Controls of temperature and mineral growth rate on Mg incorporation in aragonite

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Abstract

The incorporation of Mg in aragonite was experimentally investigated as a function of mineral growth rate at 5, 15 and 25 °C using the constant addition technique. Aragonite growth rate was found to be the major parameter affecting the Mg partitioning coefficient

(i.e. $D_{Mg} = \frac{(\frac{Mg}{Ca})_{solid}}{(\frac{Mg}{Ca})_{fluid}}$) between aragonite and fluid, whereas the effect of temperature is

smaller but measurable. At similar surface normalized growth rates, D_{Mg} values decrease as temperature increases from 5 to 25 °C. The magnitude of decrease as a function of temperature is similar for all the experiments of this study where growth rate varied in the range $10^{-8.6} \leq r_p \leq 10^{-7.1}$ (mol/m²/s). The combined effect of aragonite growth rate and temperature on D_{Mg} can be described by the linear equation:

$$\text{Log } D_{Mg} = 0.583(\pm 0.020) \text{ Log } r_p - 0.026(\pm 0.001) T + 0.863(\pm 0.153); R^2 = 0.97$$

where T is the temperature in degrees Celsius.

The increase of D_{Mg} values at decreasing temperatures in experiments conducted at similar growth rates is consistent with the increase of fluid supersaturation with respect to aragonite. Thus, it can be inferred that increased Mg incorporation at higher supersaturation is associated with the greater presence of defect sites on the growing mineral surface, similar to the incorporation of other incompatible ions in carbonate minerals. Overall, the relationship between Mg content of aragonite with the degree of saturation of the fluid with respect to this mineral phase suggests that D_{Mg} values or Mg/Ca ratio in natural aragonites can be used as a proxy for saturation degree of the formation fluid with respect to CaCO₃ minerals.

Keywords: Mg distribution, aragonite, growth rate, temperature effect, defect sites

1. Introduction

The presence of foreign ions in calcite and aragonite of marine and terrestrial origin in the geological record, provides a means for the reconstruction of the environmental conditions that occurred at the time of mineral formation. Owing to its high concentration in oceanic waters and its presence in naturally occurring calcites, the controls Mg exerts on CaCO_3 mineral formation have been extensively studied over the last five decades. For example, it is well-known that during abiotic CaCO_3 mineral formation, the presence of Mg in the aqueous fluid controls the mineralogy of the forming phase (e.g. Plummer and Busenberg, 1982; Morse et al., 1997; Goetschl et al., 2019). Additionally, Mg is incorporated as a trace/impurity in the structure of the forming mineral phase. Actually, the presence of Mg in naturally occurring calcite and aragonite is of great importance for paleo environmental reconstruction studies, because its ratio to other cations in these mineral phases (e.g. Mg/Ca, Mg/Li) has been associated with important environmental parameters such as temperature (e.g. Nürnberg et al., 1996; Raddatz et al., 2013; Montagna et al., 2014; Marchitto et al., 2018). The replacement of Ca for Mg in the calcite structure results in concentrations that vary from a few mmol/mol to several mol%, with concentrations of a few mmol/mol recorded in speleothems forming from a Mg depleted fluid (Huang and Fairchild, 2001) and Mg concentrations exceeding 20 mol% in marine authigenic high Mg-calcite (Mucci and Morse, 1983). In contrast the replacement of Ca for Mg in aragonite structure is less favourable to occur owing to the lack of solid-solution formation in the aragonite-magnesite system. Yet the presence of Mg in natural aragonites provides an intriguing question of the parameters controlling its presence in this mineral phase.

Although aragonite is a major geological archive particularly for marine environments where it occurs as coralline exoskeletons, our understanding of the mechanisms controlling the incorporation of traces/impurities in this mineral phase is rather limited. The earlier work

by Gaetani and Cohen (2006) proposed the use of Mg distribution in aragonite as a temperature proxy tool. These authors, however, did not consider the effect of mineral growth rate which has more recently been shown to affect Mg content in aragonite (Gabitov et al., 2008; 2011). Note here that mineral formation at increasing growth rates leads to deviations from the elemental ratios that would be expected under thermodynamic equilibrium conditions (e.g. Rimstidt et al, 1998). This observation is not only valid for divalent cations (i.e. Me^{2+}) that ideally replace Ca^{2+} in the structure of calcite and aragonite (e.g. Lorens, 1981; Mucci and Morse, 1983; Mucci et al., 1989; Dromgoole and Walter, 1990; Tesoriero and Pankow, 1996; Lakstanov and Stipp, 2007; Mavromatis et al., 2018), but also for incompatible elements such as Li, B or rare earth elements (REE^{3+}) that are not ideally substituting for Ca^{2+} or CO_3^{2-} in the $CaCO_3$ mineral lattice (e.g. Mavromatis et al., 2015; Uchikawa et al., 2015; 2017; Voigt et al., 2017; Fuger et al., 2019). Proper use of traces/impurities in aragonite as proxies for environmental conditions calls for decoupling of the effects of temperature from that of mineral growth rate because both these parameters affect the trace metal concentration in the forming $CaCO_3$ mineral. This prerequisite provides a fundamental step towards understanding the mechanisms controlling the presence of Mg in aragonite and for developing paleo-proxy tools.

The aim of this study is to investigate the effect of mineral growth rate and formation temperature on the incorporation of Mg in aragonite. For this, we used the constant addition technique to grow aragonite on seed material at 5, 15 and 25 °C as a function of mineral growth rate. Our results examine systematically the mechanisms controlling Mg uptake in aragonite and aim to ameliorate interpretation of paleoenvironmental reconstruction studies that commonly use Mg/Ca ratio in aragonite as a proxy tool.

