Calcium and strontium isotope fractionation during precipitation from aqueous solutions as a function of temperature and reaction rate; II. Aragonite

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Abstract

In order to study Strontium (Sr) partitioning and isotope fractionation of Sr and Calcium (Ca) in aragonite we performed precipitation experiments decoupling temperature and precipitation rates (R^*, μmol/m^2 h) in the interval of about 2.3–4.5 μmol/m^2 h. Aragonite is the only pure solid phase precipitated from a stirred solutions exposed to an atmosphere of NH_3 and CO_2 gases throughout the spontaneous decomposition of $(NH_4)_2CO_3$. The order of reaction with respect to Ca ions is one and independent of temperature. However, the order of reaction with respect to the dissolved inorganic carbon (DIC) is temperature dependent and decreases from three via two to one as temperature increases from 12.5 and 25.0 to 37.5 °C, respectively. Strontium distribution coefficient (D_{Sr}) increases with decreasing temperature. However, R^* responds differently depending on the initial Sr/Ca concentration and temperature: at 37.5 °C D_{Sr} increase as a function of increasing R^* but decrease for 12.5 and 25 °C. Not seen at 12.5 and 37.5 °C but at 25 °C the D_{Sr}-R^* gradient is also changing sign depending on the initial Sr/Ca ratio. Magnesium (Mg) adsorption coefficient between aragonite and aqueous solution (D_{Mg}) decreases with temperature but increases with R^* in the range of 2.4–3.8 μmol/m^2 h. Strontium isotope fractionation ($\Delta^{88/86}Sr_{aragonite-aq}$) follows the kinetic type of fractionation and become increasingly negative as a function of R^* for all temperatures. In contrast Ca isotope fractionation ($\Delta^{44/40}Ca_{aragonite-aq}$) shows a different behavior than the Sr isotopes. At low temperatures (12.5 and 25 °C) Ca isotope fractionation ($\Delta^{44/40}Ca_{aragonite-aq}$) becomes positive as a function of R^*. In contrast, at 37.5 °C and as a function of increasing R^* the $\Delta^{44/40}Ca_{aragonite-aq}$ show a Sr type like behavior and becomes increasingly negative. Concerning both the discrepant behavior of D_{Sr} as a function of temperature as well as for the Ca isotope fractionation as a function of temperature we infer that the switch of sign in the trace element partitioning as well as in the direction of the Ca isotope fractionation is probably due to the switch of complexation from a Ca^{2+}-NH_3 complexation at and below 25 °C to an Ca^{2+}-H_2O aquacomplex at 37.5 °C. The D_{Sr}–$\Delta^{88/86}Sr_{calcite-aq}$ correlation for calcite is independent of temperature in contrast to aragonite. We interpreted the strong D_{Sr}-temperature dependency of aragonite, the smaller range of Sr isotope fractionation as well as the shallower $\Delta^{88/86}Sr_{calcite-aq}$–$R^*$ gradients to be a consequence of the increased aragonite solubility and the "Mg blocking effect". In contrast to Sr the Ca isotope fractionation values in calcite and aragonite depend both on the complexation in solution and independent on polymorphism.
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Keywords: Aragonite; Calcite; Strontium; Magnesium; Calcium; Isotopes; Fractionationation; Blocking effect

1. INTRODUCTION

From the three main calcium carbonate ($CaCO_3$) polymorphs, aragonite, calcite and vaterite, aragonite is

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the second most abundant in the marine environment (c.f. Morse and Mackenzie, 1990; Morse et al., 2007) where it is produced either by uni- and multicellular calcifying organisms or by inorganic precipitation processes. Aragonite preferentially incorporates alkaline-earth metals like Sr^{2+} and Ba^{2+} as trace elements of which their concentrations and ratios reflect the chemical conditions in the adjacent water during mineral precipitation (Eisenhauer et al., 2009). Being of particular interest in paleoceanography for the reconstruction of seawater temperatures Sr/Ca ratios usually expressed as the distribution coefficient D_{Sr} ($[Sr/Ca]_{CC}/[Sr/Ca]_{SW}$; CC = Calcium carbonate, SW = Seawater) shows an inverse relationship with temperature during calcification (c.f. Weber, 1973; Smith et al., 1979; De Villiers et al., 1994). In biologically mediated $CaCO_3$ the D_{Sr} values tend to be different from the inorganic thermodynamically expected value, an effect generally known as the "vital effect". The latter effect reflects the physiological control of the calcifying organisms and the species dependent biomineralization pathways for $CaCO_3$ precipitation. The Sr/Ca ratios in coral skeletons are not only dependent on temperature (c.f. Beck et al., 1992) but also on the Sr/Ca ratio in seawater itself which can also be used to reconstruct the composition of paleo-water as well as the diagenetic reactions that involve carbonate sediments (Scherer and Seitz, 1980; Enmar et al., 2000). Many experimental studies have been carried out to examine the kinetics of precipitating aragonite (e.g. c.f. Kinsman and Holland, 1969; Burton and Walter, 1987; Dietzel et al., 2004; Gaetani and Cohen, 2006; Gabitov et al., 2008; Niedermayr et al., 2013; Gabitov, 2013; Kim et al., 2014), however most of these studies focused on the effect of temperature on the Sr/Ca ratio in aragonite in terms of D_{Sr} showing that these values decrease with increasing temperature.

