep clay}} - 26F_{\text{adv OUT}} - 26F_{\text{diff OUT}} \]

-----(Eq.B.17)

Substituting the values of \( \frac{dN_{26}^{26}}{dt} \) from eq (Eq.B.16) in eq (Eq.B.17):

\[ N_{24}^{24} \star \frac{dr_{pf}}{dt} + r_{pf} \star \frac{dN_{24}^{24}}{dt} = r_{\text{calcite diss}} \star 24F_{\text{calcite diss}} + r_{\text{clay diss}} \star 24F_{\text{calcite diss}} + r_{\text{adv IN}} \star 24F_{\text{adv IN}} + r_{\text{diff IN}} \star 24F_{\text{diff IN}} + r_{\text{prep calc}} \star 24F_{\text{prep calc}} + r_{\text{prep clay}} \star 24F_{\text{prep clay}} - r_{\text{adv OUT}} \star 24F_{\text{adv OUT}} - r_{\text{diff OUT}} \star 24F_{\text{diff OUT}} \]

-----(Eq.B.18)

Considering the dissolution and precipitation processes involving fractionation of Mg isotopes (\( ^{26}\text{Mg} \) and \( ^{24}\text{Mg} \)):

\[ \alpha_{\text{calcite diss}} = \frac{r_{\text{calcite diss}}}{r_{\text{carb}}} \Rightarrow r_{\text{calcite diss}} = \alpha_{\text{calcite diss}} \star r_{\text{carb}} \]

\[ \alpha_{\text{clay diss}} = \frac{r_{\text{clay diss}}}{r_{\text{carb}}} \Rightarrow r_{\text{clay diss}} = \alpha_{\text{clay diss}} \star r_{\text{carb}} \]

\[ \alpha_{\text{prep calcite pf}} = \frac{r_{\text{prep calcite pf}}}{r_{\text{pf}}} \Rightarrow r_{\text{prep calcite}} = \alpha_{\text{prep calcite pf}} \star r_{\text{pf}} \]

\[ \alpha_{\text{prep clay pf}} = \frac{r_{\text{prep clay pf}}}{r_{\text{pf}}} \Rightarrow r_{\text{prep clay}} = \alpha_{\text{prep clay pf}} \star r_{\text{pf}} \]

Evolution of the calcite

Precipitation flux:

\[ F_{\text{prep calcite}} = \frac{1}{N_{\text{carb}}} \star 24F_{\text{prep calcite}} \star (\alpha_{\text{prep calcite pf}} \star r_{\text{pf}} - r_{\text{prep calcite}}) \]

Dissolution flux:

\[ F_{\text{calcite diss}} = \frac{1}{N_{\text{carb}}} \star 24F_{\text{diss}} \star (\alpha_{\text{diss}} - 1) \star r_{\text{carb}} \]

\[ \frac{dr_{\text{carb}}}{dt} = F_{\text{prep calcite}} + F_{\text{calcite diss}} \]
Evolution of the clay

Ratio of nuclides in the bulk of secondary clay $= r_{\text{clay}} = \frac{N_{\text{Clay}}^{26}}{N_{\text{Clay}}^{24}}$

Precipitation flux:

$F_{\text{prep.clay}} = \frac{1}{N_{\text{Clay}}^{24}} \times 24 F_{\text{prep.clay}} (\alpha_{\text{prep.clay-pf}} \times r_{pf} - r_{\text{prep.clay}})$

Dissolution flux:

$F_{\text{clay_diss}} = \frac{1}{N_{\text{Clay}}^{24}} \times 24 F_{\text{diss}} (\alpha_{\text{diss}} - 1) \times r_{\text{clay}}$

$\frac{dr_{\text{carb}}}{dt} = F_{\text{prep.clay}} + F_{\text{clay_diss}}$

Diffusive flux between layer 1 and layer 2:

$F_{\text{diffiso.IN}(1-2)} = (F_{\text{diff}(1-2)} / N_{pf1}^{24}) \times (\alpha_{\text{Diffusion}} \times r_{pf1} \times r_{pf2})$