2.Methods

2.1 Precipitation experiments

The incorporation of Mg in aragonite has been studied using the mixed flow reactor experimental setup that has previously been described in Gautier et al. (2014) and Mavromatis et al. (2015). In this study, overgrowth experiments were performed on synthetic aragonite seeds at 5, 15 and 25 °C under continuous bubbling of atmospheric air, using the experimental setup that is illustrated in Fig. 1. Aragonite growth was induced by continuous pumping at similar rates of two separate inlet solutions into the reactor using a peristaltic pump. The pumping rates of the inlet solution in this study varied among runs between 9.2 and 23.1 mL/24h. One inlet solution contained CaCl_2 , MgCl_2 , and LiCl , and the second contained Na_2CO_3 and NaCl . The concentrations of Mg, Li and Na in the inlet solutions were double compared to those present in the reactor in order to avoid changes in concentrations of the reactive fluid due to dilution. In all experimental runs, the background electrolyte concentration was kept the same at ~10 mM LiCl , ~25 mM MgCl_2 and ~270 mM NaCl . The concentrations of CaCl_2 and Na_2CO_3 in the inlet solutions varied between 40 and 240 mM and in combination with variation in the pumping rates and the amount of the seed material, experimental work could be conducted over a wide range of aragonite growth rate. All reacting solutions were prepared using analytical grade chemicals and high purity deionized water (Millipore Integral 3: $18.2 \text{ M}\Omega \text{ cm}^{-1}$). The reactor was placed into a temperature cabinet prior to the runs to equilibrate at the experiment temperature. In the temperature cabinets the temperature of the experimental solutions remained constant throughout the experimental runs. Shortly before the onset of each run a known amount of aragonite seeds was added to the reactor. The pH of the reactive fluid (i.e. $8.1 \leq \text{pH} \leq 8.4$) was controlled by the continuous bubbling of atmospheric air through the reactive fluid. In order to minimize evaporation during the experimental runs, air was bubbled in a 300 mM NaCl solution prior to its introduction into the reactors. Each reactor contained 500 mL of solution and was

equipped with a Teflon floating stir bar rotating at 240 rpm. During the course of a run, introduction of inlet solutions induced an increase of the volume of the reactive fluid. Thus, every 12 or 24 h, a volume of reactive fluid, equal to the sum of the volumes of the inlet solutions added in the previous 12 or 24 h respectively, by the peristaltic pump, was sampled from the reactor so that the variations of the volume of the reactive fluid would remain roughly constant to within ± 4 %. In order to reduce aragonite removal from the reactor during sampling and to keep the solid/fluid ratio quasi constant during the course of an experiment, stirring was stopped shortly prior to sampling to allow the aragonite to settle. Immediately after sampling, the fluid was filtered through a 0.2 μm VWR cellulose acetate membrane filter and a sub-sample was acidified for cation concentration analyses. Reactive fluid carbonate alkalinity was determined in a second sub-sample, whereas the fluid pH was measured in-situ. At the end of the experimental run, the entire reactive fluid was vacuum filtered through a 0.2 μm membrane filter (Sartorius, cellulose acetate). The solids were rinsed with deionized water and dried at 40 °C.

2.2 Chemical and mineralogical analyses

Sodium elemental concentrations of the inlet solutions and the reactive fluids were measured using a Perkin Elmer Optima 8300 DV inductively coupled plasma optical emission spectrometer (ICP-OES) with an analytical precision of $<\pm 3$ % (RSD), whereas Ca and Mg concentrations were determined by Inductively Coupled Plasma Mass Spectrometer (ICP-MS; Agilent 7500CX) with an analytical precision better than 2 % (RSD). The alkalinity of fluid samples was measured by standard HCl titration using an automatic Schott TitroLine alpha plus titrator with an uncertainty of ± 2 %. The pH was measured using a SenTix[®] 945 pH gel electrode from WTW, calibrated against NIST standard buffers. Aqueous speciation, ion activities and saturation states of the reactive fluids with respect to

aragonite (i.e. $\Omega_{\text{aragonite}}$) were calculated using PHREEQC software together with its MINTEQ.V4 database (Parkhurst and Appelo, 2013) after the addition of the solubility products of magnesite (Benezeth et al., 2011), hydromagnesite (Gautier et al., 2014) and nesquehonite (Harrison et al., 2019).

The mineralogy of seed material and collected solids was defined using X-ray powder diffraction (XRD) patterns that were recorded using a PANalytical X'Pert PRO diffractometer and Co-K α -radiation (40 mA, 40 kV) in the 2θ range from 15° to 60° and with scan speed of 0.03° s⁻¹. The qualitative characterization of crystalline products conducted using the PANalytical HighScore Plus software together with the ICSD database (aragonite: de Villiers, 1971; calcite: Markgraf and Reeder, 1985) and the mineral phases were quantified by Rietveld refinement. Analytical uncertainty of this quantification was better than 1 wt.%. The precipitates were gold-coated and imaged using a ZEISS DSM 982 Gemini scanning electron microscope (SEM) equipped with a field emission gun operating at 5 kV accelerating voltage. The specific surface area of selected solids was measured with 11-point Kr isotherm using a Micromeritics TristarII plus surface area analyzer (Brunauer et al., 1938). The Ca and Mg concentrations of the solids were determined using an Agilent 7500CX ICP-MS with an analytical precision better than 2% (RSD). Instrumental drift was corrected by using a mixture of Sc, Se, and Ge internal standard normalization, while the accuracy of the measurements was ensured by repeated measurement of SPS-SW1 reference material, XXI multi-element standard solution (Merck) and of an in-house artificial solution. For the analysis ~80 mg of solid sample was digested in concentrated bi-distilled HNO₃. The digestions were performed in duplicates to avoid potential heterogeneity of the powder and thus ensure the repeatability of the measurements.

