NICKEL ISOTOPE FRACTIONATION AS A FUNCTION OF CARBONATE GROWTH RATES DURING NI COPRECIPITATION WITH CALCITE

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Abstract

The fractionation of Ni isotopes during Ni coprecipitation with calcite was measured at pH = 6.2 and pCO₂ = 1 atm as a function of calcite growth rate. Light Ni isotopes are preferentially incorporated into calcite during its coprecipitation, which is likely due to a longer Ni-O bond length in calcite compared to that of the Ni aquo complex. The extent of Ni isotope fractionation between Ni in the solid and the aqueous fluid phase increases from -0.3 to -0.9 ‰ as the calcite growth rate slows from 10^{-7.3} to 10^{-8.3} mol m⁻² s⁻¹. This behaviour can be attributed to the strong hydration of the Ni²⁺ aqueous ion. As mineral growth rates depend strongly on the degree of supersaturation of the fluid relative to the mineral, the results of this study suggest that the Ni isotopic composition of natural calcite can potentially provide insight into the saturation state of seawater with respect to calcite at the time that this mineral formed. In addition, calculations based on our results suggest that the incorporation of Ni into calcite could be a significant sink of light Ni in the ocean.

1. INTRODUCTION

A large number of past studies have focused on the composition of divalent cations substituted for Ca in calcite and aragonite (Lorens, 1981; Mucci and Morse, 1983; Tesoriero and Pankow, 1996; Lakshtanov and Stipp, 2007; von Allmen et al., 2010). The motivation for such efforts stems from the potential use of the divalent metal compositions of calcium carbonates as proxies of past environmental conditions. Notably as divalent cations substitute for Ca, they record information on the composition of the reactive fluid from which they precipitated (Mavromatis et al. 2013, 2020; Rodler et al. 2015).

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35 The influence of calcite growth rates on the isotope fractionation of divalent metals have
36 also been investigated for its potential application in paleoceanography (Lemarchand et al., 2004;
37 Tang et al., 2008; Böhm et al., 2012; Schott et al., 2014; AlKhatib and Eisenhauer, 2017;
38 Mavromatis et al., 2019). Indeed, as the rate of attachment of lighter isotopes to growing crystals
39 is faster than that of the heavier isotopes, the isotopic signatures of divalent trace elements in
40 marine calcites can provide insight into calcite growth rate, the saturation state of seawater
41 relative to this mineral and, potentially, the associated $p\text{CO}_2$ at the time of this mineral's
42 precipitation. Interestingly, whereas the extent of isotope fractionation of Sr and Ba (Tang et al.
43 2008; Böhm et al. 2012; Mavromatis et al. 2020) increases with increasing calcite growth rates,
44 that of Mg decreases (Mavromatis et al. 2013). This behavior has been attributed to the
45 differences in the desolvation rates of these metals relative to Ca^{2+} (Mavromatis et al., 2013). Note
46 that whereas the Sr^{2+} and Ba^{2+} desolvation rates are similar to that of Ca^{2+} , the Mg^{2+} desolvation
47 rate is nearly 4 orders of magnitude slower. This results in the incorporation of partially hydrated
48 Mg cations into rapidly growing calcite. As a consequence, less isotope fractionation is observed
49 between aqueous Mg and the Mg incorporated into calcite as calcite growth rates increase
50 (Mavromatis et al., 2013). It seems, therefore, that by measuring the isotopic compositions of two
51 or more of its divalent metals exhibiting contrasting fractionation behaviors further constraints on
52 the chemical environments in which marine calcites formed could be obtained.

53 The Ni^{2+} aquo ion has the slowest exchange rate of water molecules in its hydration sphere
54 among the divalent metals. This exchange rate is ~ 5 orders of magnitude slower than that of
55 Ca^{2+} . As with the case of Mg^{2+} , it seems likely that the isotopic fractionation of Ni^{2+} during its
56 incorporation into the calcite structure will have a distinct and strong dependence on calcite
57 growth rates. The Ni isotope signatures of marine calcites, therefore, have the potential to be a
58 useful proxy of these rates. Evaluation and calibration of this potential proxy requires the
59 quantification Ni isotope fractionation during its coprecipitation with calcite and the dependence
60 of this fractionation on calcite growth rates. The present study presents the first experimental
61 investigation of Ni isotope fractionation between aqueous fluids and abiotic calcite as a function
62 of its growth rate at Earth's surface conditions. The results of this study show a clear and
63 systematic variation of the Ni isotopic composition as a function of the calcite growth rate,
64 demonstrating the potential of Ni isotope compositions to illuminate the ocean saturation state
65 with respect to calcite and $p\text{CO}_2$ at the time of mineral formation.

