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Effect of growth rate on Nickel and Cobalt incorporation in aragonite

Jean-Michel Brazier^{1*}, Vasileios Mavromatis (Βασίλειος Μαυρομάτης)²

¹ Institute of Applied Geosciences, Graz University of Technology, Rechbauerstrasse 12,
8010 Graz, Austria

² Geosciences Environnement Toulouse (GET), Observatoire Midi-Pyrénées, Université de
Toulouse, CNRS, IRD, UPS, 14 Avenue Edouard Belin, 31400 Toulouse, France

*corresponding author: j.brazier@tugraz.at

Abstract

The incorporation of Ni and Co in aragonite was experimentally investigated as a function of mineral growth rate using the constant addition technique at 25°C and 1 bar $p\text{CO}_2$. The distribution coefficients of Ni and Co (i.e., $D_{Me} = \frac{(Me/Ca)_{solid}}{(a_{Me^{2+}}/a_{Ca^{2+}})_{fluid}}$) exhibit a linear correlation with mineral growth rate in the range ($-9.1 \leq \text{Log } r_p \leq -7.5 \text{ mol/m}^2/\text{s}$). The obtained results suggest a stronger dependency of D_{Ni} to growth rate compared to that observed for D_{Co} . These dependencies can be described as:

$$\text{Log } D_{Ni} = 1.247 (\pm 0.152) \text{Log } r_p + 7.448 (\pm 1.212); R^2=0.82$$

$$\text{Log } D_{Co} = 0.312 (\pm 0.047) \text{Log } r_p + 1.664 (\pm 0.383); R^2=0.81$$

The $D_{Me\text{-aragonite}}$ values for both Ni and Co are systematically lower than unity and their increase with increasing growth rate is in agreement with the incorporation of elements incompatible with the host mineral structure. Using the dependency of D_{Ni} and D_{Co} to the saturation indices (SI) of the reactive solution with respect to aragonite, the D_{Me} under equilibrium were estimated. These estimates yield equilibrium $\text{Log } D_{Me}$ values of -3.9 and -1.0 for Ni and Co, respectively. These experimentally defined D_{eq} values are 1.3 to 4.3 orders of magnitude lower compared to theoretical estimates that were earlier published in the literature. Similar to other incompatible elements, the observed increase of D_{Ni} and D_{Co} values with degree of saturation points towards an incorporation related to the density of defect sites on the mineral surface. Finally, the dependencies recorded in this study suggest that D_{Ni} and D_{Co} have the potential to be used as a proxy for saturation degree of the reactive solution.

Keywords: nickel, cobalt, aragonite, distribution coefficient, growth rate

1. Introduction

Trace elemental composition of terrestrial and marine carbonates can provide essential information for the environmental and climatic conditions occurring at the time of mineral formation. Indeed, empirical observations on natural samples have revealed various correlations between the concentration of foreign ions in carbonate minerals/rocks and the prevailing physicochemical parameters during deposition time. Thus, studying the mechanisms controlling foreign ion incorporation in CaCO_3 minerals has been an area of great interest over the last 50 years (e.g., Kitano et al., 1975; Lorens, 1981; Mucci and Morse, 1983; Dromgoole and Walter, 1990; Paquette and Reeder, 1995; Mavromatis et al., 2013, 2018). Most of these works focused on the experimental determination of factors affecting trace element concentration in calcite formed under abiotic conditions. For example, it was shown that physico-chemical parameters such as temperature, pH, ionic strength, saturation degree of the forming fluid with respect to the precipitating mineral phase and growth rate, play a determining role in the concentration of foreign elements in calcite (e.g., Morse and Bender, 1990; Temmam et al., 2000; Tang et al., 2008; Fuger et al., 2019; Goetschl et al., 2019). Among these parameters, it appears that the growth rate exerts an important control on the distribution of elements between the newly formed carbonate minerals and the reactive solution (Lorens, 1981; Lee and Reeder, 2006; Lakshtanov and Stipp, 2007; Tang et al., 2008; Mavromatis et al., 2015; 2018; Voigt et al., 2017; Fuger et al., 2019).

Interestingly however, the majority of these earlier works focused on the study of calcite, resulting in a limited understanding of the mechanisms of trace elements incorporation into aragonite. Yet the latter is the second most abundant CaCO_3 polymorph on Earth, it readily forms in contemporaneous marine environments and comprises an important geological archive for oceanic and continental environments where it is precipitated, for example, as

coral exoskeletons or speleothems, respectively. Furthermore, due to the high Mg content of the present seawater, aragonite is also formed abiotically (i.e., ooids, cements), especially in shallow warm water (e.g., Bahamas, Belize; see Zhang et al., 2017). Similar to calcite, several studies have shown that foreign elements can be incorporated into aragonite (e.g., Sr, Ba, Mg, Mn, Na, K, REE) and that their ratios to Ca can be used as useful paleoenvironmental reconstruction proxies (Raiswell and Brimblecombe, 1977; White, 1977; Terakado and Masuda, 1988; Dietzel et al., 2004; Gaetani and Cohen, 2006; Gabitov et al., 2008; Mavromatis et al., 2018). Beyond their use as paleoenvironmental proxies, the incorporation of foreign elements in aragonite indicates that it could have the capacity to immobilize, in small amounts, certain elements which are deleterious for the organisms living in the aquatic system at which the mineral are formed. In this way, understanding the parameters controlling the incorporation of such elements in aragonite and, in a follow up step understanding the associated isotope fractionation, can lead to the development of robust environmental proxies for toxic elements.

Aragonite crystallizes in the orthorhombic system and Ca^{2+} in this mineral phase occurs in 9-fold coordination which makes it difficult to substitute with smaller ions, indicating that most of the trace elements it incorporates are not the result of ion-to-ion substitution (Dietzel, 2011). These “so-called” incompatible ions with the crystal structure are defined by a distribution coefficient between the solid and the reactive solution always inferior to 1, that is increasing with increasing growth rate. In absence of diluted solid-solution formation, it appears important to experimentally quantify the effect of growth rate on the incorporation of incompatible elements and also to provide fundamental understanding on the mechanisms and sites of incorporation in aragonite.

Nickel and cobalt are both trace elements encountered in many environmental compartments and are essential to many species in terms of physiology (Domingo, 1989;

Harasim and Filipek, 2015; Li et al., 2018 and references therein). Nevertheless, these two elements become highly toxic when their concentrations increase in the environment, which raises major questions about the survival of living organisms (e.g., Anderson et al., 1973; Macomber and Hausinger., 2011; Leyssens et al., 2017; Sun et al., 2020). Both these elements are contaminants found in industrial wastewater and an increase in their concentration in the natural environment seems to be expected as these industries continue to expand (Ramrakhiani et al., 2017). Similar to many other transition metals, Ni and Co exhibit affinities to adsorption and incorporation onto or into calcite (Reeder, 1996; Lee and Reeder, 2006; Lakshtanov and Stipp, 2007; Katsikopoulos et al., 2008; Alvarez et al., 2020, 2021). The characterization of the removal processes of these metals through incorporation into CaCO₃ minerals seems therefore essential to understand and characterize the Ni and Co cycle on a large spatial and temporal scale. Considering the large abundance of aragonite in aquatic environments studying its potential to incorporate Ni and Co can provide an important step in understanding the fate of these two elements in natural environment.

The aim of this study is to determine the effect of the growth rate on the incorporation of Ni and Co in aragonite. Thus, co-precipitation experiments on aragonite seed material were performed at 25°C and 1 bar *p*CO₂ following the constant addition method. The results allow a quantitative approach of the distribution between aragonite and reactive solution as well as the dependence on the growth rate and the saturation state and thus contribute to the understanding of the mechanisms of incorporation of incompatible elements in aragonite.