2.3 Seed material

The aragonite seeds used in this study were synthesized prior to the experimental work. The majority of aragonite synthesis protocols use Mg as background electrolyte owing to the fact that this element inhibits calcite nucleation or growth (e.g., Bischoff, 1968; Zhang and Dawe, 2000). In order to reduce the presence of Mg in the synthesized aragonite, in the protocol developed in this study, aragonite seeds were synthesized in the absence of Mg. During synthesis, ~130 mL of a 1.52 M CaCl_2 solution were titrated into a borosilicate reactor containing 1.5 L of a 0.066 M Na_2CO_3 solution, with the aid of a peristaltic pump operating at a flow rate of 0.6 mL/min. The temperature of the reactive solution was kept constant at 80 ± 2 °C using a heating mantle system (series WMOTM, Mohr & Co) and it was continuously stirred at 300 rpm. The solution was filtered using a 0.2 μm cellulose acetate filter to recover the precipitates. After filtration, solids were rinsed three times with 200 mL of deionized water to remove NaCl residue and then dried at 80 °C for at least 24 h. The synthesized solid was aragonite with traces of calcite (<2 wt.%) as determined by X-ray diffraction analysis. Scanning Electron Microscopy (SEM) images of the synthetic aragonite seeds revealed needle shaped aragonite crystals of 20-100 μm in length and 2-10 μm diameter (Fig. 2A). The specific surface area of the seed material was 0.38 m²/g, whereas wet chemical analyses revealed that the seed contained ~0.5 $\mu\text{mol/g}$ (i.e. ~13 ppm) Mg. The source of Mg can be assigned to impurities in the CaCl_2 salts used during synthesis.

3. Results

3.1 Mineralogy and chemical composition of the precipitated solids

The XRD patterns of all the solid samples in this study are indicative of aragonite with trace amounts of calcite. Note here that the proportion of calcite in the bulk solids was lower than that measured in the seed material (i.e. < 2 wt. %) consistent with overgrowth of only aragonite in the experimental runs. X-ray diffraction patterns of selected samples can be

seen in Fig. S1 of the Electronic Supplement. The synthesized aragonite seeds exhibit needle-like structure typical of this mineral phase (Fig. 2A). The solid materials recovered from the reactors at the end of each run exhibit surface features indicative of mineral overgrowth on seed material. As it can be seen in Figs. 2B-2F, the aragonite precipitates exhibit surface features typical for mineral overgrowth, including surface roughness, presence of steps and surface porosity and are noticeably different in surface morphology than the seed material displayed in Fig. 2A which appears to have a smooth surface. Note here that in experiments conducted at 5 °C SEM microphotographs depict aggregates of a few 10s of nm in size present on the precipitates (e.g. Fig. 2E and 2F). The presence of these features is not associated with aragonite growth rate as can be deduced from a comparison of Fig. 2E and 2F displaying experiments LiAr-23 ($r_p=10^{-7.6}$ mol/m²/s) and LiAr-28 ($r_p=10^{-7.2}$ mol/m²/s), respectively. Note here that such features were not observed in experiments conducted at 15 and 25 °C at similar growth rates. Moreover, their presence did not increase the reactive surface area of the precipitate. In fact, as can be seen in Table S1 of the Electronic Supplement, the reactive surface for samples LiAr-23 (Fig. 2E) and LiAr-28 (Fig. 2F) are 0.41 and 0.34 m²/g, respectively, and within error identical to the seed material (i.e. 0.38 m²/g).

The amount of aragonite overgrowth has been estimated based on mass balance considerations using the concentration of Ca in the inlet solutions and the reactive fluid under steady-state conditions. The mole fraction of Mg in aragonite overgrowths has been estimated using the measured Mg concentration of bulk sample corrected for the moles of Mg in the seed material. This calculation assumes that overgrowth consists only of aragonite, consistent with the reduction of calcite presence in the bulk solid as defined by XRD techniques. The Mg concentration of the bulk precipitate in each run can be found in Table 1. In the aragonite overgrowths, Mg concentrations achieve minimum values of 0.10, 0.16 and 0.27 mmol/mol

for experiments performed at 25, 15 and 5 °C, respectively. The maximum Mg concentrations of the overgrowths achieve values of 0.69, 0.97 and 1.47 mmol/mol for experiments performed at 25, 15 and 5 °C, respectively. This observation suggests an inverse correlation of Mg content in the precipitated aragonite with increase in the growth temperature.

3.2 Chemical composition of the reactive fluids and growth rate calculations

An example of the temporal evolution of Ca and Mg concentrations and the prevailing pH of the reactive fluid can be seen in Fig. 3 for experiment LiAr-20. Chemical steady-state conditions with respect to aqueous Ca and Mg concentration occur in the total duration of the experimental runs. At these chemical steady-state conditions aragonite growth rate can be estimated based on mass balance considerations. The amount of aragonite precipitated can be approximated by the moles of Ca introduced in the reactor per time unit corrected for the moles of Ca removed from the reactor during sampling similar to Mavromatis et al. (2019) as:

$$r_p = \frac{n_{Ca(add)} - n_{Ca(rem)}}{86,400} / S \quad (1)$$

where S is the reactive surface of aragonite in m^2 and 86,400 is the number of seconds per time unit (i.e. 24 h). In Eq. (1) r_p is expressed in $mol/m^2/s$ and the estimated uncertainty is ~ 0.1 log units. The reactive surface S has been corrected for the mass of aragonite overgrowths precipitated during the course of each run based on mass balance considerations using the mass of the overgrowth and the reactive surface of the bulk sum of overgrowth and seed (see Table S1). In cases that the reactive surface area was not measured, it was assumed to be equal to that of the seed material (i.e. $0.38 m^2/g$). In addition, Eq. (1) does not consider the amount of Mg present in the solid phase, due to its low concentration in aragonite

overgrowths. As can be seen in Table 1, aragonite growth rate in the experiments conducted in this study varies about 1.5 orders of magnitude within the range $10^{-8.6} \leq r_p \leq 10^{-7.1}$ (mol/m²/s).