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67 2. MATERIAL AND METHODS

2.1 Experimental design

The experiments performed in this study were designed to measure Ni partition coefficients (D_{Ni}) and the isotopic fractionation ($\Delta^{60}\text{Ni}_{\text{calcite-fluid}}$) between calcite and its co-existing aqueous fluid by growing Ni-bearing calcite onto calcite seeds. Experiments were performed in mixed flow reactors using the constant addition method, as described in Tesoriero and Pankow (1996) with a few adaptations (see Fig. 1). In this method, the precipitation of Ni bearing calcite is induced by adding two separate aqueous fluids to the reactors, one containing Ni and Ca ions and the other containing carbonate ions. When these two fluids are pumped into the reactor, their mixing leads to calcite supersaturation in the aqueous reactor fluid resulting in the growth of Ni bearing calcite on the calcite seeds. The degree of calcite supersaturation, and consequently the calcite growth rates were modified by varying the inlet fluid flow rates, the calcium and carbonate concentrations of the injected fluids, and the mass of calcite seeds present initially in the reactor. Three modifications to the Tesoriero and Pankow (1996) experimental design were made in this study. First, a peristaltic pump was used to inject fluid into the reactors. Second, Ni was added to the injected fluids at the beginning of the experiments without having first reached steady-state reactor fluid concentrations. Third, Ni was added to the reactor fluid in some of the experiments before the pumping of the fluids began.

Synthetic high purity Merck EMSURE® calcite was used as seed material in all experiments. This calcite had a surface area of $0.28 \pm 0.03 \text{ m}^2/\text{g}$ as determined by triple-point krypton adsorption according to the BET method (Brunauer et al. 1938), using a Quantachrome Autosorb-1MP instrument. Scanning Electron Microscope (SEM) images were obtained of this initial calcite using the JEOL JSM 6700F spectrometer at the Raimond Castaing Center for Microcharacterization in Toulouse, France. These SEM images show the rhombohedral morphology of the initial calcite crystals, as well as intergrowth and agglomeration. The average length of the calcite crystals was about $6 \text{ }\mu\text{m}$. The composition of these calcite seeds was determined by digestion in concentrated HCl followed by analysis of the resulting fluid by Atomic Absorption Spectrometry. The Ni concentrations of these fluids was below the detection limit of the analyses, such that the Ni concentration of the seeds was negligible compared to that of the calcite precipitated in the growth experiments.

All aqueous solutions used in this study were prepared using high purity (>99 %) reagents and deionized MQ water (resistivity $18.2 \text{ M}\Omega \text{ cm}^{-1}$) obtained from a Millipore system. All acids used during the experiments were double-distilled, and all used commercial reagents were either suprapure or normapure grade. The aqueous Ni stock solution used during this study was prepared by dissolving Sigma-Aldrich, 99.99 %, trace metal basis $\text{Ni}(\text{NO}_3)_2$ to obtain a 10,000 ppm Ni solution.