$F_{\text{diffiso.OUT}(1-2)} = (F_{\text{diff}(1-2)} / N_{pf1}^{24}) \times (\alpha_{\text{Diffusion}} \times r_{pf1})$

Constant terms:

$\alpha_{\text{adv}} = 1$

$\alpha_{\text{calcite_diss}} = 1$

$\alpha_{\text{calcite_ppt}} = 0.9940$

$\alpha_{\text{clay_diss}} = 1$

$\alpha_{\text{clay_ppt}} = 1.0005$

$\alpha_{\text{Diff}} = 1$

Weight % of carbonate = 80%

Initial porosity % = 60

Calcite recrystallization rate = 5%/Ma

$K_{\text{Mg_calcite_ppt}} = 2.5$

Concentration of Mg in clay = 5 wt. %
Appendix Tables

Table B.1. Mg isotopic composition of modern seawater and standards measured in this study

<table>
<thead>
<tr>
<th>Samples /Standards</th>
<th>$\delta^{26}$ Mg$_{DSM3}$ (‰) Measured</th>
<th>2 SD</th>
<th>n</th>
<th>$\delta^{26}$ Mg$_{DSM3}$ (‰) Accepted</th>
</tr>
</thead>
<tbody>
<tr>
<td>FZT Mg-Std</td>
<td>-2.26</td>
<td>0.06</td>
<td>25</td>
<td>-2.28</td>
</tr>
<tr>
<td>Cambridge-1</td>
<td>-2.59</td>
<td>0.07</td>
<td>30</td>
<td>-2.58</td>
</tr>
<tr>
<td>Modern seawater</td>
<td>-0.81</td>
<td>0.05</td>
<td>5</td>
<td>-0.84</td>
</tr>
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</table>

Table B.2. Ca isotopic composition of modern seawater and standards measured in this study

<table>
<thead>
<tr>
<th>Samples /Standards</th>
<th>$\delta^{44/42}$ Ca$_{SRM-915a}$ (‰) Measured</th>
<th>2 SD</th>
<th>n</th>
<th>$\delta^{44/42}$ Ca$_{SRM-915a}$ (‰) Accepted</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRM915b</td>
<td>0.35</td>
<td>0.07</td>
<td>10</td>
<td>0.35 ± 0.06</td>
</tr>
<tr>
<td>SRM3109a</td>
<td>0.36</td>
<td>0.05</td>
<td>5</td>
<td>NA</td>
</tr>
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</table>

Table B.3. Instrument operating condition during Ca and Sr isotope analysis using Thermo Scientific Neptune Plus MC-ICP-MS (MIL Penn State)

<table>
<thead>
<tr>
<th>Instrument Parameter</th>
<th>Ca isotope analysis</th>
<th>$^{87}$Sr/$^{86}$Sr isotope analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample introduction</td>
<td>Aridus II, dry plasma</td>
<td>Quartz spray chamber Wet Plasma,</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>100 µl/min desolvating nebulizer</td>
<td>33 µl/min ESI PFA micro-flow nebulizer</td>
</tr>
<tr>
<td>Sample cone</td>
<td>Spectron Jet cone</td>
<td>Spectron regular cone</td>
</tr>
<tr>
<td>Skimmer cone</td>
<td>Spectron H-cone</td>
<td>Spectron H-cone</td>
</tr>
<tr>
<td>RF power</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>Cooling gas (Ar)</td>
<td>15.12</td>
<td>15.12</td>
</tr>
<tr>
<td>Auxiary gas (Ar)</td>
<td>0.70</td>
<td>0.70</td>
</tr>
<tr>
<td>Sample gas (Ar)</td>
<td>0.850 - 0.870</td>
<td>0.98 – 1.050</td>
</tr>
<tr>
<td>Additional Gas (Ar)</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$N_2$</td>
<td>4.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Mass Resolution</td>
<td>Medium</td>
<td>Low</td>
</tr>
</tbody>
</table>

Table B.4. Geochemical conditions and run parameters for CrunchTope model simulations:

