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Calcium isotopic evidence for rapid recrystallization of bulk marine carbonates and implications for geochemical proxies

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Abstract

Strontium and calcium isotopic data for bulk carbonate solids and pore fluids from ODP Sites 1170 and 1171 are presented. The data suggest that bulk carbonate sediments actively exchange with coexisting pore fluids over tens of millions of year time scales. Recrystallization rates constrained by Sr isotopes and Sr elemental data are ~3% per Ma at 1170A and ~7% per Ma at 1171A. The pore fluid chemistries at both sites are affected by advection, which occurs in the downwards direction at 1170 (~−25 m/Ma) and upwards at 1171A (~250 m/Ma). Both the direction and the rate of advection are reflected by the width of the diffusive boundary layer for Sr at both 1170A (~300 m) and 1171A (~50 m), compared to ODP Site 807A (~150 m) where no chemically-detectable advection is occurring. Recrystallization is supported not only by interpretations of pore fluid data, but also by the alteration of the bulk solid. This is especially true at 1171A, where advection drives significant alteration of Sr/Ca, Mg/Ca, and ^{87}Sr/^{86}Sr. Numerical simulations of pore fluid geochemical and isotopic evolution over tens of millions of years, conducted with a depositional, time-dependent reactive transport model, suggest that recrystallization rates in the upper tens of meters of the sedimentary section at both sites are more rapid than suggested by the Sr geochemical data. When the Sr-constrained rates are applied to the pore fluid Ca isotope data, the model does not predict pore fluid δ^{44}Ca within analytical uncertainty. The simulations indicate rates that are initially ~20% to 40% per Ma in young, <1 Ma sediments. The Ca isotope data cannot be explained by either inaccurate diffusion coefficients, inaccurate temporal evolution of pore fluid Ca concentrations, or upwards advection. Ultimately, such high rates in young sediments can impact paleoclimate and paleoenvironmental proxies used by geoscientists to study the past. Diagenetic effects due to rapid recrystallization, demonstrated for the oxygen isotope and Mg/Ca paleotemperature proxies, can alter paleotemperature reconstructions by as much as 4 °C. This suggests a means for affecting not only absolute temperature estimates but also systematic differences between the two paleotemperature tools.

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1. INTRODUCTION

The rates at which proxy materials, such as marine calcite, interact with coexisting pore fluids over million-year time scales is critical to assumptions regarding the fidelity of geochemical proxies. Though in local equilibrium with respect to calcite, marine pore fluids and coexisting solids can, in many cases, be in a state of trace elemental and isotopic disequilibrium, providing leverage to alter proxy archives. This state of disequilibrium is exemplified by the characteristic increase in pore fluid Sr concentrations with increasing depth in carbonate-rich sections, a consequence of the exclusion of Sr from the solid phase during diagenetic recrystallization (e.g., Gieskes, 1975; Baker et al., 1982; Richter and DePaolo, 1988; Richter and Liang, 1993; Fantle and DePaolo, 2006; Fantle et al., 2010).

The extent to which elemental and isotopic leverage is expressed as an actual "diagenetic effect" depends heavily

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on the rate of exchange between solid and fluid. Factors such as the difference in isotopic composition between the solid and fluid (δ_s–δ_f), the diagenetic equilibrium fractionation factor (or elemental partition coefficient) between the solid phase and the fluid (α_{s-f} or Δ_{s-f}, Eq. 1) also play important roles in determining both the leverage to alter and the extent of alteration (Fantle and DePaolo, 2007; Fantle et al., 2010):

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

The rate of exchange not only determines the extent of alteration of the solid but, when considered alongside transport phenomena, also dictates the length scales over which alteration occurs in the sedimentary column. The larger the length scale, the greater the potential for diagenetic alteration. The pore fluid–sediment system can be considered effectively closed over length scales similar to the advective (L_a) or diffusive (L_d) reaction lengths (e.g., Fantle et al., 2010), which assess the relative effects of advection, diffusion, and reaction in a system and, therefore, describe the distance (i.e., depth and, by extension, time) over which the solid and fluid equilibrate. For example, in a monomineralic system in which diffusion and recrystallization are active, the diffusive reaction length can be estimated as $L_d \sim (D/RMK)^{1/2}$, where D is the diffusion coefficient and RMK is a reaction term that takes the partitioning behavior (K) of a given element into account. This formulation indicates that the length scales over which major and trace elements equilibrate in the sedimentary section can be vastly different. By extension, this suggests that (1) diagenetic constraints are not simply shared between major and trace elements, and (2) there is potential to generate discrepancies over various time scales between major and trace element proxies that share a common factor (such as temperature; e.g., δ^{18}O and Mg/Ca). Relatedly advection, whose reactive length scale can be estimated as $L_a \sim v/RMK$, does occur in the marine sedimentary environment and can significantly alter interpretations of reaction rates if not taken into account (Baker et al., 1991; Richter, 1993). Thus, constraining not only reaction rates but also advection velocities is critical to understanding the extent to which diagenesis can alter proxy archives and how these effects might vary from one site at the ocean floor to another.