3.3 Magnesium partitioning between aragonite and the reactive fluid

The Mg distribution coefficient between formed aragonite and reactive fluid at chemical steady-state conditions can be estimated from the bulk Mg content of aragonite overgrowths and the molarities of aqueous Ca and Mg concentrations at chemical steady state conditions using the expression:

$$D_{Mg} = \frac{(\frac{Mg}{Ca})_{solid}}{(\frac{Mg}{Ca})_{fluid}} \quad (2)$$

where the subscript *fluid* denotes steady-state concentrations in the reactive fluid. Note here that the use of Eq. (2) is based on the assumptions that the presence of Mg in aragonite can be described as a diluted solid-solution that assumes random distribution of Mg in aragonite structure. Although XAFS data of Mg in coralline aragonite suggest that the latter is rather unlikely to occur and Mg is likely accommodated in nanodomains (Finch and Allison, 2008), the use of Eq. (2) allows for a systematic treatment of bulk Mg composition in aragonite and direct comparison with other divalent cation (i.e. Me²⁺) replacement reactions in CaCO₃ minerals where solid-solutions form. Additionally, the estimation of the Mg distribution coefficient in aragonite using Eq. (2) and the activities of free ions in the reactive fluid (i.e. Ca²⁺ and Mg²⁺), produces D_{Mg}^* values that are within error identical to those estimated with bulk concentrations (i.e. D_{Mg}) as can be seen in Table 1. The estimation of D_{Mg}^* assumes that only free ions are incorporated in the growing mineral phase as is dictated by the classical mineral growth model (Burton, 1951). Owing to the similar values of D_{Mg}^* and D_{Mg} in all the

runs only the latter parameter is discussed below. The minimum D_{Mg} values estimated in this study at 25, 15 and 5 °C are 1.69×10^{-5} , 2.52×10^{-5} and 5.47×10^{-5} , respectively, whereas the maximum D_{Mg} values at the same temperatures were 1.33×10^{-4} , 2.20×10^{-4} , and 4.12×10^{-4} , respectively. Similar to the Mg content of aragonite overgrowths, the lowest D_{Mg} values are observed at the highest overgrowth temperature in this study (i.e. at 25 °C).

The dependence of D_{Mg} on aragonite growth rate as it has been calculated with Eq. (2) for experiments at 25, 15 and 5 °C respectively, can be numerically described with the aid of the linear equations:

$$\text{Log } D_{Mg,25} = 0.586 (\pm 0.029) \text{ Log } r_p + 0.231 (\pm 0.225); R^2=0.96 \text{ (3a)}$$

$$\text{Log } D_{Mg,15} = 0.578 (\pm 0.041) \text{ Log } r_p + 0.438 (\pm 0.312); R^2=0.95 \text{ (3b)}$$

$$\text{Log } D_{Mg,5} = 0.584 (\pm 0.039) \text{ Log } r_p + 0.738 (\pm 0.302); R^2=0.95 \text{ (3c)}$$

and are valid for aragonite growth rate of $10^{-8.6} \leq r_p \leq 10^{-7.1}$ (mol/m²/s). The obtained results of the co-precipitation experiments conducted in this study are plotted as a function of aragonite growth rate in Fig. 4. These trends suggest that the temperature dependence of D_{Mg} values is the same within error for all of the temperatures examined in this study.

Overall, the dependence of Mg distribution coefficient on growth rate, described with Eqs (3a-3c), comes in agreement with the general behavior of incompatible Me^{2+} during their incorporation in $CaCO_3$ minerals for which an increase in D_{Me} value can be observed at increasing growth rate (e.g. Zhong and Mucci, 1989; Tesoriero and Pankow, 1996; Mavromatis et al., 2018; Goetschl et al., 2019).

Finally, regression analysis of the obtained results (least squares method) allows for the development of a numerical expression that combines the effects of temperature and growth rate on D_{Mg} and can be described by the linear equation:

$$\text{Log } D_{Mg} = 0.583(\pm 0.020) \text{ Log } r_p - 0.026(\pm 0.001) T + 0.863(\pm 0.153); R^2 = 0.97 \quad (4)$$

where T is the temperature in degrees Celsius. Note here that Eq. (4) is only valid for the temperature and growth rate ranges of this study, and any application to other systems should be handled with caution.

4. Discussion

4.1 The role of growth rate in Mg incorporation in aragonite

The results of this study suggest that mineral growth rate is likely the major parameter controlling the incorporation of Mg in aragonite overgrowths. As can be seen in Table 1, for experiments conducted at 25 °C, an increase of r_p from $10^{-8.6}$ to $10^{-7.1}$ (mol/m²/s) results in an increase in D_{Mg} values of about an order of magnitude from 1.69×10^{-5} to 1.33×10^{-4} . A similar dependence of D_{Mg} on growth rate can be seen also for experiments conducted at 15 and 5 °C as is depicted in Fig. 4. Actually, the slopes of Eqs (3a-3c) are identical within uncertainty, implying that the same mechanism is controlling D_{Mg} in the temperature range between 5 and 25 °C.

