



## Quantifying early marine diagenesis in shallow-water carbonate sediments

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### Abstract

Shallow-water carbonate sediments constitute one of the most abundant and widely used archives of Earth's surface evolution. One of the main limitations of this archive is the susceptibility of the chemistry of carbonate sediments to post-depositional diagenesis. Here, we develop a numerical model of marine carbonate diagenesis that tracks the elemental and isotopic composition of calcium, magnesium, carbon, oxygen, and strontium, during dissolution of primary carbonates and re-precipitation of secondary carbonate minerals. The model is ground-truthed using measurements of geochemical proxies from sites on and adjacent to the Bahamas platform (Higgins et al., 2018) and authigenic carbonates in the organic-rich deep marine Monterey Formation (Blättler et al., 2015). Observations from these disparate sedimentological and diagenetic settings show broad covariation between bulk sediment calcium and magnesium isotopes that can be explained by varying the extent to which sediments undergo diagenesis in seawater-buffered or sediment-buffered conditions. Model results indicate that the covariation between calcium and magnesium isotopes can provide a semi-quantitative estimate of the extent and style (fluid-buffered vs. sediment-buffered) of early marine diagenesis. When applied to geochemical signatures in ancient carbonate rocks, the model can be used to quantify the impact of early marine diagenesis on other geochemical proxies of interest (e.g. carbon and oxygen isotopes). The increasing recognition of early marine diagenesis as an important phenomenon in shallow-water carbonate sediments makes this approach essential for developing accurate records of the chemical and climatic history of Earth from the chemical and isotopic composition of carbonate sediments.

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### 1. INTRODUCTION

Marine carbonate sediments are one of the most important archives of Earth's history because they are abundant, span 3 billion years, and have no significant detrital compo-

nent – generally they are interpreted as being precipitated from cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ , etc.) and carbonate ions ( $\text{CO}_3^{2-}$ ) in equilibrium with contemporaneous seawater. The chemical and isotopic composition of carbonate sediments has been widely used to reconstruct the global carbon and oxygen cycles and the history of Earth's surface environment (Broecker, 1970; Knoll et al., 1986; Hayes and Waldbauer, 2006). However, to develop accurate

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records of Earth's past surface environment, it is essential to recognize that all carbonate sediments have experienced some post-depositional diagenetic alteration of their primary chemistry during the transformation from unlithified sediments into rocks (Bathurst, 1976; Swart and Eberli, 2005; Higgins et al., 2018). These diagenetic reactions can alter and in some cases completely reset the primary major, minor, and trace element chemistry of the sediment (Allan and Matthews, 1982; Banner and Hanson, 1990).

The extent to which carbonate diagenesis alters the chemical and isotopic composition of the sediment depends on four features of the diagenetic environment: (1) the composition of the diagenetic fluid, (2) the reactivity of the carbonate minerals over time, (3) the mechanism of solute transport (e.g. diffusion vs. advection), and (4) pressure and temperature. Previous studies of carbonate diagenesis have focused on two particular diagenetic environments: meteoric and deep-burial. Both of these diagenetic regimes leave visible traces of alteration, such as exposure surfaces that can be easily identified in the field or textural changes that can be observed petrographically (Bathurst, 1976; Allan and Matthews, 1982; Dyer et al., 2015). While these regimes are important, they are not the focus of this study. Rather, we are interested in early marine diagenesis associated with the transformation of metastable carbonate polymorphs such as high-Mg calcite and aragonite to diagenetically stabilized low-Mg calcite and dolomite (Malone et al., 2001; Melim et al., 2002; Higgins et al., 2018). Early marine diagenetic alteration, involving seawater or seawater-derived fluids, is widespread in shallow-water marine carbonate sediments and involves mass fluxes between sediments and local pore-fluids that are capable of significantly altering the chemical and isotopic composition of the primary sediment (Fantle and Higgins, 2014; Higgins et al., 2018).