Each experiment was begun by first making a pre-equilibrated aqueous fluid prepared by adding approximately 2 g of calcite seeds to a 0.2 mol/kg NaCl aqueous fluid and while bubbling the fluid with 1 atm CO_2 for 12 hours. The equilibrated fluid was then separated from the calcite using a Merck Millipore $0.2 \text{ }\mu\text{m}$ Teflon syringe filter. The pre-equilibrated aqueous fluid then was added together with new calcite seed crystals to a Nalgene polycarbonate reactor. The mass of these initial calcite seed crystals ranged from 0.75 to 4 g. The initial aqueous fluid and the calcite seeds were then allowed to equilibrate overnight while bubbling 1 atm pure CO_2 in the reactor fluid. This assured the mineral-fluid system was close to equilibrium prior to starting the fluid flow. After this equilibration step, the two inlet fluids were injected into the reactor at constant rates. The two inlet fluids used during the flow experiments consisted of 1) a CaCl_2 and $\text{Ni}(\text{NO}_3)_2$ bearing aqueous solution and 2) a Na_2CO_3 bearing aqueous solution. The CaCl_2 and NaCO_3 concentrations of these inlet fluids ranged from 0.06 to 0.2 mol/kg, and the concentration of Ni ranged from 4.8 to 28 ppm. The inlet fluid Ca and Ni concentrations for the experiments are provided in Table 1. The aqueous Ni concentration was kept as low as possible while taking into account the requirements of the isotope measurements, namely that at least 600 ng of Ni was present in all collected fluid samples. Moreover, the Na/Ni ratio of the sampled aqueous fluids was kept lower than 20 so not to hamper the subsequent Ni chemical separation procedure based on ion exchange chromatography. Consequently 2.6 mg of a sampled 0.2 M NaCl fluid must contain at least 600 ng of Ni.

The total ionic strength of the inlet fluids was fixed to 0.2 mol/kg to be consistent with that of the initial reactive fluid; to adjust their ionic strength, NaCl was added to these fluids. The two inlet fluids were pumped into the reactor at equal flow rates using a peristaltic pump. The flow rates ranged from approximately 10 to 40 g/day depending on the experiment; these fluid flow rates were regularly verified during each experiment by weighing the inlet fluid reservoirs. The mass of aqueous fluid in the reactor was kept constant by removing a volume of aqueous fluid

equal to that added each 24 hrs (or 48 hrs in the case of slower growth rate experiments), so that the fluid volume in the reactor varied by less than 10 % throughout the experiments.

In some coprecipitation experiments, a small volume of the aqueous Ni stock solution was added to the reactive fluid in the reactor at the beginning of the experiments. This was done to accelerate the attainment of steady-state Ni concentrations in the reactor fluid. The concentration of Ni added to each reactor at the beginning of an experiment was determined by modeling the Ni concentration at steady state from the experimental parameters and assuming that the distribution coefficient, D_{Ni} , equaled 1 (Lakshtanov and Stipp 2007). Preliminary experiments showed that there was no effect of adding Ni at the beginning of the experiment on the reactive fluid Ni concentration or on the isotopic composition of the Ni in these fluids at steady state.

The reactor temperature was kept at 25 ± 2 °C using a Fisher thermostatic bath. The calcite seeds were kept in suspension using a Teflon floating stirring bar, which prevents grinding of the calcite against the bottom of the vessel. Fluid pH and alkalinity were maintained at constant values by constantly bubbling pure CO₂ through the reactor. To minimize evaporation during the experiments, the CO₂ gas was passed through a 0.2 M NaCl solution before entering the reactor – see Fig. 1.

Figure 1 Schematic illustration of the experimental design used for the coprecipitation experiments. The reactor was placed in a thermostatically controlled vessel and the aqueous reactor fluid was mixed using a suspended stirring bar. A constant CO₂ partial pressure of 1 atm was achieved by bubbling pure CO₂ into the reactor. Inlet fluids were pumped into the reactor at a constant rate using a peristaltic pump.

Fluids were regularly sampled from the reactor to monitor reaction progress. To avoid removing calcite from the reactor during the experiments, stirring was stopped to allow the solids to settle for a few minutes prior to aqueous fluid sampling. Sampled fluids were immediately filtered through a 0.22 µm Merck Millipore Teflon syringe filter. Three sub-samples were taken: one for alkalinity determination, one for dissolved element concentration measurement, and one for nickel isotopic composition analysis. The fluids collected for elemental and for isotopic analysis were acidified shortly after sampling, using double distilled HNO₃ for the bulk chemical composition analysis or using distilled HCl for the isotopic analysis.

Pumping of the input fluids was continued until a steady state fluid composition was attained in the reactor. At steady state, the addition of calcium and nickel via inlet fluid injection is equal to that precipitated as calcite, so the composition of the reactor fluid remains constant. The pH, alkalinity, aqueous Ca and Ni concentrations were measured regularly and used to verify the attainment of steady state. Steady state was considered to be reached once three consecutive measurements of the sampled fluids compositions remained constant within analytical uncertainty. Once steady state was confirmed the experiments were stopped. The duration of the experiments ranged from 8 to 21 days.

