Fractionation of oxygen isotopes and trace metals during Ca-Mg carbonate transformation in diagenetic conditions

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Ca-Mg carbonates in geologic archives are commonly used as paleoenvironmental proxies to reconstruct paleoclimatic conditions, through measurement of stable isotope compositions (e.g., δ^{18} O), Mg/Ca ratios, and trace metal compositions (e.g., Li, Sr).¹ Yet, direct precipitation of dolomite $[CaMg(CO_3)_2]$ and magnesite (MgCO₃) is kinetically inhibited at ambient conditions owing to the high energy required to dehydrate $Mg^{2+}_{(aq)}$. As a result, metastable Ca-Mg carbonate phases preferentially form and recrystallize over time to more thermodynamically stable phases.² Post-deposition changes such as introduction of saline fluid and increasing diagenetic temperatures (> 40 °C) can also induce transformation reactions of Ca-Mg carbonates, which can overprint primary trace element or isotopic signatures.³ The objective of this study is to examine time-dependent mineral transformation and recrystallization pathways for Ca, Mg, and Ca-Mg carbonates in saline conditions, between 40 and 80 °C, to determine the effects on trace metal partitioning (Li and Sr) and oxygen isotope fractionation.

Here, we performed batch experiments at 40, 60 and 80 °C by mixing highly concentrated Na₂CO₃, MgSO₄ and CaCl₂ solutions, similar to Kelleher and Redfern⁴. Initial solutions also contained trace concentrations of Li (0.09 mM) and Sr (0.04 mM). Changes in δ^{18} O, major and trace elements in fluids and solids, mineralogy by X-ray diffraction (XRD) and scanning electron microscopy (SEM), and mol% MgCO₃ (X_{Mg}) were monitored throughout each experiment for 104 days. Overall, our work describes the geochemical evolution of Mg- and Ca-Mgcarbonate precipitation and transformation pathways with varying temperature. These results have implications for cycling of Mg in saline environments that may lead to dolomitization over time and fractionation of trace metals and isotopes used as indicators for paleoenvironmental conditions.

[1] Mucci and Morse (1983) *Geochim. Cosmochim. Acta*, **47**, 217–233 [2] Chaka (2018) *ACS Earth Sp. Chem.*, **2**, 210–224. [3] Harrison et al. (2020) *Geochim. Cosmochim. Acta*, **293**, 507–524. [4] Kelleher and Redfern (2002) *Mol. Simul.*, **25**, 557-572.