The sensitivity of elements in carbonate sediment to early marine diagenesis is determined, to a first order, by the abundance of the element in seawater-derived pore-fluids compared to bulk carbonate sediment. Carbon isotope values ( $\delta^{13}\text{C}$ ) are regarded as the most diagenetically robust of the geochemical systems, due to the high concentration of carbon in carbonate sediments relative to most diagenetic pore-fluids (Banner and Hanson, 1990; Derry, 2010). It should be noted that remineralization of organic carbon is an important factor (although not considered explicitly in this paper) that may change the sensitivity of  $\delta^{13}\text{C}$  values to early marine diagenesis by affecting both pore-fluid chemistry and dissolution rates (Patterson and Walter, 1994; Irwin et al., 1977). Other major constituents such as calcium isotopes ( $\delta^{44/40}\text{Ca}$ ) in limestone and both calcium and magnesium isotopes ( $\delta^{26}\text{Mg}$ ) in dolomite are expected to be similarly or somewhat less resistant to diagenesis than carbon as calcium and magnesium are more abundant than carbon in seawater and seawater-derived fluids. On the other hand, the isotopic composition of oxygen ( $\delta^{18}\text{O}$ ), another major constituent in carbonates, is easily reset due to the abundance of oxygen in water ( $\text{H}_2\text{O}$ ).

Solute transport is perhaps the second most important variable in many diagenetic systems as it determines, in part, the extent to which diagenesis is dominated by the

chemistry of the fluid (fluid-buffered) or the chemistry of the sediment (sediment-buffered). Diagenetic systems where diffusion dominates tend to favor sediment-buffered diagenesis, whereas systems with significant advective fluid-flow tend to favor fluid-buffered conditions. Potential sources of fluid flow include tidal pumping, wave action, geothermal convection, evaporative reflux, and mixing with meteoric water (Simms, 1984; Kaufman, 1994; Kohout, 1977; Hughes et al., 2007). Critically, fluid flow in shallow-water carbonate systems can create diagenetic systems that are capable of altering even the most robust primary chemical and/or isotopic signals (e.g.  $\delta^{13}\text{C}$ ,  $\delta^{44/40}\text{Ca}$ , Higgins et al., 2018). Compounding the problem, early marine diagenetic alteration is difficult to identify using either petrographic (Grotzinger and Reed, 1983; Melim et al., 2002) or traditional geochemical indicators (e.g. Mn/Sr; Brand and Veizer, 1980). Generally, this style of diagenesis goes unrecognized and undiscussed in studies of the geochemistry of carbonate sediments in the geologic record.

In this study, we develop a numerical model of mineral dissolution and re-precipitation within the pore space of platform and periplatform carbonates. The model quantifies the resetting of  $\delta^{44/40}\text{Ca}$ ,  $\delta^{26}\text{Mg}$ ,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$  in combination with elemental concentrations of Sr during neomorphism (aragonite-to-calcite), recrystallization (calcite-to-calcite), and dolomitization (calcite-to-dolomite). The model is ground-truthed using published measurements of Bahamian carbonates and authigenic carbonates from the Monterey Formation where the boundary conditions, degree of fluid-rock interaction, and composition of seawater are relatively well known (Supko, 1977; Vahrenkamp et al., 1988; Eberli et al., 1997; Ginsburg, 2001; Swart and Eberli, 2005; Blättler et al., 2015; Higgins et al., 2018). Model results provide quantitative constraints on (1) the composition of the primary mineralogical end-member, (2) the diagenetic end-member, and (3) the composition of the diagenetic fluid. Application of this diagenetic model to ancient carbonate sediments with large datasets of calcium, magnesium, carbon, and oxygen isotopes and major/minor element chemistry will lead to more robust records of secular change for a wide range of carbonate-bound geochemical proxies (e.g.  $\delta^7\text{Li}$ ,  $\delta^{11}\text{B}$ ,  $\delta^{34}\text{S}_{\text{CAS}}$ ,  $\delta^{88/86}\text{Sr}$ ,  $\delta^{238/235}\text{U}$ , I/Ca) and more accurate reconstructions of the history of the global carbon and oxygen cycles.

## 2. METHODS

### 2.1. Model setup

Building on published modeling efforts (Banner and Hanson, 1990; Fantle and Higgins, 2014; Blättler et al., 2015), we construct a numerical model that simulates early marine diagenesis of carbonate sediments by stoichiometrically recrystallizing aragonite to low-Mg calcite (neomorphism) or aragonite/calcite to dolomite (dolomitization) assuming conservation of mass of carbon in the sediment. The model transforms one carbonate mineral into another through dissolution and re-precipitation reactions that exchange mass between the sediment and the pore-fluid.

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