2. Material and methods

2.1. Experimental procedures

Experiments of nickel and cobalt co-precipitation with aragonite were performed on synthetic aragonite seeds at 25°C and 1 bar *p*CO₂ using a mixed flow reactor (see Fig. 1).

This experimental set-up has been adapted from Tesoriero and Pankow (1996) and has been broadly used over the last decades to investigate the incorporation of traces/impurities in carbonate minerals, because it allows for a wide variation in growth rate and pH of the reactive solution (e.g., Fuger et al., 2019; Goetschl et al., 2019; Mavromatis et al., 2013, 2018, 2022). The use of high $p\text{CO}_2$ in this study ensures that Ni and Co oxides or hydroxides do not form during our experiments. All the reactive solutions were prepared using deionized water (Millipore Integral 3; 18.2M Ω /cm) and analytical grade chemicals. For Ni coprecipitation experiments, all reactor solutions were prepared shortly prior to the runs and contained 300 mM of NaNO₃, 25 or 55-65 mM of Mg(NO₃)₂, 20 mM of Ca(NO₃)₂ and 0.2 mM of Ni(NO₃)₂. Nitrate-bearing salts were chosen here to allow for direct comparison with earlier works (e.g. Lakhstanov and Stipp, 2007; Alvarez-Castillo et al., 2021). Note here however that the runs NiAr-1 to NiAr-6, which investigated the lowest growth rate, were prepared with 25 mM of Mg(NO₃)₂ whereas for higher growth rate (i.e. NiAr-13 to NiAr-24), Mg(NO₃)₂ concentrations in the reactors were increased to ~55-65 mM to avoid calcite formation. For Co coprecipitation experiments, all reactor solutions contained 300 mM of NaNO₃, ~53-60 mM of Mg(NO₃)₂, 20 mM of Ca(NO₃)₂ and 0.1 mM of Co(NO₃)₂.

Between 1 and 5 g of aragonite seeds were then added to each reactor. This was followed by addition of two distinct inlet solutions by a peristaltic pump at similar flow rates (10 to 20 ml/day) to induce aragonite overgrowth. The first solution contained Ca(NO₃)₂, Mg(NO₃)₂ and Ni(NO₃)₂ or Co(NO₃)₂, whereas the second contained Na₂CO₃ and NaNO₃. Total inlet Mg(NO₃)₂, Ni(NO₃)₂, Co(NO₃)₂ and NaNO₃ concentrations were similar to the one of the initial reactive solution to avoid dilution effects. The concentrations of Ca(NO₃)₂ and Na₂CO₃ were equal in each run but varied between 60 and 150 mM among runs to investigate a range of mineral growth rate. Each reactor was equipped with a Teflon-coated floating stir bar operating at 240 rpm during the experimental runs to ensure homogeneity of the reactive

solution. The pH of the reactive solutions (6.3 ± 0.1 , 2SD) was controlled by bubbling of pure CO_2 , which was prior to its introduction in each reactor, bubbled through deionized water ($18.2\text{M}\Omega/\text{cm}$) to minimize evaporation in the reactor. Over the course of the experiments, 10 to 20 mL of each inlet solution were added per unit of time (i.e. 12h and 24h for 3.5- and 7-days experiments, respectively) and the same volume of reactive solution was removed via sampling in order to keep the total volume variation in a range of $\pm 4\%$. In order to keep the solid/solution ratio at the same variation range of $\pm 4\%$ during the experiments, the stirring was stopped to let the aragonite settle before each supernatant uptake. The latter were immediately filtered through $0.2\ \mu\text{m}$ cellulose acetate syringe filters (VWR) and the pH was measured in-situ. Aliquots were used for alkalinity measurements while the rest of the fluid samples was acidified with bi-distilled HNO_3 14N and stored for further elemental concentration measurements. At the end of each run, the reactor solutions were entirely vacuum filtered through $0.2\ \mu\text{m}$ cellulose acetate filters (Sartorius) and the solids were rinsed several times with pure deionized water ($18.2\text{M}\Omega/\text{cm}$) and dried at 40°C for 48 h.

2.2. Solution and solid characterization

The pH of the reactive solutions was measured with a SenTix 945 pH Gel pH electrode (WTW) calibrated with three NIST buffers (pH 4.01, 7.00, and 10.01). Total alkalinity was measured by 10 mM HCl titration on a Schott TitroLine alpha plus automatic titrator with an analytical precision of $\pm 2\%$. Sodium, Ca, Mg, Ni, and Co elemental concentrations of the reactive solutions were measured by inductively Couple Plasma Mass Spectrometry (ICP-MS) on an Agilent 7500CX with a precision lower than 2% (RSD). Instrumental drift was corrected by internal standard normalization using a mixture of Sc, Se and Ge. The accuracy of the measurements was ensured by repeated measurement of SPS-SW1 reference material

and XXI multi-element standard solution (Merck) during the different measurement sessions. Ion activities, aqueous speciation and saturation indices of the reactive solution with respect to aragonite ($SI = \text{Log} (IAP/K_{sp \text{ aragonite}})$) were calculated using the PHREEQC software together with its MINTEQ.V4 database (Parkhurst and Appelo, 2013), after the addition of the solubility products of nesquehonite [$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$] and dypingite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot (5 \text{ or } 8)\text{H}_2\text{O}$] from Harrison et al., (2019) and hydromagnesite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$] from Gautier et al. (2014). These results can be found on the Table A.1 and constant values are detailed in Table A.2

The mineralogy of seed material and aragonite overgrowths at the end of each run was characterized by X-ray diffraction (XRD) using a PANalytical X'Pert PRO diffractometer and a Co-K α radiation (40 mA, 40 kV) within a 2θ range of $4-85^\circ$ at $0.03^\circ \text{ s}^{-1}$. Mineral phases were determined using the PANalytical HighScore Plus software with the ICSD database and quantified by Rietveld refinement within 1 wt.% error. The specific surface area of solid materials was determined with an 11-points krypton adsorption BET method (Brunauer et al., 1938) using a Micromeritics Tristar II plus (Queen's University, Kingston). Imaging analyses of gold-coated samples were performed using a Zeiss DSM 92 Gemini Scanning Electron Microscope (SEM) operating at 5 kV acceleration voltage. For the chemical composition of solids about 50 mg of each sample were digested in 2% HNO_3 (prepared from bi-distilled HNO_3) and Co, Ni and Ca concentrations were measured on an Agilent 7500CX ICP-MS with a precision better than 2% (RSD). Instrumental drift and accuracy were corrected and ensured the same way presented for fluid analysis.

2.3. Seed materials

The aragonite seeds used in the experiments of this study were precipitated following the protocol described in Mavromatis et al. (2022). Briefly, the precipitation was performed by the titration of ~130 mL of a 1.52 M CaCl₂ solution into 1.5 L of a 0.066 M Na₂CO₃ solution with a flowrate of 0.6 mL/min. During all the process, the reactive solution was continuously stirred at 300 rpm and the temperature was kept constant at 80 ± 2°C using a heating mantle system (serie WMO, Mohr & Co). X-ray diffraction patterns of the synthesized solid indicates the presence of calcite in minor amount (i.e. 2.5 wt.%). Scanning electron microscopy images show needle-like aragonite crystals of 20-80 μm in length and 2-10 μm in diameter. The specific surface area of the aragonite was 0.50 m²/g, while wet chemical analyses showed that the seeds contained no Co and trace amounts of Ni (1.67 μmol/mol). The presence of Ni in the seeds is probably introduced from impurities of the technical grade chemicals used in the precipitation process.