<table>
<thead>
<tr>
<th>Model assumptions</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column height</td>
<td>166 m</td>
</tr>
<tr>
<td>Grid spacing</td>
<td>1 m</td>
</tr>
<tr>
<td>Upper boundary</td>
<td>Dirichlet</td>
</tr>
<tr>
<td>Lower boundary</td>
<td>Flux</td>
</tr>
<tr>
<td>Porosity</td>
<td>50%</td>
</tr>
<tr>
<td>Temperature</td>
<td>4°C at the sediment-water interface and increases</td>
</tr>
<tr>
<td>Model assumptions</td>
<td>Values</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Diffusion coefficients: cm²/sec at 4°C</td>
<td>7.03*10⁻⁶</td>
</tr>
<tr>
<td>Geochemical condition of upper boundary</td>
<td>Similar to modern seawater chemistry</td>
</tr>
<tr>
<td>Geochemical condition of lower boundary</td>
<td>The pore fluid chemistry of 762B near carbonate-silicate transition</td>
</tr>
<tr>
<td></td>
<td>Pore fluid chemistry similar to Site 762B are assigned to each grid point</td>
</tr>
<tr>
<td></td>
<td>Grid point 1-119 and 141-166: sediments are composed of 80-90% Calcite and 5-10% Quartz and K-feldspar, 0-5% Kaolinite.</td>
</tr>
<tr>
<td>Geochemical condition of lower boundary</td>
<td>Grid point 120-140: sediments contain 70% calcite, 10% Quartz, 20% Kaolinite.</td>
</tr>
<tr>
<td></td>
<td>No smectite and illite present in the initial column</td>
</tr>
<tr>
<td>Sediment composition:</td>
<td>TST</td>
</tr>
<tr>
<td>Reaction rate law:</td>
<td>TST</td>
</tr>
</tbody>
</table>

### Appendix Figures

Fig. B.1. Age-depth relationship in ODP Holes (a) 806B and (b) 762B (Haq et al., 1990; Kroenke et al., 1991; Teng, 1992; Delaney and Linn, 1993; Rai et al., 2012).
Fig. B.2. Comparison between three holes (807A, 806B, and 762B) in terms of (a) wt % of CaCO$_3$ of bulk sediments (b) porosity % and pore fluid (c) pH, (d) alkalinity, (e) calcium, (f) magnesium, (g) strontium, (h) sodium, (i) potassium, (j) lithium, (k) SiO$_2$ (aq) (l) sulfate concentrations as a function of depth (Kroenke et al., 1991; Haq et al, 1992; de Carlo, 1992 Delaney and Linn, 1993). The abbreviation “pf” stands for pore fluid.
Fig. B.3. Elution curves from ion-chromatographic separation using (a) and (b) Bio Rad AG-50W-X-8 resin, (c) Eichrom TODGA resin and (d) Eichrom Sr-Spec resin
Fig. B.4. Comparison between the depth-detrended values of $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios of bulk carbonates and pore fluids from (a) ODP Holes 806B and (b) 762B with the depth-detrended profile of global seawater $^{87}\text{Sr} / ^{86}\text{Sr}$ curve (McArthur and Howarth, 2004) as a function of depth.
Fig. B.5. The model fits to the measured data of (a) pore fluid and bulk carbonate $\delta^{44/40}{\text{Ca}}_{\text{SRM-915a}}$ from Hole 806B, (b) pore fluid and bulk carbonate $^{87}{\text{Sr}}/^{86}{\text{Sr}}$ ratios (depth-detrended) and (c) pore fluid $[\text{Sr}^{2+}]$ are presented. All model runs used 7600 m$^2$/Ma as diffusion coefficient ($D_{\text{Sr}}$ and $D_{\text{Ca}}$). The upper boundary of $\delta^{44/40}{\text{Ca}}_{\text{SRM-915a}}$, $^{87}{\text{Sr}}/^{86}{\text{Sr}}$, and $[\text{Sr}^{2+}]$ are fixed to the modern seawater compositions. The open and closed symbols represent measured pore fluids and bulk carbonates, respectively. The dashed and and solid colored lines represent the initial conditions and model results, respectively using a reaction rate of 5%/Ma ($R=0.05e^{-36/6}$).
Fig. B.6. The model fits to the measured data of (a) pore fluid and bulk carbonate $\delta^{44/40}\text{Ca}_{\text{SRM-915a}}$ from Hole 762B, (b) pore fluid and bulk carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (depth-detrended) and (c) pore fluid $[\text{Sr}^{2+}]$ are presented. All model runs used 7600 m$^2$/Ma as diffusion coefficient ($D_{\text{Sr}}$ and $D_{\text{Ca}}$). The upper boundary $\delta^{44/40}\text{Ca}_{\text{SRM-915a}}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $[\text{Sr}^{2+}]$ are fixed to the modern seawater compositions. The open and closed symbols represent measured pore fluids and bulk carbonates, respectively. The black dashed and the solid red lines represent the initial conditions and model curves, respectively using a reaction rate of 5%/Ma ($R = 0.0055 + 0.045e^{-\text{age/2.1}}$).
Appendix C