Mineral growth rate is a well-studied parameter controlling the incorporation of Me^{2+} in $CaCO_3$ minerals. As has been shown by Rimstid et al. (1998), an increase in growth rate results in a decrease of D_{Me} during the formation of $CaCO_3$ minerals for elements exhibiting $D_{Me} > 1$ at near equilibrium conditions such as Fe^{2+} , Mn^{2+} in calcite and Sr^{2+} in aragonite (e.g. Lorens, 1981; Dromgoole and Walter, 1990). In contrast an increase in D_{Me} is observed during the incorporation of incompatible ions that are characterized by $D_{Me} < 1$ at near equilibrium conditions such as Ba^{2+} and Sr^{2+} in calcite and Ba^{2+} in aragonite (e.g. Tesoriero and Pankow, 1996; Tang et al., 2008; Mavromatis et al., 2018). This dependence of D_{Me} on growth rate suggests that at increasing growth rate the composition of the growing mineral is not controlled by thermodynamic principles and tends to achieve a composition similar to

that of the forming fluid. Similar to other Me^{2+} , the presence of Mg^{2+} in calcite is also affected by mineral growth kinetics (Mavromatis et al., 2013). Interestingly however, the dependence of Mg partitioning in calcite on mineral growth rate is significantly weaker compared to that observed in this study for Mg incorporation in aragonite. The incorporation of Mg in calcite exhibits an increase of roughly half an order of magnitude in $D_{\text{Mg,calcite}}$ for an order of magnitude increase in growth rate (Goetschl et al., 2019). The absolute value of $D_{\text{Mg,calcite}}$ reported in the literature at 25 °C however, at similar surface normalized growth rates to those measured in this study for aragonite (i.e. $1.69 \times 10^{-5} \leq D_{\text{Mg,aragonite}} \leq 4.12 \times 10^{-4}$, see Table 1), is 2-3 orders of magnitude larger (i.e. $0.01 \leq D_{\text{Mg,calcite}} \leq 0.04$; Oomori et al., 1987; Mucci, 1987; Howson et al., 1987; Burton and Walter, 1991; Hartley and Mucci, 1996; Huang and Fairchild, 2001; Mavromatis et al., 2013; 2017).

The observed dependence of D_{Mg} on growth rate that can be seen in Fig. 4, comes in excellent agreement with the earlier observations by Gabitov et al. (2008). These authors conducted experiments of nucleation and growth of aragonite crystals using the ammonium carbonate diffusion technique and reported increasing D_{Mg} values as a function of growth rate. The D_{Mg} values reported by Gabitov et al. (2008) lay in the range $1.9\text{--}7.5 \times 10^{-5}$ and are in good agreement with the results of this study. In contrast to the growth rate dependence of D_{Mg} values observed in this study and by Gabitov et al. (2008), the earlier work by Zhong and Mucci (1989) found no growth rate effects on D_{Mg} values. Using a chemo-stat technique, similar to that used in this study, Zhong and Mucci (1989) estimated an average D_{Mg} value of $6.9 \pm 1.3 \times 10^{-4}$. The rather high D_{Mg} value was assigned by these authors to the presence of calcite in the aragonite seed and/or to differences in the analytical techniques used for the estimation of Mg in the solid (Gabitov et al., 2008). Additionally, it is likely that the higher D_{Mg} values reported by Zhong and Mucci (1989) are to some extent also controlled by the composition of the background electrolyte, which in their experiments was artificial seawater

of various salinities. For example, Bots et al. (2011) reported that the presence of sulphate in aragonite impacts its Mg content.

Although Mg is commonly present in natural aragonites such as corals, its presence in the crystal structure of this mineral phase is not favored according to thermodynamic considerations. The major limitation stems from the inability of Mg to increase its coordination from 6 in the Mg^{2+} (aq) ion to 9 in this mineral phase that would lead to an ideal positioning in the Ca site in the crystal lattice. Indeed, molecular dynamic simulations have shown that at thermodynamic equilibrium, Mg presence in the surface of aragonite is energetically favored, however the replacement of Ca for Mg in the bulk solid is energetically less favored (Ruiz-Hernandez et al., 2012; Kawano et al., 2015).

The high sensitivity of D_{Mg} values to growth rate (Fig. 4) suggests that the incorporation of Mg in aragonite likely occurs at defect sites on the growing mineral surface. Such behavior is common for incompatible ion incorporation in carbonate minerals (e.g., Li^+ , Na^+ , BO_4^- , SO_4^{2-}). For example, Busenberg and Plummer (1985) suggested that the incorporation of Na^+ in calcite depends on the density of crystal surface defects, which increases with the degree of saturation of the forming fluid with respect to the precipitating phase (Teng et al., 2000). As such, Na content in calcite has been observed to increase with increasing growth rate (Busenberg and Plummer, 1985; Mucci, 1988; Fuger et al., 2019). As can be seen in Fig. 5, D_{Mg} values exhibit a positive dependence to the saturation degree in the forming fluid, with the latter parameter to control mineral growth. Indeed, as has been shown by Teng et al. (2000) for calcite, at low supersaturation degrees, attachment of solutes mainly occurs at surface defect sites (i.e., dislocations, surface imperfections, grain boundaries) leading to spiral growth mechanism, whereas at increasing supersaturation mineral growth can also proceed by surface nucleation processes. Thus, it can be suggested that the increasing supersaturation of the fluid with respect to aragonite promotes the presence of

defect sites on crystal surface and subsequently augments the concentration of Mg in the solid phase.

Mechanistically the elevated concentration of Mg in aragonite at higher growth rates can be explained by the growth entrapment model (GEM) (Watson and Liang, 1995; Watson, 1996, 2004). The GEM proposes that trace elements/impurities that are incompatible with the mineral structure are enriched in the surface layer of the growing crystal. This implies that despite the lack of a diluted solid-solution formation in the magnesite-aragonite system, Mg concentration in the crystal lattice, would increase at elevated growth rates. The GEM has been successfully applied to describe the incorporation of both cations and anions between carbonate minerals and fluids in earlier studies (Gabitov and Watson, 2006; Gaetani and Cohen, 2006; Tang et al., 2008). Interestingly, Gabitov et al. (2008; 2011) applied the GEM and found that at $\sim 100\%$ Mg entrapment in growing aragonite D_{Mg} should achieve a value up to $7.5 \pm 1.7 \times 10^{-5}$. This value is roughly half compared to the maximum value measured at 25 °C in this study (i.e. 1.33×10^{-4} ; exp LiAr-17), suggesting that greater Mg entrapment in aragonite, similar to what is observed in natural samples (e.g. Montagna et al., 2014; Rollion-Bard and Blamart, 2015), is likely possible.