3. Results

3.1. Composition of the precipitated solids

The X-ray diffraction patterns of the solids recovered from the reactors at the end of the runs consist of aragonite, with minor amounts of calcite. The abundance of calcite in these samples is similar to- or lower than- that of the seed material and between 0.6 and 2.5 wt.%. This observation suggests that during the experimental runs aragonite is the only mineral precipitating in the overgrowths. Contrary to the aragonite seeds (Fig. 2A), the SEM images of the solids at the end of the experimental runs exhibit surface structures consisting of step features which are indicative of overgrowth (Fig. 2B-2C). The amount of aragonite overgrowth (in g) under steady-state conditions can be calculated following:

$$Overgrowth = [(nC_{a_{add}}) - (nC_{a_{rem}})] \times M_{aragonite} \times N_{days} \quad (1)$$

where $nC_{a_{add}}$ and $nC_{a_{rem}}$ denote the number of moles of Ca added by pumping and removed by sampling in the reactors every 24h, respectively, while $M_{aragonite}$ is the molar mass of aragonite in g/mol (i.e. 100.0869 g/mol) and N_{days} is the number of days of the experimental run. Following Eq. (1), Ni and Co concentrations of the precipitated solids were calculated based on mass balance considerations and are presented in Table 1. In the case of Ni co-precipitation experiments corrections for the amount of Ni in the seed were applied. Nickel concentrations in aragonite precipitate range from 0.0003 to 0.0521 mmol/mol, whereas the Co concentrations exhibit values that range between 0.0541 to 0.1086 mmol/mol.

3.2. Composition of the reactive solutions

Two examples of the temporal evolution the concentrations of Ca and Ni or Co in the reactive solutions are displayed in Fig. 3A and 3B for NiAr-17 and CoAr-11 experiments, respectively. As it can be seen in Fig. 3, Ca concentrations of the reactive solutions reach steady-state conditions between 24 h and 48 h of the experimental runs, while Ni and Co concentrations are stable during the whole duration of the runs. Note here that the pH is stable all along the experiments. More details on the composition of the different reactive solutions can be found on the Table A.3.

The aragonite growth rate (r_p) at steady-state conditions can be estimated by mass balancing the number of moles of Ca added to the reactors and removed during sampling. This growth rate, expressed in mol/m²/s, is calculated following the equation proposed by Mavromatis et al. (2018):

$$r_p = \frac{(nCa_{add}) - (nCa_{rem})}{\frac{86400}{S}} \quad (2)$$

where nCa_{add} and nCa_{rem} represent the number of Ca moles added and removed from the reactor every 24 h, respectively, S denotes the total specific surface area of the mineral (i.e., seed + precipitate) in m^2 and 86400 represents the number of seconds in 24h. Due to the low concentrations of Ni and Co in the solids, they were not considered in rate estimation using Eq. (2). It has to be noted that the specific surface area of the solids collected at the end of the runs is somewhat lower ($\sim 0.34 \text{ m}^2/\text{g}$) compared to the $0.50 \text{ m}^2/\text{g}$ of the seed material and thus correction in rate estimation using Eq. (2) were applied. The uncertainty associated to Eq. (2) based on the Ca concentration and specific surface area evolutions was determined as ± 0.1 Log unit. The ranges of investigated growth rate are $-7.5 \geq \text{Log } r_p \geq -9.1$ and $-7.6 \geq \text{Log } r_p \geq -8.7$ mol/ m^2/s for Ni and Co experiments, respectively.

3.3. Nickel and Cobalt distribution between aragonite and solution

In this study distribution coefficient has been estimated as:

$$D_{Me} = \frac{(Me/Ca)_{solid}}{(a_{Me^{2+}}/a_{Ca^{2+}})_{fluid}} \quad (3)$$

where Me/Ca represents the ratio between the Me and Ca content in the solid and $a_{Me^{2+}}/a_{Ca^{2+}}$ represent the ratio of the activities the free aqueous ions of these metals in the reactive solution under steady-state conditions and is independent of background electrolyte composition. The use of Eq. (3) assumes that mineral growth proceeds via the attachment of free ions on the growing mineral surface as it is postulated in the classic TLK crystal growth model (Burton, 1951). It thus assumes that incorporation of Ni and Co in aragonite, proceeds via a change of their coordination from 6-fold in the aqueous phase to 9-fold in the solid in

order to ideally replace Ca in this mineral structure. This approach was previously used by several studies describing the presence of Me^{2+} in $CaCO_3$ as a diluted solid-solution between $MeCO_3$ and $CaCO_3$ (e.g., Dromgoole and Walter, 1990; Tesoriero and Pankow, 1996; Mavromatis et al., 2013, 2018, 2019). In this study, the formation of solid-solution between $NiCO_3$ or $CoCO_3$ and aragonite is rather unlikely to occur. Here the use of the same approach and Eq. (3) allows a direct comparison of the results with other elements. Note here that the free aqueous ions activities were preferred over the total ion concentration because a significant portion of Ca, Ni and Co are under aqueous complex form (i.e., ~40 % of the Ca (notably $CaHCO_3^+$ and $CaNO_3^+$), ~60 % of the Ni (notably $NiHCO_3^+$ and $NiNO_3^+$) and ~15% the Co of the total concentrations (notably $CoHCO_3^+$ and $CoNO_3^+$)). Distribution coefficients expressed with the aid of the total ion concentration in the reactive solution (i.e., referred as $D^*_{Ni/Co}$ in this study) can be nevertheless found in Table 1 and show difference in absolute values but similar dependency to growth rate compared to the $D_{Ni/Co}$ values.

The calculated $\text{Log } D_{Ni}$ values range between -4.2 and -1.9, while the $\text{Log } D_{Co}$ values range between -1.0 and -0.7. As it can be seen in Figs 4A and 4B, a linear dependency between Ni and Co distribution coefficients in aragonite and mineral growth rate exists. These dependencies are linear in a Log-Log space and can be mathematically described by linear regression using the equations:

$$\text{Log } D_{Ni} = 1.247 (\pm 0.152) \text{Log } r_p + 7.448 (\pm 1.212); R^2=0.82 \quad (4)$$

$$\text{Log } D_{Co} = 0.312 (\pm 0.047) \text{Log } r_p + 1.664 (\pm 0.383); R^2=0.81 \quad (5)$$

These equations are valid for both Ni^{2+} and Co^{2+} under the conditions (i.e., chemical composition of the reactive solutions, temperature, pCO_2 , pH) and growth rates ranges investigated in this study. The obtained results suggest a positive correlation between

distribution coefficients and growth rate, which is in accordance with incompatible element incorporation behaviour in CaCO_3 minerals. Finally, a measurable difference in the slopes of Eqs. (4) and (5) can be observed for the dependence of $\text{Log } D_{Me}$ values on $\text{Log } r_p$. These difference in the slope suggests a higher dependency of Ni incorporation in aragonite on growth rate compared to that measured for Co.