Additional information for Chapter 4

C.1. Description of a simple box model for equilibrium exchange reaction

A simple box model is developed to estimate the exchange reaction rate involved for each type of sample and reactor. The model primarily built to simulate the dissolution-precipitation process, which is linked to the mass exchange of $^{45}$Ca tracer between the solid and the solution. Therefore, the model has two main components: (1) a mass model and (2) and $^{45}$Ca radiotracer model. Another secondary component is added to the model to link the dissolution-precipitation reaction to the mass exchange of trace metals, specifically Mg and Sr between the solid and the solution.

In the Ca mass model, there are three main reservoirs, the fluid, the exchanged solid and the un-exchanged solid. The initial mass of Ca in the fluid reservoir is linked to the initial mass of Ca in the un-exchanged solid reservoir by the solid to fluid ratio ($\frac{Ca_{solid}}{Ca_{fluid}}$) specified in the model. The dissolution flux ($F_{diss-unexch}$) of Ca between the un-exchanged solid and fluid reservoir is defined by the following equation:

$$F_{diss-unexch} = \frac{\%diss \cdot Ca_{unexch}}{100 \cdot time}$$  ---- (Eq.C.1)

where the % diss is defined by the % rate of dissolution.

The precipitation flux of Ca between the fluid and the exchanged solid reservoir ($F_{ppt-exch}$) is related to the rate of dissolution (% diss) by a constant term k.

Therefore, in case of an equilibrium exchange reaction the precipitation flux is defined by:

$$F_{ppt-exch} = k \cdot F_{diss-unexch} = k \cdot \frac{\%diss \cdot Ca_{unexch}}{100 \cdot time}$$  ---- (Eq.C.2)

The mass model also has two different modes of operation:
1) heterogeneous mode, where the dissolution flux into the fluid only exist between the un-
exchanged solid and the fluid reservoir. No dissolution flux from the exchanged solid reservoir to
the fluid is allowed.

2) homogeneous mode, where the dissolution flux from the exchanged solid reservoir to the fluid
is permissible and that flux is dependent on a certain threshold value of the total mass of Ca in
the exchanged solid reservoir. Therefore, in case steady state scenario, the precipitation flux is
balanced by the combined dissolution fluxes using the equation below:

\[ F_{ppt-exch} = F_{diss-unexch} + F_{diss-exch} \]  \hspace{1cm} (Eq.C.3)

The homogeneous mode of the model allows us to simulate the effect of back reaction,
where the precipitated solid reservoir is re-equilibrating with the fluid and the mass flux from the
exchanged solid reservoir is expressed by the product of total mass of Ca exchanged and the %
exchange (\% exch) of the mass of Ca relative to the initial mass of Ca in the solid (\( C_{a_{exch}} \)):

\[ F_{diss-exch} = \frac{\% exch \cdot C_{a_{exch}}}{100 \cdot \text{time}} \]  \hspace{1cm} (Eq.C.4)

