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Isotope fractionation during Mg-carbonate mineral phase transformations

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The isotopic compositions of carbonate minerals are routinely used to help reconstruct environmental conditions such as temperature, pH, and primary productivity that occurred in the geologic past. They also allow tracking of reaction processes and element sources in historical and modern environments. To correctly interpret measured isotopic compositions, knowledge of the mechanism of isotopic fractionation and the factors that influence its degree is vital. A number of factors influence isotopic fractionation under isothermal conditions, including the strength of the metal-oxygen bond in the mineral compared to that of the aqueous ion, which can be accompanied by changes in coordination, and the speciation of the aqueous ion in solution. The mineral growth rate, or pathway of mineral formation, for example via direct precipitation versus transformation of a precursor, are also potentially important factors controlling the isotopic composition of the stable phase. In this study, we investigate the isotopic fractionation of Mg and C isotopes in the hydrous Mg-carbonate minerals, nesquehonite [$MgCO_3 \cdot 3H_2O$] and dypingite [$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$] and the factors that control fractionation. These minerals are of interest because they form in ultramafic weathering settings, can be used to sequester CO_2, and have numerous metastable precursor phases that transform at low temperature. The fractionation of both Mg and C isotopes during the transformation of nesquehonite to the thermodynamically more stable phase, dypingite was tracked at 5°C, 25°C, and 35°C in closed-system experiments. Solubility products for both phases were also determined, which were previously unavailable for dypingite. Although the rates of the phase transformation differed between 25°C and 35°C, as shown by X-ray diffraction and electron microscopy, a similar equilibrium distribution of Mg and C isotopomers between dypingite and the fluid is reached at both temperatures. No phase transformation was recorded at 5°C owing to slow reaction kinetics. During the phase transformation, fluids were progressively depleted in ^{13}C relative to solids, resulting in an equilibrium fractionation factor between dypingite and dissolved inorganic carbon (DIC) of $\Delta^{13}C_{dyp-DIC} \approx$ +4.65±0.06‰ at 25°C, and +4.47±0.16‰ at 35°C, similar to that reported by Wilson et al. (2010) [1]. Conversely, δ^{26}Mg of the solids decreased during the mineral phase transformation, with a $\Delta^{26}Mg_{dyp-fluid} \approx$ -0.76±0.07‰ and -0.97±0.18‰ at 25°C and 35°C, respectively. The difference in isotopic composition between $Mg_{(aq)}$ and nesquehonite is small compared to dypingite, with values of $\Delta^{26}Mg_{nsq-fluid} \approx$-0.12±0.07, -0.18±0.05‰ and -0.11±0.08‰ at 5°C, 25°C, and 35°C, respectively. The high proportion of aqueous $MgCO_3$ complexes in solution implied that aqueous speciation must be considered to interpret Mg isotope compositions [2], with fractionation also controlled by Mg-O bond strengths in the solids. These experimental results provide insights to the factors controlling fractionation of Mg and C in different Mg-carbonate minerals, and allow more robust interpretation of isotopic signatures measured in the field.

[1] Wilson et al. (2010) *Environ Sci Technol.* 44, 9522-9529; [2] Schott et al. (2016) *Chem Geol.* 445, 120-134.