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(CO$_3$)$_2$] by systematic synthesis experiments. Norsethite is a model double carbonate, with a general formula of AB(CO$_3$)$_2$, 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 (∆$^{26}$Mgsolid-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 ∆$^{26}$Mgsolid-aq decreasing to –2.12‰ at 30 °C and –1.56‰ at 70 °C. In the ripening stage, norsethite became isotopically heavier, with ∆$^{26}$Mgsolid-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

INTRODUCTION

Carbonates comprise a major component of the ancient sedimentary records (e.g., Morse and Mackenzie 1990) and they are of great importance in geological record, as they document a variety of geological, environmental, and biological processes. Carbonate is a ubiquitous material and plays an essential role in human society, such as construction, agriculture, and mechanical engineering (e.g., Børja and Nilsen 2009; De Muynck et al. 2008; Gu et al. 2008; Jin and Yue 2008; Wang et al. 2021). For a better interpretation of carbonate geochemical records and industrial applications, it is important to understand the mechanism that controls carbonate nucleation and growth.

Carbonates could grow via different mechanisms. Numerous studies have been conducted to study the formation of carbonate minerals, focusing on the classic crystal growth mechanism of ion-by-ion attachment (e.g., Davis et al. 2000; De Yoreo et al. 2013; Hong et al. 2016; Nielsen et al. 2016; Teng et al. 2000). However, the formation of carbonate minerals could proceed via an alternative, yet fundamental pathway, which is the transformation of amorphous carbonate precursor (e.g., Giuffre et al. 2015; Liu and Li 2020; Loste et al. 2003; Mavromatis et al. 2017b; Rodriguez-Blanco et al. 2017), a kind of metastable material with the microscopic structure that lacks long-range order. Carbonate formation via the pathway of transformation of amorphous carbonate is particularly important for biomineralization. Phenomena of amorphous carbonate transformation have been reported in many biologically precipitated carbonates (Gower 2008 and references therein), such as foraminifera (Jacob et al. 2017; Mor Khalifa et al. 2018), coral skeletons (Mass et al. 2017;