The objective of research aimed at quantifying reaction rates is to improve both the ability to target those sedimentary sections that are optimal for proxy work and the accuracy of proxy-based reconstructions of the past. From a more general perspective, bulk carbonate recrystallization rates provide critical context for interpreting proxy records that are being generated from increasingly smaller proxy archives (e.g., dissolution and laser ablation/ion microprobe analyses of individual foraminiferal tests). Such context allows for a quantitative consideration of error estimation and even a means of correcting systematic offsets in proxy records, and can help substantiate hypotheses regarding trace elemental and isotopic distributions at small spatial scales. Diagenetic alteration, properly quantified, may help reconcile the disagreement between proxy records and improve the use of complementary proxy records to constrain the past (e.g., application of the Mg/Ca paleotemperature proxy to invert δ^{18}O records for ice volume or source water δ^{18}O).

Reaction rates in carbonate-rich sediments have been quantified in marine sedimentary sections, for instance, through reactive transport modeling of Sr concentrations and Sr isotopic composition (Richter and DePaolo, 1987, 1988; Richter and Liang, 1993; Richter, 1996; Fantle and DePaolo, 2006). Such work has demonstrated that Sr geochemical data are consistent with recrystallization (i.e., dissolution–precipitation) and that the diffusive reaction length, the length scale over which pore fluid Sr effectively averages reaction, is on the order of hundreds of meters. Accordingly, the Sr chemistry of pore fluids is not particularly sensitive to reaction in young sediments deposited in the upper tens of meters of the sedimentary section.

Given that Ca is a major constituent in calcite, the Ca isotopic composition of marine pore fluids should be sensitive to reaction over substantially smaller length scales than Sr in carbonate-rich sections. Recent work, which provided the first estimates of bulk carbonate recrystallization rates in sediments over the first million year or so following deposition, suggests that the diffusive reaction length for Ca is on the order of meters (Fantle and DePaolo, 2007). As a result, the Ca isotopic composition of marine pore fluids should reflect recrystallization over meter to tens of meter length scales and, by inference, sub-million year time scales.

The initial work on pore fluids from ODP Site 807A on the Ontong Java Plateau indicated that recrystallization rates of Pleistocene-age bulk sediments are ten to twenty times faster than previously thought (Fantle and DePaolo, 2007). The implication is that the carbonate mass affected by diagenesis is also considerably greater than previously thought, with as much as 60% of the bulk sediment recrystallized over tens of millions of years. Given the difficulty with accommodating this extent of reaction on surfaces alone, such a finding is significant for geochemical proxy work: it implies considerably more diagenetic alteration than has been considered previously, especially for those elements that are out of trace elemental (Sr, Mg) and isotopic (δ^{18}O, δ^{13}C) equilibrium in the upper tens of meters of the sedimentary column.

The current work extends the observations made at ODP Site 807A to two additional ODP Sites: 1170A and 1171A on the South Tasman Rise. These sites were chosen because they are comparable in many respects to the ideal sites used to reconstruct the past: they are carbonate-rich, relatively continuous, and have no overt, massive dissolution horizons. By contrast to 807A, 1170A and 1171A are thinner sections, and offer a useful comparison in this regard. If one accepts the substitution of space for time, the contemporaneous progression from ~1000 m (807A) to ~500 m (1170A) and ~200 m (1171A) sections could be used to investigate the temporal geochemical evolution of a carbonate-rich column. At each site, Pleistocene carbonates, and associated pore fluids, were sampled and their Sr and Ca isotope geochemistry and elemental (Sr, Mg) compositions analyzed. The collected data were then modeled using a depositional, time dependent reactive transport