Similar to the mass model, the \(^{45}\)Ca radiotracer model also has all three components and
two modes of operation. The mass fluxes of \(^{45}\)Ca in the tracer model are scaled to the mass fluxes
Ca in the mass model in respective reservoirs by equations below:

\[ F^{45}_{ppt-exch} = \frac{C_{a_{fluid}}^{45}}{C_{a_{fluid}}} \cdot F^{\prime}_{ppt-exch} \]  \hspace{1cm} (Eq.C.5)

\[ F^{45}_{diss-unexch} = \frac{C_{a_{unexch}}^{45}}{C_{a_{unexch}}} \cdot F_{diss-unexch} \]  \hspace{1cm} (Eq.C.6)

\[ F^{45}_{diss-exch} = \frac{C_{a_{exch}}^{45}}{C_{a_{exch}}} \cdot F_{diss-exch} \]  \hspace{1cm} (Eq.C.7)

In the model, all masses are in moles and fluxes are in mole/day unit. The initial value of
\(^{45}\)Ca in the total solid (exchanged + un-exchanged) reservoir is set to be 0. Multiple model
simulations using both homogeneous and heterogeneous reaction mode are performed to estimate
the exchange rate required to reproduce the observed uptake of $^{45}$Ca at a given solid to fluid ratio in the experiments.

Additionally, to investigate the effect of dissolution – reprecipitation on the Mg and Sr concentration of the fluid two parallel tracer models are set up which are similar to the $^{45}$Ca radiotracer model, except the initial mass of Mg and Sr in the solid are calculated from Mg/Ca and Sr/Ca ratios specified to the model and mass of total Ca present in the solid. The initial values of Mg/Ca and Sr/Ca ratios are chosen based on natural variability of Mg/Ca and Sr/Ca ratios in foraminiferal carbonates. Two additional parameters, $K_{Mg}$ and $K_{Sr}$, are used to regulate the amount of Mg and Sr uptake from the solution during precipitation of calcite into the exchanged reservoir.

Another four-box model is also constructed to test the effect of chemical heterogeneity in the initial solid in terms of Mg/Ca ratio and Sr/Ca ratio on the atom exchange process. In this model instead of one un-exchanged solid, two separate un-exchanged solid reservoirs are set up with different initial Mg/Ca and Sr/Ca ratio. Therefore, the steady state scenario will have the precipitation flux balanced by the combined dissolution fluxes from two solid un-exchanged and one solid exchanged reservoir using the equation below:

$$F_{ppt-exch} = F_{diss-unexch-1} + F_{diss-unexch-2} + F_{diss-exch} \quad \text{---- (Eq.C.8)}$$

The radiotracer and trace element components of the second model are adjusted accordingly in the similar manner as the previous model.

**C.2. Model sensitivity to various model assumptions**

At first considering the steady state scenario, where the dissolution flux from the un-exchanged solid reservoirs to the fluid is balance by the precipitation flux from the fluid reservoir to the exchanged solid reservoir we attempt to model the activity of $^{45}$Ca in solid and fluid and $[Ca^{2+}]$, $[Mg^{2+}]$, and $[Sr^{2+}]$ in the fluid. A steady state simulation of this model could only
reproduce similar increase in fluid [Mg$^{2+}$], and [Sr$^{2+}$] in the reactors with an assumption that the Mg and Sr uptake of the exchanged solid during precipitation is significantly smaller than the release of Mg and Sr in the fluid during dissolution of the un-exchanged solids (Appendix. Fig.C.4). The model could not reproduce the observed increase in Ca in the solution.