4.2 The role of temperature in Mg incorporation in aragonite

As can be seen in Fig. 4, at similar surface normalized growth rates, D_{Mg} values appear systematically lower as aragonite formation temperature increases. This observation is likely to be associated to the higher supersaturation of the reactive fluid with respect to aragonite at decreasing temperatures (Fig. 5), although surface normalized growth rates are similar among the three temperatures at which experiments were conducted in this study. Note here that in all the runs of this study the availability of ions in the reactive fluid is controlled by the titration of the inlet solutions which was kept similar for all the three

temperatures explored. Thus, the difference in the saturation of the fluid with respect to the aragonite among the three temperatures explored can be assigned to the retrograde solubility of aragonite (Plummer and Busenberg, 1982). For example, in experiments LiAr-18, LiAr-36 and LiAr-30 conducted at 25, 15 and 5 °C, respectively the measured surface-normalized growth rate was the same for all the three runs (i.e. $\sim 10^{-7.1} \text{ mol/m}^2/\text{s}$). Yet, in these three runs $\Omega_{\text{aragonite}}$ was 3.98, 4.66 and 5.29, respectively, exhibiting a systematic increase as formation temperature decreases. As has been observed earlier, a direct link occurs between supersaturation of the fluid from which carbonate mineral form and the presence of defect sites (e.g. McDermott et al., 1999; Frisia et al., 2000; Wynn et al., 2018). The presence of these defect sites promotes incorporates of incompatible ions in carbonate minerals (e.g. Pingitore and Eastman, 1986; Uchikawa et al., 2017; Wynn et al., 2018). Thus, it can be inferred that the elevated supersaturation of the fluid with respect to aragonite observed in this study for experiments conducted at similar growth rates but different temperatures, promotes the incorporation of Mg in this mineral phase. This likely occurs as a result of the greater presence of surface defects promoted by the higher $\Omega_{\text{aragonite}}$ values that occur at lower temperatures.

Interestingly, differences in D_{Mg} values are not only associated with differences of $\Omega_{\text{aragonite}}$ at different formation temperatures, but are also directly controlled by the temperature of aragonite formation. This is observed in experiments conducted at very low growth rate when the degree of supersaturation of the fluid with respect to aragonite is similar among the three formation temperatures. For example, in experiments LiAr-1, LiAr-31 and LiAr-25 conducted at 25, 15 and 5 °C, respectively, the measured $\Omega_{\text{aragonite}}$ was ~ 1.1 . Despite the similarity in $\Omega_{\text{aragonite}}$ a significant variation in D_{Mg} values occurs with an increase from $10^{-4.77}$ at 25 °C (LiAr-1) to $10^{-4.09}$ at 5 °C (LiAr-25). Thus, at near equilibrium conditions, temperature is directly controlling the Mg incorporation in aragonite, although the exact

mechanism promoting the incorporation of this cation in aragonite at lower temperatures requires further investigation. The decrease of D_{Mg} values with increasing temperature are consistent with the results of Gabitov et al. (2008), who reported reduced Mg/Ca ratio in aragonite overgrowths formed at 53 °C compared to those formed at 22 °C. Moreover, a similar correlation between D_{Mg} values and temperature was reported earlier by Gaetani and Cohen (2006) in aragonite nucleation experiments. Actually, Gaetani and Cohen (2006) proposed an exponential relationship between D_{Mg} and temperature in the range between 15 and 75 °C, suggesting a significant impact of temperature on Mg incorporation in aragonite. We note here that overall the D_{Mg} values reported in Gaetani and Cohen (2006) are about an order of magnitude higher than the maximum value measured in this study at 25 °C and about two orders of magnitude higher for experiments conducted at 5 °C. Likely the observed discrepancies in absolute D_{Mg} values can be assigned to differences in the experimental design. In this study, aragonite precipitation occurred via overgrowth on seed material at relatively low $\Omega_{\text{aragonite}}$ (~1 to 5), whereas in Gaetani and Cohen (2006) mineral formation occurred at $\Omega_{\text{aragonite}} > 25$. The relatively high $\Omega_{\text{aragonite}}$ values in the experiments of Gaetani and Cohen (2006) were induced by the titration of a carbonate-bearing solution in the forming fluid that promoted an increased entrapment of traces/impurities in the initial nucleating and later growing aragonite crystals. Despite differences in experimental design impacting the magnitude of the estimated D_{Mg} values, the temperature trends observed in this study and Gaetani and Cohen (2006) are consistent. A similar discrepancy in the magnitude of distribution coefficients due to differences in experimental setups has been observed in the Ba content of aragonite nucleated by Dietzel et al. (2004) and Gaetani and Cohen (2006) compared to overgrowth experiments of Mavromatis et al. (2018). Alternatively, the high supersaturation degrees of CaCO_3 formation in these earlier studies likely led to mineral

formation through an amorphous precursor, which could impact the extent of Me incorporation (Purgstaller et al. 2016; 2017).