At the end of each experiment the solids were separated from the reactor fluid via suction filtration using a 0.22 µm Teflon filter (Millipore). The solids were rinsed with water to remove any Ni adsorbed on the calcite surface and allowed to dry at room temperature. To verify the precipitation of calcite during the experiments, the collected solids were examined by X-ray Diffraction (XRD) and SEM. XRD analyses were performed using an INEL CPS-120 diffractometer with Co K α -radiation having a detection limit of ~5 %. The obtained diffraction patterns were compared to the characteristic profile for calcite taken from the RRUFF database (Lafuente et al. 2016). A representative XRD pattern of the reaction products is provided in the Supplementary Material. After these analyses, the total mass of collected solids were dissolved using 4 M HCl, which generated a homogeneous fluid sample used for further analyses.

2.2 Chemical analysis of the fluid phases

The alkalinity of collected fluids was measured shortly after sampling via 0.05 M HCl acidimetric titration using a Schott TA 10 plus volumetric automatic titrator. The measurements were performed following the Gran method (Stumm, 1996) and had an uncertainty of ± 1 % with a detection limit of 5×10^{-5} eq/l. The pH of the reactor fluids was measured in situ using a Mettler Toledo glass pH electrode calibrated before each measurement using Thermo Fisher buffers (pH=4.006, 6.865 and 9.183 at 25 °C). The buffers used for electrode calibration were kept in a thermostated bath at the same temperature as the reactors. The uncertainty of the measured pH values is estimated to be ± 0.02 pH-units.

The Ca and Ni concentrations of all sampled fluids were measured by flame Atomic Absorption Spectrometer (AAS) using a Perkin Elmer Analyst 400 with an uncertainty of ± 1 % and a detection limit of 7×10^{-7} mol/kg. Standards were prepared using 1000 ppm Ca or Ni standard solutions and an aqueous 2 % HNO₃ solution for dilution. This 2 % HNO₃ solution was also used to dilute the collected experimental reactor fluid samples for Ca analysis so that their concentration and pH fell within the measurement range. Calcium measurements were performed over the 0.5 to 5 ppm range, hence the samples were diluted by a factor of 200 for these analyses. Lanthanum oxide was added to all samples and standards prepared for Ca analysis to reach a final concentration of 0.409 g/kg to avoid anionic chemical interferences. Nickel measurements were performed over the 1 to 10 ppm range. Samples for nickel analysis were measured undiluted and the standards were diluted in an aqueous NaCl solution having an identical concentration as the samples to avoid potential matrix effects.

2.3 Calculation of Ni partition coefficients and calcite growth rates

The partitioning of a divalent cation, Me^{2+} , between calcite and its coexisting aqueous fluid represents the equilibrium constant of the exchange reaction between Ca^{2+} and Me^{2+} in $(Ca_{1-x}Me_x)CO_3$ solid solutions (see the Appendix). This exchange is commonly described using the Henderson and Kracek (1927) apparent partition coefficient, which implicitly assumes that aqueous Ca and Me complexation is negligible and that the activity coefficients of the $CaCO_3$ and $MeCO_3$ solid solutions are equal to one. The apparent partitioning coefficient, D_{Ni} , between calcite and the fluid is thus expressed as

$$D_{Ni} = \frac{X_{Ni} [Ca]}{X_{Ca} [Ni]} \quad (1)$$

where [Ni] and [Ca] stand for the molal concentrations of Ni and Ca in the aqueous fluid, X_{Ni} and X_{Ca} refer to the mole fractions of Ni and Ca in the solid, respectively.

The mole fraction of Ni precipitating in the solid at steady state conditions, X_{Ni} can be calculated in experiments where Ni is added into a mixed flow reactor from mass balance constraints using

$$X_{Ni} = \frac{n_{Ni(added)} - n_{Ni(removed)}}{n_{Ca(added)} + n_{Ni(added)} - n_{Ca(removed)} - n_{Ni(removed)}} \quad (2)$$

where $n_{Ca(added)}$ and $n_{Ni(added)}$ represent the number of moles of Ca and Ni, respectively, added to the reactor by fluid injection over one day, and $n_{Ca(removed)}$ and $n_{Ni(removed)}$ stand for the number of moles of Ca and Ni respectively removed by reactor fluid sampling during that day.