In order to address the effect of non-steady state mineral fluid exchange induced by chemical heterogeneity in foraminiferal calcite, we apply an imbalance in the flux in and out of the fluid reservoir. The precipitation flux from the fluid to the exchanged solid reservoir is only balance by the back reaction flux from the exchanged solid reservoir and the dissolution flux from high Mg-Sr solid and low-Mg-Sr solid is optimized to simulate the effect of preferential dissolution of Mg and Sr rich solids relative to the low-Mg-Sr solids. The model simulation suggest that the changes in the solution chemistry and concentration of $^{45}$Ca tracer in both exchanged solid and fluid reservoir can be reasonably reproduced with 90% of the dissolution flux from the high-Mg-Sr solids even without any back reaction in first 24 hours. However, the data obtained after 9 days of the experiment required 100% back-reaction and progressively increasing dissolution flux from the low-Mg-Sr solids. This observation indicates that initially the preferential dissolution of high Mg-Sr carbonates resulted the rapid increase in Mg, Ca, and Sr in the solution followed by dissolution flux from both carbonates. Hence the decrease in Mg/Ca and Sr/Ca ratio in the solution over the course of the experiment can be explained by the model.

**Appendix Table**

<table>
<thead>
<tr>
<th>Model parameters</th>
<th>Initial value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles of Ca in solution</td>
<td>$1.07 \times 10^{-7}$</td>
</tr>
<tr>
<td>% High-Mg-calcite</td>
<td>10</td>
</tr>
<tr>
<td>% Low-Mg-calcite</td>
<td>90</td>
</tr>
<tr>
<td>Mg/Ca for High-Mg-Sr-calcite</td>
<td>0.75</td>
</tr>
<tr>
<td>Mg/Ca for Low-Mg-Sr-calcite</td>
<td>0.0005</td>
</tr>
<tr>
<td>Sr/Ca for High-Mg-Sr-calcite</td>
<td>0.0035</td>
</tr>
<tr>
<td>Sr/Ca for Low-Mg-Sr-calcite</td>
<td>0.0015</td>
</tr>
<tr>
<td>Partition coefficient ($K_{Mg}$) for precipitation</td>
<td>0.0005</td>
</tr>
<tr>
<td>Partition coefficient ($K_{Sr}$) for precipitation</td>
<td>0.0005</td>
</tr>
</tbody>
</table>
C.3. Sampling method and analysis using LSC

The solid particles on the filter membrane are then rinsed with 0.5 ml of the respective equilibration solution for three times to ensure complete removal of the \(^{45}\text{Ca}\)-spiked solution from the solid residue. Following the separation of solid and fluid components from the reactor the solid residues are dissolved completely using 0.5 ml of 0.1N HCl. The parallel non-radiotracer experiments are also sampled on the same sampling days as of the radiotracer experiments. However, unlike the radiotracer experiments, the foraminiferal tests from the non-radiotracer reactors are filtered out, rinsed, and reserved for high-resolution imaging.

A 0.5 ml aliquots of both solution and dissolved calcite are added to 10 ml of VWR Ultima Gold scintillation cocktail and kept in a dark place for at least 24 hours before measurement on a liquid scintillation counter (LSC; Beckman Coulter Model LS6500 Liquid Scintillation Counter, Penn State). The activity (in counts per minute) of \(^{45}\text{Ca}\) in each sample vial is measured using the LSC in three windows during the analysis. The total measured activity of \(^{45}\text{Ca}\) in each sample is then calculated by adding up activities registered in all three windows. Three sets of 6-8 standards prepared according to the sample matrix are measured during the each analytical session.

Procedural blanks for each type of sample matrix are prepared during sampling by first passing 0.5 ml of \(^{45}\text{Ca}\)-spiked equilibration solution through the microcentrifuge filter followed by 0.5 ml of equilibrium solution three times and then collecting 0.5 ml 0.1N HCl passed through the same filter. Three separate instrumental blanks are prepared by just adding 0.5 ml of each type of equilibration solutions (not spiked with \(^{45}\text{Ca}\)) and 0.5 ml of 0.1N HCl to scintillation cocktails. The average total counts on instrumental blanks are 54 ± 4 cpm while the average counts on procedural blanks are 300 ± 39 cpm. However, as no significant decrease in the activity of procedural blanks is observed even with a thorough rinsing of solid residues in the filter unit with
an additional ~1 ml of equilibration solutions the sampling method is considered successful in removing any residual $^{45}$Ca-spiked equilibration fluid from the solids.