4. Discussion

4.1. Nickel incorporation in aragonite

As it is depicted in Fig. 4A, the results of this study suggest a strong correlation between $\text{Log } D_{Ni}$ and mineral growth rate. Indeed, an increase of ~ 2.3 orders of magnitude of $\text{Log } D_{Ni}$ (from -4.2 to -1.9) is observed when aragonite $\text{Log } r_p$ increases by ~ 1.6 orders of magnitude, from -9.1 to -7.5 ($\text{mol/m}^2/\text{s}$). The dependence of $\text{Log } D_{Ni}$ on $\text{Log } r_p$ is in good agreement with the behaviour of incompatible ions during their incorporation in minerals with structure different than that of the pure mineral phase. Generally, incompatible ion incorporation is characterized by $\text{Log } D_{Me}$ values systematically lower than zero that tend to reach zero when mineral growth departs from thermodynamic equilibrium regardless of the equilibrium value (Rimstidt et al., 1998). This effect was experimentally shown for the incorporation of several incompatible mono- and divalent metal cations in both calcite (e.g., Sr^{2+} , Ba^{2+}) and aragonite (e.g., Na^+ , K^+ , Ba^{2+} , Mg^{2+}) (White, 1977; Lorens, 1981; Tesoriero and Pankow, 1996; Lee and Reeder, 2006; Gabitov et al., 2008; Mavromatis et al., 2018, 2022). These studies have also shown that many parameters may explain the $\text{Log } D_{Me} < 0$ values, including differences in the size of ionic radii between the trace metal and the major cation, change in coordination, the hydration energy or the rate of water molecules exchange in the hydration shell.

Accordingly, the incompatibility of Ni^{2+} in aragonite can be likely partly explained by its

ionic radius. Note here that a direct comparison between 9-coordinated Ni and Ca is not possible, however a comparison of the radii of these metals in 6-fold coordination indicates that Ni is ~30% smaller than Ca^{2+} (i.e. 0.69 vs 1.00 Å; Shannon, 1976). In fact, it is well accepted that a one-to-one substitution is difficult if the ionic radius of the trace metal considered is highly different from that of the host cation. This is not only the case for small cations, such as Ni^{2+} that generally do not easily obtain a 9-fold coordination but also for cations that are significantly larger than Ca^{2+} , such as Ba. Indeed despite the formation of a diluted solid-solution $D_{\text{Ba,aragonite}}$ has been experimentally measured to exhibit values lower than unity (Mavromatis et al., 2018). Specifically, for the case of Ni, it is important to consider that the pure Ni-bearing carbonate phase gaspeite (i.e., NiCO_3) exhibits a calcite-like structure with an octahedral molecular geometry leading to a 6-fold coordinated Ni^{2+} (Pertlik, 1985; Haynes, 2014). Actually, to our knowledge Ni^{2+} in 9-fold coordination was never reported in the literature neither in solid nor in fluid phase. Aqueous Ni is usually complexed in 4-, 5- or 6-fold coordination (e.g. $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$; Varadwaj et al., 2008).

In addition to the ionic radius and coordination, other important parameters that could explain the very low D_{Ni} values recorded in this study are the high hydration of the aqueous Ni^{2+} and its affinity for the aqueous solution as highlighted by its low hydration Gibbs free energy (i.e., -1980 kJ/mol; Marcus, 1991) and by its low rate of water molecules exchange (i.e., $3.15 \times 10^4 \text{ s}^{-1}$; Lincoln and Merbach, 1995; Table 2). The incompatibility of the Ni^{2+} with the aragonite structure likely leads to an absence of solid-solution formation between NiCO_3 and aragonite.

Beyond its positive correlation to growth rate, $\text{Log } D_{\text{Ni}}$ also exhibits a strong correlation with $SI_{\text{aragonite}}$ (as seen in Fig. 5A) that can be described numerically by linear regression using the equation:

$$\text{Log } D_{Ni} = 8.893 (\pm 1.312) \text{SI}_{\text{aragonite}} - 3.859 (\pm 0.215); R^2=0.75 \quad (6)$$

Our experiments were designed to follow the evolution of the $\text{Log } D_{Ni}$ as a function of the $\text{Log } r_p$ so the reactive solutions were oversaturated with respect to aragonite making impossible to measure empirically the $\text{Log } D_{Ni}$ value at equilibrium. Nevertheless, following the linear trend in Eq. (6), it is possible to estimate $\text{Log } D_{Ni}$ values at $\text{SI}_{\text{aragonite}}=0$ assuming that this value reflects equilibrium conditions. In this case, using Eq. (6), it can be estimated that at equilibrium $\text{Log } D_{Ni} = -3.9$. Interestingly this value is significantly lower than theoretical estimates of $\text{Log } D_{Ni}$ at equilibrium that were earlier reported in the literature. Indeed, in the works by Wang and Xu (2001) and Böttcher and Dietzel (2010) the reported $\text{Log } D_{eq}$ values for Ni in aragonite of 0.46 and -0.26, respectively. The main difference between the values proposed by these two studies is likely due to the modelling approach of the $\text{Log } D_{Me}$ values. Böttcher and Dietzel (2010) used an approach correlating the solubility product of end-members to the distribution coefficient of trace metals in carbonate minerals. Although this model provides good estimation of elemental distribution during ideal solid-solution formation, its principal limitation lies in the assumption of similar crystal structure of end-members, which is not the case for example between NiCO_3 and aragonite crystallising in orthorhombic and trigonal system, respectively. On the other hand, Wang and Xu (2001) estimated $\text{Log } D_{Me}$ values by correlating the difference in the standard Gibbs free energy of formation, the difference in the standard non-solvation energy and the difference in ionic radius between the trace metal element and the host element (in our case Ni^{2+} and Ca^{2+} , respectively). This model considers element incorporation into incompatible end-member crystal structure, here aragonite, by accounting for the physical parameters of the trace metal and host elements. However, the equilibrium $\text{Log } D_{Ni}$ value calculated through this model (i.e. 0.46) is still far from the value estimated in this study (-3.9). A significant difference

between the values of this model and experimental values have for example already been shown in the case of Mg^{2+} incorporation in aragonite or for Sr^{2+} and Zn^{2+} incorporation in calcite (Rimstidt et al., 1998; Mavromatis et al., 2019, 2022).

Interestingly, the $\text{Log } D_{eq}$ value for Ni in calcite (i.e., 0.54) proposed by Wang and Xu (2001) is in closer agreement with several studies that measured the $\text{Log } D_{Ni}$ between various reactive solutions and calcite and reported values that are usually close to each other in a range of -0.4 to 0.3, for growth rate ranges approaching the ones investigated in this study (Munsel et al., 2010; Lakshtanov and Stipp, 2007; Alvarez et al., 2021). It is also interesting to note that the obtained results show a high dependence of $\text{Log } D_{Ni}$ on the $\text{Log } r_p$, while this was not observed by previous study on calcite (Lakshtanov and Stipp, 2007; Alvarez et al., 2021). Lakshtanov and Stipp (2007) explained this behaviour by the proximity of the equilibrium $\text{Log } D_{Ni}$ value to 0. According to their calculations, the high dependence of $\text{Log } D_{Ni}$ on $\text{Log } r_p$ could thus be partly explained by the important difference between the value of $\text{Log } D_{Ni,eq}$ (assumed to be close to -3.9) and the value towards which $\text{Log } D_{Ni}$ will tend when the growth rate increases (i.e., 0). This explanation is still open to discussion as very low $\text{Log } D_{Me+}$ values were already reported for monovalent elements highly incompatible with calcite (between -5.5 and -3.2 for both $\text{Log } D_{Li+}$ and D_{Na+} for example; Fuger et al., 2019) showing however a weaker dependence to growth rate compared to this observed for Ni in aragonite.