Although it has been discussed that Ca ($\delta^{44/40}Ca$) and Sr ($\delta^{88/86}Sr$) isotopes measured in calcite and aragonite may be used to reconstruct environmental conditions from the adjacent seawater (Gussone et al., 2003; Fantle and Higgins, 2014) research focused mainly on biologically precipitated calcite and aragonite. Only a few studies are available concerning Ca isotope fractionation during inorganic aragonite precipitation (c.f. Gussone et al., 2003). Even more, to our knowledge no study is yet available about Sr isotope fractionation during inorganic aragonite precipitation.

This lack of data and information is the impetus for this study, in which we precipitated aragonite at three different temperatures (12.5, 25.0 and 37.5 ± 0.2 °C) from buffered aqueous ammonium by controlled diffusion of CO_2 (g) and NH_3 (g) with a wide range of R^*. Following this experimental approach we are able to study the dependency of the precipitation from the rate (R^*) and the temperature (T) both probably the two most important parameters influencing $CaCO_3$ precipitation. Note, this study extents and completes a similar study we have performed concerning calcite (AlKhatib and Eisenhauer, 2017). Experimental setup, chemical solutions (except for the Mg concentration) and equations are identical with this earlier companion study.

2. MATERIAL AND METHODS
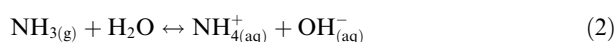
2.1. Materials and experimental setup

Except for the molar Mg/Ca ratio which was set to be 3:1 the solutions as well as the experiments performed to precipitate aragonite is completely based on the earlier set up as described in AlKhatib and Eisenhauer (2017), Fig. 1). The [Mg/Ca] ratio was set to 3.1 because any Mg/Ca above about 2:1 guarantees the precipitation of aragonite instead of calcite. This is for example the case in the ocean where the Mg/Ca ratio shows a molar ratio of 5.2.

In brief two main sets of solutions were prepared to produce aragonite in an ammonium buffered solutions (NH_4/NH_3) at three different temperatures 12.5, 25.0 and 37.5 °C (±0.2 °C). The first set is composed of 0.395 M NH_4Cl, 10.0 mM $CaCl_2$ and 0.10 mM $SrCl_2$. The second solution shows the same composition except for $SrCl_2$ set to be 0.050 mM. In order to verify differences in chemical composition three solutions were prepared differently either containing 15 or 150 mM [Ca], respectively: Solution No. 4 is composed of 0.395 M NH_4Cl, 19.84 mM $CaCl_2$ and 0.11 mM $SrCl_2$, solution No. 7 is composed of 0.395 M NH_4Cl, 149 mM $CaCl_2$ and 0.11 mM $SrCl_2$ and solution No. 8 is composed of 0.395 M NH_4Cl, 148.42 mM $CaCl_2$ and 1.5 mM $SrCl_2$. NH_4Cl is used here to buffer the solution and to adjust the ionic strength of the solutions. All the chemicals are ACS grade of Merck and all solutions were prepared using deionized water (18.2 MΩ).

In this technique 400–550 ml of NH_4Cl-$CaCl_2$-$SrCl_2$-solution and the solid $(NH_4)_2CO_3$ (ammonium carbonate) are contained within a sealed reacting chamber as it is described in AlKhatib and Eisenhauer (2017). In all experiments the reacting solution is stirred with a magnetic stirrer at 300 rounds per minute. Ammonium carbonate decomposes spontaneously and produces an ammonia/carbon dioxide atmosphere within the chamber by the reaction:

$$(NH_4)_2CO_{3(s)} \leftrightarrow 2NH_{3(g)} + CO_{2(g)} + H_2O_{(g)} \qquad (1)$$

Ammonia and carbon dioxide gases diffuse and dissolve in the experimental solution increasing pH and alkalinity by the following reactions

$$NH_{3(g)} + H_2O \leftrightarrow NH_{4(aq)}^+ + OH_{(aq)}^- \qquad (2)$$
$$CO_{2(g)} + H_2O \leftrightarrow CO_{2(aq)} \qquad (3)$$
$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \qquad (4)$$
$$H_2CO_3 \leftrightarrow HCO_{3(aq)}^- + H_{(aq)}^+ \qquad (5)$$
$$HCO_{3(aq)}^- \leftrightarrow CO_{3(aq)}^{2-} + H_{(aq)}^+ \qquad (6)$$

The overall spontaneous reaction of the steps (1)–(6) is:

$$(NH_4)_2CO_3(s) \rightarrow 2NH_4^+(aq) + CO_3^{2-}(aq)$$

The result of these reactions is the supersaturation of the reacting solution with respect to aragonite. The dynamic of the reaction was monitored by a WTW 3100 pH meter which was standardized against a buffer solutions of pH 4, 7 and 10 before each single experiment. This pH meter connected to a computer monitors the pH values and the