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Impact of amorphous precursor phases on magnesium isotope signatures of Mg-calcite

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ABSTRACT

Various marine calcifiers form exoskeletons via an amorphous calcium carbonate (ACC) precursor phase and magnesium plays an important role in the temporary stabilization of this metastable phase. Thus, the use of Mg isotope ratios of marine biogenic carbonates as a proxy to reconstruct past seawater chemistry calls for a detailed understanding of the mechanisms controlling Mg isotope signatures during the formation and transformation of ACC to the final crystalline carbonate mineral. For this purpose we have investigated the Mg isotope fractionation between $(Ca,Mg)CO_3$ solids and aqueous fluids at 25 °C and $pH = 8.3$ during (i) the direct precipitation of crystalline Mg-calcite and (ii) the formation of Mg-rich ACC (Mg-ACC) and its transformation to Mg-calcite. The outcome documents that the small Mg isotope fractionation between Mg-ACC and reactive fluid ($\Delta^{26}Mg_{ACC\text{-}fluid} = -1.0 \pm 0.1$‰) is not preserved during the transformation of the ACCs into Mg-calcite. Following a pronounced isotopic shift accompanying the transformation of Mg-ACC into Mg-calcite, $\Delta^{26}Mg_{calcite\text{-}fluid}$ progressively decreases with reaction progress from ~ -3.0‰ to -3.6‰, reflecting both the approach of isotopic equilibrium and the increase of calcite Mg content (to near 20 mol % Mg). In contrast the crystalline Mg-calcite precipitated directly from the reacting fluid, i.e. lacking a discernable formation of an amorphous precursor, exhibits only small temporal variations in $\Delta^{26}Mg_{calcite\text{-}fluid}$ which overall is affected by the precipitation kinetics. The values found in this study at the onset of Mg-ACC precipitation for Mg isotope fractionation between Mg-ACC and the fluid ($\Delta^{26}Mg_{ACC\text{-}fluid} = -1.0$‰) and between Mg-ACC and $Mg^{2+}(aq)$ ($\Delta^{26}Mg_{ACC\text{-}Mg^{2+}(aq)} = +2.0$‰) are consistent with the formation of a hydrated Ca nanoporous solid accommodating Mg bicarbonate/carbonate species in combination with hydrated magnesium. This material crossed by percolating channels filled with the reacting fluid easily converts to Mg-rich calcite via exchange and/or dissolution/precipitation reactions. The results of this study provide new insights on the acquisition of the Mg chemical and isotopic signatures by the skeletal marine carbonates precipitated in confined media from strongly supersaturated fluids. They also offer new guides for the interpretation of the isotopic signature of these organisms for paleo-environmental reconstructions.

1. Introduction

Magnesium is a major component of seawater and abundant in a large number of continental water bodies. It plays a key role in the precipitation of carbonate minerals in the ocean as well as during diagenetic reactions (Swart, 2015). As a result, much attention has been devoted in the last years to the Mg isotope composition of marine carbonates and their potential for the reconstruction of past seawater chemistry (Higgins and Schrag, 2010) and for providing new insights into the global Mg cycle and the temporal evolution of continental weathering (Higgins and Schrag, 2010; Riechelmann et al., 2012; Pogge von Strandmann et al., 2014; Beinlich et al., 2014; Mavromatis et al., 2014, 2016a).

In order to reconstruct past seawater Mg isotope signatures from carbonate archives, the Mg isotope fractionation between carbonate minerals and fluids and specifically between calcite and seawater must be known. As a result a number of recent studies have been carried out to calibrate the Mg isotope fractionation during calcite precipitation (Immenhauser et al., 2010; Li et al., 2012; Mavromatis et al., 2013). These studies have focused on the inor-

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ganic calcite crystal growth and the quantification of the impact of growth kinetics on Mg partitioning and isotope fractionation between calcite and the fluid. This raises the question, however, whether these inorganic experiments could provide a robust description of the fractionation of Mg isotopes in biogenic carbonates (Hippler et al., 2009). The answer to this question is important because (i) the biomineralization pathways differ between different groups of organisms (Immenhauser et al., 2016) and (ii) marine limestones, whether neritic or pelagic in origin, consist of a complex admixture of biogenic and abiogenic Mg-bearing carbonates (Morse and Mackenzie, 1990).

Mg concentrations in inorganic $CaCO_3$ precipitated in seawater-type fluids do not exceed 1–3 mol % (Politi et al., 2010), whereas Mg content of biogenic marine carbonates can reach up to 30 mol % (Chave, 1954). Furthermore, a large body of recent literature suggests that many groups of organisms apply amorphous precursor strategies in biomineralization (Politi et al., 2004, 2008; Immenhauser et al., 2016 and references therein) and that the confined peculiar fluid chemical environment (including high alkalinity and Mg(aq)/Ca(aq) ratio) controlling the formation and transformation of this precursor seems to be a prerequisite for the formation of Mg-rich calcite ($X_{Mg} > 10$ mol %; Raz et al., 2000; Politi et al., 2010; Purgstaller et al., 2016). In this regard, the formation of a nanoporous calcium-rich framework, accommodating hydrated Ca and Mg with reduced coordination and supporting interconnected/percolating channels containing water and carbonate molecules, likely plays a key role in the transient stabilization of the amorphous structure and its crystallization into a Mg-rich calcite (Addadi et al., 2003; Goodwin et al., 2010; Lin et al., 2015).