It is also interesting to compare the Ni^{2+} incorporation into calcite and aragonite with another highly hydrated element such as Mg^{2+} . Indeed, the $\text{Log } D_{Mg}$ at equilibrium has been experimentally estimated at -2.1 and -4.8 for calcite and aragonite, respectively (Mavromatis et al., 2013, 2022). This negative value of D_{Mg} for calcite is surprising because calcite and magnesite (MgCO_3) share the same crystal structure and Mg is therefore theoretically compatible with the structure of calcite. Mavromatis et al. (2013) showed that the factor driving this low value was in fact the dehydration rate of the aqueous Mg^{2+} . This rate is also

very low for aqueous Ni^{2+} and could partly explain, as in the case of Mg^{2+} , the low values of $\text{Log } D_{\text{Ni}}$ between reactive solution and aragonite at equilibrium (see Pokrovsky and Schott, 2002). Nevertheless, and in contrast to Mg^{2+} , the $\text{Log } D_{\text{Ni}}$ between reactive solution and calcite at equilibrium is characterized by a value higher than 1 (i.e., ~ 0.5 ; Lakshtanov and Stipp., 2007) indicating a compatibility of Ni^{2+} for the calcite structure. It thus appears that in addition to the lower rate of exchange of water molecules in the Ni^{2+} hydration sphere, another mechanism likely controls the incorporation of Ni^{2+} in the carbonate solid that is different to that affects incorporation of Mg^{2+} .

4.2. Cobalt incorporation in aragonite

Similar to Ni, Co incorporation in aragonite exhibits positive dependence on growth rate with an increase of ~ 0.3 orders of magnitude of $\text{Log } D_{\text{Co}}$ (from -1 to -0.7) for ~ 1.1 orders of magnitude of $\text{Log } r_p$ (-8.7 to -7.6 mol/m²/s) (Fig. 4B). Regarding the negative $\text{Log } D_{\text{Co}}$ values that increase towards zero at higher growth rate, the Co behaves as an incompatible element in aragonite in agreement with the absence of solid-solution between aragonite and CoCO_3 (sphaerocobaltite). Indeed, in its aquo form, Co^{2+} is mostly found in an octahedral configuration, although tetrahedral configurations are possible and both can also coexist for the same ligand (Cotton et al., 1988; Varadwaj and Marques, 2010). This octahedral configuration is also found in CoCO_3 mineral phase and the 9-fold coordination of Ca^{2+} in aragonite, therefore, does not appear to be favourable for a Co^{2+} substitution especially due its smaller ionic radius than Ca^{2+} (0.745 vs 1.00 Å in 6-fold coordination; Shannon, 1976). Furthermore, the low hydration Gibbs free energy of Co (i.e., -1915 kJ/mol; Marcus, 1991) associated to a low rate of water molecule exchange in its hydration sphere ($3.18 \times 10^6 \text{ s}^{-1}$; Lincoln and Merbach, 1995) tend to indicate an important affinity for the aqueous phase that

could also partially explain the low equilibrium $\text{Log } D_{Co}$ value estimated in this work (see Table 2). It is worth noticing that all these parameters (i.e., ionic radius, hydration Gibbs free energy, water exchange rate) are higher for Co than for Ni, similar to the equilibrium $\text{Log } D_{Co}$ and $\text{Log } D_{Ni}$ values estimated in this study. It is therefore likely that the differences between $\text{Log } D_{Ni}$ and $\text{Log } D_{Co}$ at equilibrium estimated in this work are, to some extent, the result of a positive correlation with these physical parameters. For example, the difference in $\text{Log } D_{Ni}$ and $\text{Log } D_{Co}$ observed could partially be explained by the difference in ionic radii between Co^{2+} and Ni^{2+} (0.745 vs 0.69 Å in 6-fold coordination, respectively; Shannon, 1976). The Co^{2+} is ~8% larger than the Ni^{2+} and thus close to the Ca^{2+} ionic radius, which agrees with the work of Okumura and Kitano (1986) showing that monovalent ions such as Na^+ , Li^+ , K^+ or Rb^+ seem to be incorporated into aragonite in greater quantity when their ionic radii are close to that of Ca^{2+} .

The obtained results also suggest a correlation between the $\text{Log } D_{Co}$ values and the $\text{SI}_{\text{aragonite}}$ values in our experiments. The $\text{Log } D_{Co}$ evolution as a function of SI of the reactive solution with respect to aragonite (Fig. 5B) can be numerically described by a linear regression under the form:

$$\text{Log } D_{Co} = 1.355 (\pm 0.222) \text{SI}_{\text{aragonite}} - 1.020 (\pm 0.032); R^2=0.79 \quad (7)$$

Using this equation, it is possible to calculate the $\text{Log } D_{Co}$ values corresponding to a $\text{SI}_{\text{aragonite}}=0$ and an estimation of a $\text{Log } D_{Co}$ close to equilibrium. This calculated equilibrium $\text{Log } D_{Co}$ value of -1 in aragonite is far lower to the previous calculations of 0.32 and 0.98 by Böttcher and Dietzel (2011) and Wang and Xu (2001), respectively. Beyond the differences between these two theoretical values that could be attributed to differences in calculation approach (see section 4.1), similar to Ni, the large discrepancy between theoretical and

experimental values underline the difficulties to accurately model the incorporation of trace element in non-isostructural end members. On the contrary, the predicted $\text{Log } D_{\text{eq}}$ value for Co in calcite (0.97; Wang and Xu, 2001) agrees with experimental results that previously determined a $\text{Log } D_{\text{Co}}$ between 0.3 and 0.9 (Lorens, 1981; Lee and Reeder, 2006). This $\text{Log } D_{\text{Co}}$ values difference between calcite and aragonite (i.e., calcite: $0.3 < \text{Log } D_{\text{Co}} < 0.9$ for $-7.3 < \text{Log } r_p < -5.3$ mol/m²/s; aragonite: $-1 < \text{Log } D_{\text{Co}} < -0.7$ for $-8.74 < \text{Log } r_p < -7.56$ mol/m²/s) can be explained by the formation of a solid-solution in the calcite-sphaerocobaltite system which does not occur in the aragonite-sphaerocobaltite system (Lorens, 1981; Reeder, 1996; Lee and Reeder, 2006; Katsikopoulos et al, 2008). In this sense, González-López et al. (2014) calculated that the replacement of Ca^{2+} for Co^{2+} in aragonite structure requires almost three times more energy compared to Co^{2+} incorporation into calcite, emphasizing the incompatibility of Co^{2+} for aragonite. However, in their experiment of Co co-precipitation with calcite, Katsikopoulos et al. (2008) showed that significant amounts of Co-bearing aragonite can be formed when the $\text{Co}^{2+}/\text{Ca}^{2+}$ ratios are higher than 0.1 in the reactive solution and even become the dominant phases when the $\text{Co}^{2+}/\text{Ca}^{2+}$ ratios become higher than 0.2. Thus, it seems that Co^{2+} bearing aragonite can be formed under certain conditions. Note however that to our knowledge, no study has yet provided results on the coordination of Co^{2+} in such Co-bearing aragonite.

Finally, it is worth noting that the dependence of $\text{Log } D_{\text{Co}}$ on $\text{Log } r_p$ is much lower than for $\text{Log } D_{\text{Ni}}$ (slope of 0.312 ± 0.047 and 1.247 ± 0.152 , respectively; see Eqs (4) and (5)). In fact, at the same range of growth rate (i.e., $-8.74 < \text{Log } r_p < -7.56$ mol/m²/s), the $\text{Log } D_{\text{Co}}$ values are systematically higher than the $\text{Log } D_{\text{Ni}}$, considering the high dependence of $\text{Log } D_{\text{Ni}}$ on the $\text{Log } r_p$ this trend will probably be reversed for $\text{Log } r_p$ higher than -6.2 mol/m²/s. Following the calculations proposed by Lakshatanov and Stipp (2007) for $\text{Log } D_{\text{Ni}}$, the lower dependence of $\text{Log } D_{\text{Co}}$ to $\text{Log } r_p$ would imply an equilibrium value of $\text{Log } D_{\text{Co}}$ closer to 0

than for $\text{Log } D_{Ni}$. This extrapolation seems likely regarding the large differences between $\text{Log } D_{Co}$ and $\text{Log } D_{Ni}$ values recorded at low $\text{Log } r_p$ but remains open to discussion.