4.3 Implications for the modelling of trace metal incorporation in CaCO₃ minerals and the use of Mg content in natural aragonites

The incorporation of Me²⁺ in CaCO₃ minerals is commonly modelled based on the assumption that an ideal solid-solution occurs between the pure Me-carbonate mineral and the CaCO₃ phase (e.g. Sverjensky, 1984, 1985; Rimstidt et al., 1998; Wang and Xu, 2001). For example, the model of Rimstidt et al. (1998) correlates the solubility products of pure end-member carbonates with partitioning of traces in calcite, it ignores however, that crystal structure is an important parameter that affects incorporation, as for example that of Ba and Sr in calcite. Indeed, witherite (BaCO₃) and strontianite (SrCO₃) crystallize in the orthorhombic system at ambient temperatures and thus are not isostructural to rhombohedral calcite making the modelling of their replacement somewhat complex. This complication was pointed out by Böttcher (1997) for the experimental work of Tesoriero and Pankow (1996) on the incorporation of Ba and Sr in calcite. In an effort to resolve the issue of mineral structure, Sverjensky (1984, 1985) correlated metal partitioning with the Gibbs free energy of the formation of end-member metal carbonates. Even for this theoretical consideration however, when the Gibbs free energy of formation is used for the orthorhombic magnesite-aragonite solid-solution (Sverjensky and Molling, 1992) a rather elevated D_{Mg} value of $10^{-2.93}$ at 25 °C can be estimated, which is ~2 orders of magnitude higher than the D_{Mg} value closest to equilibrium measured in this study at 25 °C (i.e $10^{-4.76}$ in experiment LiAr-1; Table 1).

Although the theoretical modeling of Me²⁺ incorporation in CaCO₃ minerals may deviate from experimental studies or natural analogues, the ideal replacement of Ca²⁺ for Me²⁺ has been shown for a large number of elements present in calcite (e.g., Ba, Co, Mg, Zn;

Reeder et al., 1999; Finch and Allison, 2007) and aragonite (e.g., Ba, Sr; Finch and Allison, 2007) based on spectroscopic techniques. In contrast the experimental results of this study suggest that during its incorporation in aragonite, Mg is behaving as an incompatible element to the mineral structure, exhibiting a high sensitivity to mineral growth rate. Similar dependencies of the distribution coefficients of incompatible ion incorporation in CaCO_3 minerals have been earlier shown for Li (Füger et al., 2019) and B (Mavromatis et al., 2015; Uchikawa et al., 2015). For these elements the exact position in the crystal lattice is still under debate and as such theoretical modelling has been proven to deviate from experimental calibrations and natural samples. Considering that the obtained relationship between D_{Mg} and growth rate is affected by temperature and most likely by background electrolyte composition, it can be suggested that the use of incompatible elements in carbonate minerals, including Mg in aragonite, requires empirical calibrations in order to be applied in biological systems.

The good correlation between mineral growth rate and D_{Mg} values numerically described using Eqs (3a-3c) including the effect of temperature (Eq. 4) likely provides the means for the potential use of aragonite Mg content or Mg/Ca ratio as a proxy tool in natural samples. For example, the high sensitivity of D_{Mg} on aragonite growth rate suggests that Mg content in this mineral phase can be used as a tool for mapping growth rate regimes in speleothems that usually form from solution with low degrees of supersaturation with respect to CaCO_3 minerals. Actually, Wassenburg et al. (2016) presented data on speleothem aragonites characterized by an average D_{Mg} value of 9.7×10^{-5} that lays well within the range estimated in this study. Similarly, the reported D_{Mg} values of a number of other aragonitic archives fall well within the range of values measured in this study, including the Manila clams *R. philippinarum* ($D_{\text{Mg}} = 4.6 - 6.2 \times 10^{-4}$; Poulain et al., 2015), fresh water mussel shells *Lampsilis cardium* ($D_{\text{Mg}} = 3 - 8 \times 10^{-4}$; Geeza et al., 2019) and scleractinian corals of

various species ($D_{Mg} = 3 - 5 \times 10^{-4}$; Montagna et al., 2014). For corals, the correlation between Mg/Ca and the calcification rates has been reported for a number of specimens grown in cultures (e.g. Inoue et al., 2007; Reynaud et al., 2007). In bio-induced carbonates however, a number of processes have been shown to affect Mg content that includes the presence of organic layers (e.g. Foster et al., 2008), pH variations in the calcifying fluid (e.g. Holcomb et al., 2009), compartmentalized precipitation (e.g. Rollion-Bard et al., 2011; Rollion-Bard and Blamart, 2015) and formation via an amorphous precursor phase (e.g. Rollion-Bard et al., 2011; Mass et al., 2017). Thus, the rate effect described in Eqs (3a-3c) may not be directly applicable in natural samples.

The results of the present study indicate that if properly calibrated, Mg in aragonite may provide pertinent information on the formation conditions of natural aragonites. As can be seen in Fig. 5, there is a linear dependence between D_{Mg} values and the degree of aragonite supersaturation in the forming fluid. Those can be numerically described for experiments conducted at 25, 15 and 5 °C, respectively, as:

$$\text{Log } D_{Mg,25} = 1.146 (\pm 0.092) \text{ Log } \Omega_{Arag} - 4.803 (\pm 0.036); R^2=0.94 \quad (5a)$$

$$\text{Log } D_{Mg,15} = 1.339 (\pm 0.144) \text{ Log } \Omega_{Arag} - 4.527 (\pm 0.062); R^2=0.88 \quad (5b)$$

$$\text{Log } D_{Mg,5} = 1.192 (\pm 0.154) \text{ Log } \Omega_{Arag} - 4.300 (\pm 0.075); R^2=0.84 \quad (5c)$$

These relations suggest that if the temperature of formation is known or can be estimated (e.g., $\delta^{18}\text{O}$ compositions of the samples), the Mg content of aragonite can provide insights for the degree of supersaturation of the forming fluid and/or the carbonate ion concentration if the chemical composition of the forming fluid can be hypothesized (e.g., seawater). Such correlation between Mg/Ca ratio and carbonate ion concentration has been earlier shown in the aragonitic foraminifera species *Hoeglundina elegans* (Rosenthal et al., 2006). Note however that the range of $\Omega_{\text{aragonite}}$ is not the same among the three temperatures groups explored (see Table 1) thus the use of Eqs. (5a-5c) may require further calibration that reflect

conditions met in natural systems. Overall, the relationship between Mg content of aragonite with the degree of saturation of the fluid with respect to this mineral phase suggest that in the case of proper calibration (e.g., for seawater-like fluids), D_{Mg} or Mg/Ca ratio in the forming solid can be used as a proxy for saturation degree of the fluid with respect to CaCO_3 minerals.