The elementary mechanisms that control the formation of Mg-calcites from a metastable ACC are clearly different from the classical ion-by-ion attachment of solutes to advancing steps involved in the inorganic crystal growth of Mg-calcite in slightly supersaturated forming solutions. The ways of acquisition and evolution of Ca and Mg isotopic signatures in calcites formed from an ACC precursor are also expected to be distinctly different from those operating during calcite inorganic crystal growth. To our knowledge, no study until now has monitored the evolution of the Mg isotope composition of the forming fluid and the precipitated solid phases during the formation of Mg-bearing ACCs (Mg-ACC) and their transformation to crystalline Mg-calcite. This is remarkable, as without this information, any attempt to reconstruct past seawater composition from marine biogenic carbonates must remain poorly constrained.

In an effort to characterize Mg isotope fractionation between aqueous solutions and Mg-calcites formed from ACC precursors, as well as during and after the transformation of these amorphous phases to Mg-calcites, we have measured the Mg isotope signatures of Mg-ACC, Mg-calcite, and fluids during the experimental runs performed under controlled pH conditions as reported earlier by Purgstaller et al. (2016). The intention of this study is not to simulate biomineralization in its complex and individual behavior, but to decouple the distinct effects of ACC (trans)formation on Mg isotope fractionation between aqueous Mg and Mg-calcite at well-defined physicochemical experimental conditions.

2. Methods

2.1. Experimental setup and analytical procedures

The experimental setup and the analytical methods have been described in detail in Purgstaller et al. (2016). Briefly, the experiment was hosted in a temperature controlled (25.00 ± 0.03 °C) Easy MaxTM 102 system (Mettler Toledo) within a 150 ml borosilicate glass reactor. Mg-ACC formation was induced by titration of 50 ml of a 0.6 M $(Ca,Mg)Cl_2$ solution via an automatic titrator (702 SM Titrino; Methrom) at a rate of 2 ml/min into 50 ml of a 1 M $NaHCO_3$ solution (stirred at 200 rpm). The pH of the reactive fluid was kept constant at 8.3 ± 0.1 by automatic injection of a 1 M NaOH solution (Schott; TitroLine alpha plus). The temporal evolution of mineral precipitation was monitored by in situ Raman spectroscopy (Raman RXN2^{TM} analyzer, Kaiser Optical Systems). After 60 min of reaction time the reactive solution was transferred into a 150 ml glass bottle and was placed air-tight on a compact shaker (Edmund Bühler GmbH; KS-15) operating at 150 rpm in a temperature controlled room at 25 ± 1 °C. The evolution of the chemical and Mg-isotope composition of the reactive fluids and the precipitated solids were followed via homogeneous sampling of 5 ml that were subtracted from the reactor at 5, 12.5, 25, 60, 180 min and after 1, 3 and 14 days of reaction time. In addition after 1, 9 and 18 min of reaction time, 1 ml aliquots of the experimental solution were sampled and filtered only for solution analyses. The solids were separated by a 0.2 μm cellulose acetate filter using a suction filtration unit and were immediately analyzed using Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR; Perkin Elmer Spektrum 100). Afterwards the solids were dried in a desiccator containing silica gel at room temperature. The mineralogy of the dried precipitates was determined using X-ray diffraction (PANalytical X´Pert PRO). Aqueous Mg and Ca concentrations were measured using an ion chromatography unit (Dionex IC S 3000) and the total alkalinity of the solutions was determined by a Schott TitroLine alpha plus titrator. The Mg contents of the solids (in mol %), calculated based on mass balance calculations (see Purgstaller et al., 2016, for further details) are in excellent agreement with the Mg contents of solid measured by digestion of selected solid samples in 6 % HNO_3.

In total, 4 experiments were carried out in the presence of Mg. The Mg/Ca ratios used in the 0.6 M $(Ca,Mg)Cl_2$ solutions were 1:4, 1:5, 1:6 and 1:8, thus, the experiments are labeled as MgCa4, MgCa5, MgCa6 and MgCa8, similar to Purgstaller et al. (2016). Note here that this ratio does not reflect the composition of reactive fluids and solids after the onset of the runs.

The apparent growth rate (mol/s) of the precipitating solid phase over time for these experimental runs can be estimated by mass balance of Ca and Mg introduced in the reactor by the titration of the inlet $(Ca,Mg)Cl_2$ solution and the actual aqueous Ca and Mg concentrations according to the equation:

$$\mathrm{Rate}_{\mathrm{app}} = \frac{\mathrm{Ca}_{\mathrm{add}} - \mathrm{Ca}_{\mathrm{meas}} + \mathrm{Mg}_{\mathrm{add}} - \mathrm{Mg}_{\mathrm{meas}}}{t} \qquad (1)$$

where the subscripts *add* and *meas* denote the moles of Ca and Mg added and measured respectively in the reactor and t is the elapsed reaction time in seconds from the onset of the experimental run. The temporal evolution of the apparent growth rate is illustrated in Fig. 1.

2.2. Magnesium isotope analyses

Magnesium isotope analyses of reacting solutions and precipitated solids followed the protocol described earlier by Immenhauser et al. (2010) and detailed in Geske et al. (2015). Solid and fluid samples were eluted with 1.25 M HNO_3 through the BioRad ion exchange resin AG50W-X12 (200–400 mesh) for chemical separation of matrix elements (i.e. Na, Ca). The ratios of Mg isotopes in the samples were determined with a Thermo Fisher Scientific Neptune MC-ICP-MS in a 500 ppb Mg 3.5 % HNO_3 solution at the facilities of the Ruhr-University-Bochum (Germany). The Mg concentration of the analyzed sample was kept within ±15% of the standard, which proved to minimize potential isobaric interferences from matrices. A positive effect on signal stability