4.3. Mechanisms of Ni and Co incorporation in aragonite

The modelling of trace metal incorporation in carbonate minerals is of great importance for assessing environmental conditions of mineral formation and so far, two models have been extensively used in the literature to describe this process. The growth entrapment model (GEM) developed by Watson (Watson and Liang 1995; Watson, 1996; 2004), can likely qualitatively explain the dependence of distribution coefficients on growth rate observed in this study. In fact, it has been previously used to describe the incorporation of both mono- and divalent foreign elements (such as Mg^{2+} , Ba^{2+} , Li^+ , Na^+) in CaCO_3 (e.g., Gabitov et al., 2008, 2011, 2021; Mavromatis et al., 2013, 2018; Fuger et al., 2019; Goetschl et al., 2019). This model proposes an enrichment or depletion of the trace element in a structurally distinct solid near surface region between the mineral and the bulk reactive solution. The extent of enrichment or depletion deviates from near equilibrium values when diffusivity of ions in this near surface region is lower (or less effective) than crystal growth rate (and hence the rate of incorporation of traces in the freshly precipitated mineral layer). This model, therefore, implies that despite the absence of solid solution formation between the two end members considered here, the incorporation of incompatible elements remains possible and comes in agreement with many studies that have explored this topic experimentally (e.g. Gabitov and Watson, 2006; Tang et al., 2008; Mavromatis et al., 2018; Fuger et al., 2019; Goetschl et al., 2019).

Another mechanistic way to describe the incorporation of trace elements in carbonates as function of growth rate is provided by the surface reaction kinetic model (SRKM) of

DePaolo (2011). This model considers only the aqueous phase at which mineral grow and treats the deviation from equilibrium conditions of the end-member carbonate minerals in order to correlate distribution coefficients with growth rate making use of the expression:

$$D_{Me} = \frac{D_f}{1 + \frac{R_p}{r_p + R_b} \left(\frac{D_f}{D_{eq}} - 1 \right)} \quad (8)$$

where the D_{Me} represents the distribution of the trace metal between the reactive solution and aragonite, the D_{eq} represents distribution under equilibrium conditions, R_b stands for the dissolution rate of aragonite, r_p denotes growth rate and D_f the forward kinetic distribution coefficient.

Here we make an effort to fit this theoretical model in our experimental findings. In Table 3 three scenarios are presented that fit different combinations of the parameters R_b , D_{eq} and D_f of Eq. (8). Note here that R_b , i.e. the dissolution rate of aragonite at far from equilibrium conditions should be considered as a constant during the application of Eq. (8). A closer look in the literature however suggests significant variations in the R_b value. For example, Chou et al. (1989) propose a $R_b = 10^{-5.9}$ mol/m²/s at pH~6.2, whereas under the same pH conditions Cubillas et al. (2005) proposed a value of $10^{-6.3}$ mol/m²/s. This half an order of magnitude difference likely stems from the estimation of surface area in the dissolving mineral phase. Indeed, in their work, Chou et al. (1989) estimated the specific surface area from grain geometry, an approach that can lead to high uncertainties. Consequently, the value proposed by Cubillas et al. (2005), and calculated using a BET measured specific surface area, was chosen for the scenarii 1 and 2 (see Figs. 6A and 6B). The D_{eq} values for Ni and Co were taken from Eqs. (6) and (7) at $SI_{aragonite} = 0$ as $10^{-3.9}$ and 10^{-1} , respectively, and were used for the Scenarii 1 and 3. The D_f values were fit to the data and took values equal to 0.05 and 0.6 for Ni and Co, respectively, in Scenarii 1 and 3 as they are representing the values of the best fit in our Scenario 3 (see Fig. 6C). From these three

scenarii it can be observed that the experimental data measured in this study are far from the trend proposed by the model independently of the D_{eq} or D_f chosen. Actually, best fits to the SRKM model are provided when the R_b value is modified. Interestingly, a similar R_b value to that for Co (i.e., $10^{-7.8}$) was determined to fit the Mg incorporation data of Mavromatis et al. (2022), that used the same material as in this study, with the SRKM model. Surprisingly, all these values (see the column “best fit” in the Table 3) are far lower than the one proposed by Cubillas et al. (2005) and notably they are different between the two sets of experiments performed with Ni and Co in this study. Similar deviations during the fit of SRKM model to calcite have also been reported in the literature (e.g. Farmer et al., 2019; Mavromatis et al., 2020; Füger et al., 2022). A possible explanation for the observed deviation during the fitting of Eq. (8) in the experimental data, can be assigned to inhibition effect of Ni and Co on the dissolution rate of aragonite, as it was already showed by Gutjahr et al. (1996) for Zn, Cu, Sr or Ba. It is however highly unlikely that the very low concentrations of both Ni and Co in our reactive solutions could explain differences up to ~3.3 orders of magnitude between the values proposed by Cubillas et al. (2005) and the values needed to fit our data using the SRKM model. Furthermore, Gutjahr et al. (1996) observed that the presence of Mg does not affect the dissolution rate of aragonite and regarding the R_b value needed to fit the experimental Mg data with the model, it tends to indicate that the SRKM model is probably not suitable to explain the incompatible trace metals in aragonite.

On a different approach, Teng et al. (2000) highlighted the importance of defects (e.g., vacancies, dislocations, stacking faults, precipitates or collection of vacancies) and of their structures as a mineral growth starting point. They also showed that the growth mechanisms at calcite surface are related to the saturation state (i.e., Ω) of the reactive solution. It appears that for low supersaturation state between 0 and 0.8 (i.e., $SI = 0$ to 0.35), growth occurs mainly by steps that are initiated only at dislocations, crystal imperfections or

grain boundaries. But when the supersaturation state is higher than 0.8 (i.e., $SI > 0.35$) surface nucleation processes can also occur (Teng et al., 2000). Consequently, the increase of the saturation state of the reactive solution is an important driver of new defects site formation in the freshly precipitated material leading to a defect density increase. The positive correlation between $\text{Log } D_{Ni}/D_{Co}$ and the saturation of the reactive solution with respect to aragonite observed in this study (see Figs. 5A and 5B) tend thus to indicate that Ni and Co incorporation is closely related to the amount of defect sites. This was incidentally one of the conclusions of Busenberg and Plummer (1985) to explain the positive correlation between the growth rate and the Na^+ incorporation in calcite. The saturation indices of the reactive solutions with respect to aragonite in this study being comprised between 0.02 and 0.28, it seems logical that we were unable to observe nucleation on the mineral surfaces. Even if it is difficult to describe the growth as a spiral in our SEM images, a growth by steps is visible consisting of several successive steps layers that do not show the same geometry in all directions of the growth planes. Indeed, the lateral edges of the steps show relatively linear geometries while the direction towards which the steps seem to grow show more sinuous borders suggesting a bonding anisotropy generating a high kink density (De Yoreo and Vekilov, 2003). These rough steps are known to form mostly weak bonds and to grow 10 times faster than smooth steps for the same saturation rate. They, therefore, seem to be the main drivers of mineral growth and potentially efficient entrappers of incompatible elements in aragonite such as Ni and Co. An alternative hypothesis is that Ni and Co are not incorporated as traces in aragonite but under the form of Ni or Co bearing mineral phases nanodomains. Indeed, this was one of the conclusions of Finch and Allison (2007) in their study about Mg coordination in aragonite. Further studies by EXAFS spectroscopy would be valuable to determine precisely the location of Ni and Co in aragonite.

