

Isotopic responses of magnesium to two types of dissolution-reprecipitation processes for the growth of the double-carbonate mineral norsethite

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ABSTRACT

An important mechanism of carbonate mineral growth is dissolution-reprecipitation, including the transformation of amorphous precursor to crystalline carbonates, and coarsening (ripening) of fine carbonate crystals. However, the mechanistic details of cation exchange associated with carbonate mineral growth via a dissolution-reprecipitation process are still not well understood. In this study, we used Mg isotopes to probe the exchange of Mg between aqueous solutions and norsethite [BaMg(CO₃)₂] by systematic synthesis experiments. Norsethite is a model double carbonate, with a general formula of AB(CO₃)₂, where A and B stand for two different divalent ions. Formation of norsethite is comprised of three stages, including: (1) precipitation of barium-magnesium (Ba-Mg) amorphous carbonate; (2) transformation of Ba-Mg amorphous carbonate to nano-crystalline norsethite by fast dissolution-reprecipitation; and (3) coarsening (ripening) of nano-norsethite by slow dissolution-reprecipitation. Magnesium isotopes displayed distinct fractionation behaviors in each of the three stages. The Mg isotope fractionation factors ($\Delta^{26}\text{Mg}_{\text{solid-aq}}$) associated with precipitation of Ba-Mg amorphous carbonate were slightly negative and temperature-dependent, from -0.83‰ at 30 °C to -0.53‰ at 70 °C. During the transformation of Ba-Mg amorphous carbonate to nano-crystalline norsethite, isotopically light Mg isotopes were further enriched in the solid phase, with apparent $\Delta^{26}\text{Mg}_{\text{solid-aq}}$ decreasing to -2.12‰ at 30 °C and -1.56‰ at 70 °C. In the ripening stage, norsethite became isotopically heavier, with $\Delta^{26}\text{Mg}_{\text{solid-aq}}$ increasing up to -1.95‰ at 30 °C and -1.17‰ at 70 °C. The experimental results show that non-equilibrium isotope fractionation occurred during the transformation of amorphous carbonate to nano-crystalline norsethite (i.e., fast dissolution-reprecipitation). By contrast, the subsequent ripening of the norsethite led to the evolution toward isotopic equilibrium of the system by slower exchange with a longer reaction time (i.e., slow dissolution-reprecipitation). Moreover, our first-principles calculation results indicate that the equilibrium isotope fractionation was approached, but not attained, even after 276 days of recrystallization at temperatures below 70 °C. In short, this study has identified two different types of dissolution-reprecipitation process during the carbonate mineral growth and highlights the importance of understanding formation mechanism and post-depositional history of carbonate in interpreting the isotopic data of carbonate minerals.

Keywords: Norsethite, amorphous carbonate, dissolution-reprecipitation, transformation, recrystallization, Mg isotope