5. Conclusions

The experimental work performed in this study documents that the presence of Mg in aragonite is predominantly affected by mineral growth rate and to a lesser extent by temperature. The strong increase of D_{Mg} values at increasing growth rate suggests that Mg in aragonite can be a robust indicator of mineral growth rate, if formation temperature is known. Additionally, the results provide insights on the mechanisms controlling the presence of Mg in aragonite overgrowths. Indeed, the inverse correlation between D_{Mg} values and temperature for experiments performed at similar surface normalized growth rates together with the observed higher degree of saturation at lower formation temperatures suggests that incorporation of Mg in this mineral phase might be associated with the presence of surface defect sites. Here the retrograde solubility of aragonite at lower temperatures promotes a larger number of defect sites due to higher saturation of the fluid with respect to the growing mineral at decreasing temperatures. This feature suggests that D_{Mg} values and Mg/Ca ratio in natural aragonite have the potential to be used as a proxy of fluid saturation degree with respect to CaCO_3 minerals. Finally, and in contrast to the behavior of other divalent cations during their incorporation in CaCO_3 minerals, the co-precipitation of Mg with aragonite cannot be modelled as a diluted solid-solution using thermodynamic considerations. Similar to the presence of other incompatible ions in carbonate minerals presence of Mg in aragonite

requires empirical calibrations, specific for the background electrolyte composition of the forming fluid.

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Table 1: Temperature, Mg/Ca ratio in aragonite overgrowths, saturation state of the forming fluid with respect to aragonite (i.e. $\Omega_{\text{aragonite}}$), aragonite growth rate and distribution coefficient of Mg in aragonite based on concentrations (i.e. D_{Mg}) and activities of free ions (i.e. D_{Mg^*}) in the reactive fluid.

Experiment	Temperature (°C)	Mg/Ca _{aragonite} (mmol/mol)	$\Omega_{\text{aragonite}}$	Log r_p (mol/m ² /s)	Log D_{Mg}	Log D_{Mg^*}
LiAr-1	25	0.13	1.13	-8.6	-4.77	-4.76
LiAr-2	25	0.20	1.25	-8.2	-4.55	-4.54
LiAr-3	25	0.28	1.44	-7.9	-4.40	-4.39
LiAr-4	25	0.30	1.85	-7.6	-4.29	-4.27
LiAr-5	25	0.36	2.56	-7.5	-4.19	-4.18
LiAr-6	25	0.33	2.67	-7.5	-4.25	-4.24
LiAr-13	25	0.14	1.25	-8.3	-4.70	-4.68
LiAr-14	25	0.26	1.69	-7.9	-4.43	-4.40
LiAr-15	25	0.53	2.67	-7.4	-4.13	-4.10
LiAr-16	25	0.69	4.00	-7.1	-3.90	-3.87
LiAr-17	25	0.67	3.93	-7.1	-3.88	-3.85
LiAr-18	25	0.60	3.98	-7.1	-3.89	-3.86
LiAr-37	25	0.10	1.36	-8.5	-4.73	-4.70
LiAr-39	25	0.22	1.92	-7.8	-4.33	-4.30
LiAr-40	25	0.30	2.76	-7.7	-4.21	-4.19
LiAr-42	25	0.38	3.79	-7.4	-4.05	-4.02
LiAr-7	15	0.16	1.23	-8.6	-4.60	-4.57
LiAr-8	15	0.35	1.47	-8.2	-4.27	-4.24
LiAr-9	15	0.43	2.19	-7.9	-4.11	-4.08
LiAr-10	15	0.57	2.81	-7.7	-3.92	-3.89
LiAr-11	15	0.81	3.60	-7.4	-3.75	-3.72
LiAr-12	15	0.62	3.80	-7.4	-3.86	-3.83
LiAr-31	15	0.26	1.07	-8.3	-4.40	-4.38
LiAr-32	15	0.40	1.68	-7.9	-4.19	-4.16
LiAr-33	15	0.82	2.68	-7.4	-3.83	-3.80
LiAr-34	15	0.80	3.28	-7.2	-3.79	-3.76
LiAr-35	15	0.76	3.63	-7.1	-3.78	-3.75
LiAr-36	15	0.97	4.66	-7.1	-3.66	-3.62
LiAr-19	5	0.61	1.29	-8.6	-4.26	-4.23
LiAr-20	5	0.81	1.70	-8.2	-4.10	-4.07
LiAr-21	5	1.04	2.42	-7.9	-3.88	-3.86
LiAr-22	5	0.93	2.97	-7.7	-3.87	-3.84
LiAr-23	5	1.21	3.63	-7.6	-3.72	-3.69
LiAr-24	5	1.20	4.55	-7.6	-3.66	-3.63
LiAr-25	5	0.27	1.14	-8.3	-4.09	-4.05
LiAr-26	5	0.45	1.68	-7.9	-3.83	-3.80
LiAr-27	5	0.79	3.44	-7.4	-3.52	-3.49
LiAr-28	5	0.87	4.31	-7.2	-3.47	-3.44
LiAr-29	5	1.07	4.43	-7.1	-3.51	-3.47
LiAr-30	5	1.47	5.29	-7.2	-3.38	-3.35