4.4. Implications for natural environment

Both Ni and Co are of high societal importance due to their deleterious effect on the environment. Nickel is for example toxic to many marine species (see Gissi et al., 2016) and notably to *Acropora Muricata* corals which have shown signs of health deterioration (e.g., bleaching due to loss of *Symbiodinium*) when Ni^{2+} concentrations in the aqueous medium are high (i.e., $>200 \mu\text{g/L}$) (Gissi et al., 2019). Beyond its effects on their health, it also appears that Ni is stored in corals at various concentrations depending on the type of biological material that decreases from zooxanthellae to tissue and finally skeleton. This accumulation appears to be species dependent and Denton and Burdon-Jones (1986) have shown, for example, that octocorallian corals (soft corals, $<0.92 \mu\text{g/g}$) show higher average values than the scleractinian corals (hard corals, $<0.56 \mu\text{g/g}$). Moreover, Reichelt-Bruschette and McOrist (2003) showed a greater variation in skeletal Ni concentrations between 0.05 and 249 $\mu\text{g/g}$ in corals collected from the Great Barrier Reef in agreement with results reported by Gillmore et al. (2020). Although limited amount of data are available, similar values have been reported in stalagmite aragonite from Hüttenbläuserschachthöhle in Germany showing Ni concentrations of 0.37 $\mu\text{g/g}$ and for six inactive aragonite stalactites (2 to 8 $\mu\text{g/g}$) from the Pierre Saint-Martin cave in the Pyrenees (France) (Ortega et al 2005; Jochum et al., 2012). These recorded concentrations of Ni in both biotic and abiotic aragonite imply that, despite its incompatibility, this metal can be incorporated in aragonite. Regarding our results, it appears thus possible that $\text{Log } D_{\text{Ni}}$ can be used as a tracer of fluid saturation state and of mineral growth rate specially in the case of abiotic aragonite. This application has however to be taken with caution because of potential spatiotemporal variability of aqueous Ni and Co concentrations in natural environment, as well as, because Ni forms aqueous complexes with organic and inorganic ligands (e.g. Cl^- , SO_4^{2-}) that have to be considered during estimation of

D_{Ni} values in natural samples. For coralline aragonite, the application of our findings must be used even more carefully as the vital effects are not constrained for Ni incorporation and are likely species dependent. Thus, incorporation of Ni into biotic and abiotic aragonite also provides an opportunity to follow up on the work of Alvarez et al. (2021) who showed that Ni incorporation into calcite and the associated isotope fractionation contributed to the resolution of the Ni imbalance in the ocean. In fact, aragonite being the second most abundant calcium carbonate polymorph, it likely plays an important role in the global oceanic Ni cycle despite the small amount of Ni it can incorporate.

Similar to Ni, cobalt has important detrimental effects on marine calcifiers as it was for example noticed on a coccolithophoridae specie (*Cricosphaera carterae*) showing a decrease or even a stop in cell division when Co solution concentration is high ($>100 \mu\text{M Co}$; Blankenship and Wilbur, 1975). Biscéré et al. (2015) also showed that Co can reduce the calcification rate of some corals up to 70 % by inhibiting photosynthetic efficiency and can be incorporated in their biological tissues. Veeh and Turekian (1968) measured very low Co concentrations (between 0.001 and 0.012 $\mu\text{g/g}$) in corals from Hawaii, while Anu et al. (2007) showed that cobalt is predominantly incorporated in the skeleton (values comprised between 0.79 and 9.82 $\mu\text{g/g}$) compared to soft tissue on the five corals species they studied from Lakshadweep Archipelago. To our knowledge, no study has investigated the presence of cobalt in inorganic aragonite. Beyond these results, which highlight the incorporation of cobalt into biogenic aragonite despite its theoretical incompatibility, it appears that aragonite can play an important role in the remediation of cobalt. Indeed, Barber et al. (1975) highlighted the potential of cobalt as an inhibitor of calcite formation when concentration in solution is higher than $5 \times 10^{-3} \text{ mol/L}$. A similar effect was also shown by Wada et al. (1995) who demonstrated a correlation between the Co concentration of solutions ($\text{Co}^{2+}/\text{Ca}^{2+}$ ratios ranging from 3.3×10^{-2} to 0.5) and the amount of aragonite precipitated. It appears that in the

case of high Co concentration solutions, aragonite precipitation is favoured and can thus play an important role in Co^{2+} remediation. Furthermore, Katsikopoulos et al. (2008) also showed that in the case of highly concentrated Co solutions, Co-bearing aragonite phases were formed despite the absence of solid solution between aragonite and sphaerocobaltite. Thus, even if a small amount of Co is incorporated into aragonite compared to calcite (e.g., Lee and Reeder, 2006), the formation of aragonite appears to be favoured by the presence of Co^{2+} and therefore appears to have potential in the purification of highly cobalt enriched solutions.

5. Conclusion

The experiments carried out in this study have shown for the first time that Ni and Co can be incorporated in a small amount into abiotic aragonite overgrowths. These incorporations follow the classical behaviour of elements incompatible with the structures of the host mineral showing an increase in distribution when the growth rate increase. This incompatibility tends to indicate an absence of solid-solutions formations in the gaspeite-aragonite and sphaerocobaltite-aragonite systems likely resulting from the smaller ionic radius of Ni^{2+} and Co^{2+} than Ca^{2+} making difficult to fulfil the 9-fold coordination of aragonite in case of ion-to-ion substitution. A strong difference in dependence was however observed between $\text{Log } D_{\text{Ni}}$ vs $\text{Log } r_p$ and $\text{Log } D_{\text{Co}}$ vs $\log r_p$ potentially related to their physical and chemical properties such as ionic radius, hydration energy, and rate of water exchange in their hydration shells. A high dependence was also recorded between $\text{Log } D_{\text{Ni}} / D_{\text{Co}}$ and the SI of the reactive solution with respect to aragonite. Based on our results it seems that the equilibrium $\text{Log } D_{\text{Ni}}$ and $\text{Log } D_{\text{Co}}$ values (i.e., estimated from $\text{SI}=0$) are at least inferior to -3.9 and -1, respectively, which is far below the values previously proposed in the literature. In both cases, the important dependences of their distribution values with the

growth rate and with the SI of the reactive solution with respect to aragonite suggest that they can both be considered as proxies of these two parameters.

It appears that the evolutions of the $\text{Log } D_{\text{Ni}} / D_{\text{Co}}$ values as a function of the $\text{Log } r_p$ recorded in this study require important modifications of the dissolution rate value of aragonite in order to be modelled with the Surface Reaction Kinetic Model (SRKM). The incorporation of Ni^{2+} and Co^{2+} is likely related to the defect site of the aragonite crystals. As the supersaturation increases, the number of defects in the freshly formed mineral is assumed to increase, which agrees with the positive correlation observed between the $\text{Log } D_{\text{Ni}} / \text{Log } D_{\text{Co}}$ and the SI of the reactive solution with respect to aragonite. Furthermore, the collected SEM images of the solids highlight the formation of rough step, which are likely the main driver of crystal overgrowth and thus of Ni^{2+} and Co^{2+} incorporation. Despite these results, the form under which Ni and Co are incorporated into aragonite is still debatable and new analyses, in particular EXAFS, would be necessary to improve our understanding of their incorporation processes.

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Figure captions

Fig. 1. Experimental setup.

Fig. 2. Scanning electron microscope (SEM) images of (A) the aragonite seeds used in this study, (B) overgrowth aragonite from experiments NiAr-6, and (C) overgrowth aragonite from experiments CoAr-4.

Fig. 3. Example of Ca, Ni and Co concentrations of the reactive fluid for experiments NiAr-17 and CoAr-11.