**C.4. Analysis of elemental concentration using Quadrupole ICP-MS**

The elemental concentration analysis of the fluid samples recovered from each reactor after filtering out the solids is conducted using a Thermo X-Series II Quadrupole ICP-MS. All the fluid samples are dried down and re-suspended to a desired volume using 0.3 N HNO$_3$. A set of 6 single element standards is prepared gravimetrically using the same matrix for each element of interest (e.g., Ca, Mg, Sr, Na, and Si). Another set of 6 multi-element standards is prepared to correct for any isobaric interference on the desired nuclides. The instrumental drift is corrected using the counts on an internal standard ($^{115}$In) introduced simultaneously with the samples. The calibration curves developed from each set of standards are then used to calculate the concentration of Ca, Mg, Sr, and Si in the samples from the drift-corrected counts for respective nuclides.

Surface area estimation of the individual tests are done based on micro-CT scans of foraminiferal tests using a GE Phoenix V|tome|x m instrument. The 3-D images are processed using the Avizo Fire software packages where a smoothening factor of 2 is used to consider most of the variability in surface roughness and pores in the surface area estimation (Appendix C. Fig.C-2). Additionally, a FEI Quanta 200 Environmental SEM and a FEI Nova NanoSEM 630 FESEM are used to obtain high-resolution images of the foraminiferal tests and microstructures.
Appendix Figures

Fig. C.1. ESEM images for the foraminiferal tests. (a) Full surface view and (b) micro-structures and pores of *Orbulina universa* and (c) full surface view of *Globigeninoides ruber* from the Cariaco basin sediment trap before experiment; (d) full surface view and (e) micro-structures and pores and of *Orbulina universa* and (f) full surface view of *Globigeninoides ruber* from the Cariaco basin sediment trap after 97 days of partial dissolution; (g) and (h) full surface view and (i) micro structures showing presence of nanofossils attached onto the surface of fossilized *Orbulina universa* recovered from the sediment cores (0-100) mbsf depth from ODP Hole 807A at Ontong Java Plateau from the reactors sampled at day1 during partial dissolution experiments; (j) and (k) full surface view and (l) micro structures of fossilized *Orbulina universa* recovered from the sediment cores (0-100) mbsf depth from ODP 807A at Ontong Java Plateau from the reactors sampled at the day 32 and the day 97 during partial dissolution experiments, respectively.
Fig. C.2. Micro-CT images for the foraminiferal tests used in partial dissolution experiment: (a) full surface view and (b) inside of *Orbulina universa* tests same as Fig. C-1(a). (c) Surface appearance of *Orbulina universa* tests after applying surface smoothening factor 2 to estimate total surface area of the tests. (d) full surface view and (e) inside of *Orbulina universa* tests (Post experiment, day 97), (f) Surface appearance of *Orbulina universa* tests after applying surface smoothening factor 2 to estimate total surface area of the tests.

Fig. C.3. Model construct to simulate dissolution and precipitation reaction in a close system with heterogeneous Mg and Sr concentration of the initial solid. The subscripts “diss”, “ppt”, and “back-react” stand for dissolution, precipitation and back reaction.
Fig. C.4. Model simulation for (a) mass of $^{45}$Ca tracer in solids and (b) mass of Ca in fluids assuming steady-state vs non-steady state condition. Effect of back reaction on the model simulation for (c) mass of $^{45}$Ca tracer in the solid and (d) mass of Ca in the fluid.
VITA

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Education

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• Paul D. Krynine Award, Department of Geosciences, Penn State University, 2012-2015.
• Hiroshi and Koya Ohmoto Graduate Fellowship, Department of Geosciences, Penn State University, 2012, 2013.
• Charles E. Knopf Sr. Memorial Scholarship, Department of Geosciences, Penn State University, 2011.
• Junior Research Fellowship, Council of Scientific and Industrial Research, India, 2009-2010.

Publications

• [with M. S. Fantle] Quantifying diagenetic alteration of marine carbonate $\delta^{26}$Mg in an open system influenced by advection, (submitted, under review).

