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The role of recrystallization in shaping the geochemical signature of dolomite: an experimental study

COLE A. MCCORMICK[1], DALTON HARDISTY[2], CHELSEA L. PEDERSON[3], WATTS L DIETRICH[2], ISAAC BONDZIE-SELBY[3], MOHAMMED HASHIM[4] AND KIMBERLY V. LAU[5]

[1]The University of Manchester
[2]Michigan State University
[3]University of Southern Mississippi
[4]University of Southern California
[5]The Pennsylvania State University

Carbonate minerals that formed in marine settings can incorporate the geochemical composition of seawater from the time at which they precipitated. This is mostly true for aragonite and high-Mg calcite – two polymorphs of $CaCO_3$ that form a significant proportion of modern carbonate sediments – due to their well-constrained partition coefficients and isotopic fractionation factors. However, aragonite and high-Mg calcite are metastable minerals that transform into low-Mg calcite and dolomite [$CaMg(CO_3)_2$], which dominate ancient carbonate rocks. Such diagenetic alterations can also result in geochemical changes. Constraining how dolomitization impacts the geochemistry of carbonate minerals can be challenging because ordered dolomite is notoriously difficult to precipitate in the laboratory at 25°C, and it has yet to be observed to form in nature under near-surface, ambient conditions. Thus, it is often unclear whether the geochemical signature of dolomite reflects the precursor $CaCO_3$, the diagenetic fluid, or an intermediate composition between these endmembers. To address these knowledge gaps, we use high-temperature, replacement dolomitization experiments to evaluate the mechanisms by which Sr and U partition between the $CaCO_3$ reactant, the diagenetic fluid, and the dolomite product. First, we compare their partition coefficients during the dolomitization of aragonite ([Sr] = 8800 ppm; [U] = 2900 ppb) versus the dolomitization of calcite ([Sr] = 250 ppm; [U] = 290 ppb). Next, we assess how different reaction conditions (e.g., temperature and fluid composition) determine the structural parameters and geochemical composition of dolomite. We test the hypothesis that dolomite stoichiometry, cation ordering, and unit cell volume exert a first-order control on the amount of Sr and U that can fit within its crystal structure, which in turn dictates the partitioning coefficient. Our experimental results provide novel insights into the role of diagenesis in shaping the geological record, with future work that will investigate the isotopic fractionation of Sr and U.