Fig. 4. Dependence of (A) $\text{Log } D_{\text{Ni}}$ and (B) $\text{Log } D_{\text{Co}}$ on Log aragonite growth rate (r_p). The describing equations are given in the text as Eqs. 4 and 5, respectively.

Fig. 5. Dependence of (A) $\text{Log } D_{Ni}$ and (B) $\text{Log } D_{Co}$ on SI of the fluid with respect to aragonite. The describing equations are given in the text as Eqs. 6 and 7, respectively.

Fig. 6. Experimental D_{Ni} and D_{Co} (blue diamond) plotted against log rate and comparison with the SRKM model predictions (red line). The parameters used for the SRKM model are given in Table 2.

Table captions

Table 1. pH at steady state, Ni/Ca and Co/Ca ratio in the precipitated solids, saturation indices of the reactive solutions with respect to aragonite at steady state ($SI_{\text{aragonite}}$), growth rate ($\text{Log } r_p$), distribution coefficient of Ni and Co between the fluid and aragonite calculated from activities of free ions (D_{Ni} and $\text{Log } D_{Ni}$, and D_{Co} and $\text{Log } D_{Co}$) and from total Ni and Co concentration (D^*_{Ni} and $\text{Log } D^*_{Ni}$, and D^*_{Co} and $\text{Log } D^*_{Co}$).

Table 2. Values of the ionic radius in 6- and 9-fold coordination, of the hydration Gibbs free energy and of the rate of water molecule exchange at 298 K under aquo ion form for Ca^{2+} , Ni^{2+} and Co^{2+} .

Table 3. Values of $\text{Log } R_b$, $\text{Log } D_{eq}$ and D_f chosen for the three scenarii performed to fit our experimental D_{Ni} and D_{Co} data with the SRKM model. The best fit parameters are given in the third columns.

Table A.1. Calcium, Ni, Co and Mg concentration in the reactive solutions at steady state and saturation indices of the reactive solutions with respect to calcite, Ni(OH)₂, NiCO₃, NiO, CoCO₃, Co(OH)₂ and CoO at steady state.

Table A.2. Complexation reactions involving Ca²⁺-Ni²⁺-Co²⁺ relevant with this study and their associated stability constant (Log K) at 25°C and 0 ionic strength as given in the MINTEQ.V4 database.

Table A.3. Calcium, Ni, Co and Mg concentrations of the inlet solutions, amount of seed in the reactors at the beginning of each experiment, duration of experiments, total flow rate, and Ca, Ni, Co and Mg concentration in the reactive solution at t=0 and at steady state.

Table 1:

Experiments	pH	Ni/Ca _{aragonite} (mmol/mol)	SI _{aragonite}	Log r_p (mol/m ² /s)	D_{Ni}	Log D_{Ni}	D_{Ni}^*	Log D_{Ni}^*
NiAr-1	6.19	0.0003	0.04	-9.09	6.8E-05	-4.2	4.4E-05	-4.4
NiAr-2	6.27	0.0065	0.17	-7.95	1.6E-03	-2.8	1.0E-03	-3.0
NiAr-3	6.27	0.0129	0.16	-8.32	3.0E-03	-2.5	2.0E-03	-2.7
NiAr-4	6.28	0.0176	0.20	-7.58	4.7E-03	-2.3	2.9E-03	-2.5
NiAr-5	6.27	0.0521	0.20	-7.83	1.4E-02	-1.9	8.6E-03	-2.1
NiAr-6	6.32	0.0201	0.20	-7.82	4.8E-03	-2.3	3.0E-03	-2.5
NiAr-13	6.21	0.0015	0.05	-8.75	3.5E-04	-3.5	2.4E-04	-3.7
NiAr-14	6.25	0.0248	0.11	-8.17	6.0E-03	-2.2	4.1E-03	-2.4
NiAr-15	6.23	0.0010	0.03	-8.60	2.3E-04	-3.6	1.6E-04	-3.8
NiAr-16	6.25	0.0113	0.10	-8.27	2.6E-03	-2.6	1.8E-03	-2.8
NiAr-17	6.29	0.0166	0.17	-7.88	4.1E-03	-2.4	2.8E-03	-2.6
NiAr-18	6.37	0.0481	0.24	-7.65	1.2E-02	-1.9	7.9E-03	-2.1
NiAr-20	6.32	0.0220	0.14	-7.67	6.0E-03	-2.2	3.9E-03	-2.4
NiAr-21	6.34	0.0196	0.15	-7.74	5.3E-03	-2.3	3.4E-03	-2.5
NiAr-22	6.36	0.0242	0.20	-7.61	6.5E-03	-2.2	4.0E-03	-2.4
NiAr-23	6.32	0.0349	0.21	-7.45	1.1E-02	-2.0	6.6E-03	-2.2
NiAr-24	6.34	0.0427	0.21	-7.46	1.2E-02	-1.9	7.8E-03	-2.1

Experiments	pH	Co/Ca _{aragonite} (mmol/mol)	SI _{aragonite}	Log r_p (mol/m ² /s)	D_{Co}	Log D_{Co}	D_{Co}^*	Log D_{Co}^*
CoAr-1	6.19	0.0560	0.02	-8.74	1.0E-01	-1.0	1.8E-02	-1.8
CoAr-2	6.23	0.0877	0.13	-8.02	1.8E-01	-0.8	3.0E-02	-1.5
CoAr-3	6.21	0.0541	0.08	-8.40	1.0E-01	-1.0	1.7E-02	-1.8
CoAr-4	6.28	0.1058	0.25	-7.61	2.2E-01	-0.7	3.8E-02	-1.4
CoAr-5	6.26	0.0779	0.18	-7.92	1.5E-01	-0.8	2.6E-02	-1.6
CoAr-6	6.30	0.0881	0.24	-7.73	1.9E-01	-0.7	3.2E-02	-1.5
CoAr-7	6.23	0.0764	0.05	-8.29	1.3E-01	-0.9	2.3E-02	-1.6
CoAr-8	6.23	0.0744	0.04	-8.19	1.2E-01	-0.9	2.2E-02	-1.7
CoAr-9	6.23	0.0637	0.07	-8.56	1.0E-01	-1.0	1.9E-02	-1.7
CoAr-10	6.24	0.0575	0.07	-8.22	9.8E-02	-1.0	1.8E-02	-1.7
CoAr-11	6.23	0.0724	0.07	-8.00	1.3E-01	-0.9	2.2E-02	-1.6
CoAr-12	6.29	0.1086	0.21	-7.56	2.1E-01	-0.7	3.5E-02	-1.5

Table 2:

Ions	Ionic radius CN=6 (Å)	Ionic radius CN=9 (Å)	Hydration Gibbs free energy (kJ/mol)	Rate of water molecule exchange at 298 K under aquo ion form (s⁻¹)
Ca²⁺	1.00 [*]	1.18 [*]	-1505 ^{**}	~10 ^{9***}
Ni²⁺	0.69 [*]	n.d.	-1980 ^{**}	3.15 x 10 ^{4***}
Co²⁺	0.745 [*]	n.d.	-1915 ^{**}	3.18 x 10 ^{6***}

* Shannon, 1976

** Marcus, 1991

*** Lincoln and Merbach, 1995

n.d. = no data

Table 3:

	Scenario 1		Scenario 2		Scenario 3 (Best fit)	
	Ni	Co	Ni	Co	Ni	Co
Log R_b	-6.3*	-6.3*	-6.3*	-6.3*	-9.6	-7.8
Log D_{eq}	-3.86**	-1.02**	-3	-1.2	-3.86**	-1.02**
D_f	0.05	0.6	0.5	1	0.05	0.6

*From Cubillas et al., 2005

**Calculated from Eqs. (6) and (7) of this work considering SI=0