Calcite growth rates (R_p) at steady state can be calculated using

$$R_p = \frac{[Ca_{in}] - [Ca_{removed}]}{FR \cdot S} \quad (3)$$

where $[Ca_{in}]$ and $[Ca_{removed}]$ stand for the overall Ca concentration of the combined inlet fluids and that in the fluids removed from the reactor during sampling, FR refers to the fluid flow rate, and S denotes the total surface area of calcite in the reactor. The specific surface area of precipitated calcite at the end of the experiments was identical, within uncertainty, to that of the original calcite seeds. Note that rates calculated using Eq. 3 do not take account of Ni incorporated into the precipitated calcite, as its mass is negligible compared to that of Ca.

2.4 Isotopic analysis

Samples were prepared for Ni isotopic analyses by ion exchange chromatography. All collected steady state reactor fluid and solid samples, as well as the starting Ni-components and some standards aliquots were processed identically except for a calcium separation step, which was performed only on the fluids generated from the aqueous HCl digestion of the solid calcite samples. This calcium separation step preceded the ion exchange chromatography process. During this initial separation stage, the calcium was precipitated as CaF_2 to reduce the amount of dissolved calcium loaded onto the columns to avoid surpassing the resin capacity.

For this calcium separation a 100 μ L aliquot of the fluid generated from calcite digestion was first evaporated. Chloride was then replaced by fluoride by taking up this residue in 5 mL of a 1 M aqueous HF solution, refluxing the sample at 120 °C for 2 hrs, and then evaporating it. This process was repeated a second time except for the evaporation step. The resulting liquids were then centrifuged for 10 minutes at 4500 rpm and the supernatant was placed in a Teflon beaker while the residue was rinsed with water. After a vigorous agitation, the residue bearing water was again centrifuged. The resulting supernatant was added to the previously collected supernatant in the Teflon beaker. The combined liquid samples were evaporated and then taken up in 2 M HCl. Afterwards, these fluids were treated identically as the originally fluid samples. To ensure that this CaF_2 precipitation step has no effect on the Ni isotope composition, an Aldrich Ni standard was added to a carbonate sample devoid of Ni. This Ni-doped sample was then processed the same way as any other solid samples: it displays the same isotope composition as the original unprocessed Ni standard.

Nickel was separated from other matrix elements prior to isotope analysis using a 5 step separation procedure adapted from Quitté and Oberli (2006). The details of this separation are described in Castillo Alvarez et al. (2020). The first two steps require the Bio-Rad AG 1-X8 anion exchange resin and aimed to remove Fe and Zn, the main isobaric interferences for Ni. The third step was performed using a Triskem Nickel specific resin and is based on the complexation of Ni with Dimethylglyoxime (DMG) to form Ni-DMG. The fourth step used the Bio-Rad AG50W-X8 cation exchange resin to purify the sample. The last step uses the Bio-Rad AG1-X8 anion exchange resin to remove the Fe introduced during the previous steps. The fluid recovered after the completed separation procedure was dried and the final residue retained for analysis.

This residue was dissolved in 0.1 M HCl for isotope analysis. Nickel isotope measurements were performed at the Observatoire Midi Pyrenees analytical platform in Toulouse France, using a Thermo-Finnigan Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS). The MC-ICPMS was equipped with an Apex desolvating system connected to a glass nebulizer, and fitted with a standard sample cone and a X skimmer cone. Samples were measured in medium resolution mode, using the sample-standard bracketing technique and Cu doping to correct for mass bias. The Ni concentration of the measured samples was 200 ppb while the Cu concentration was 100 ppb. The 2σ (two standard deviations) of the $\delta^{60}\text{Ni}$ measurements was calculated based on multiple (typically 3) measurements of each liquid and ranged between 0.016

and 0.188‰. Some of this variation may be due to minor Fe and/or Zn contamination present in some samples. As mentioned above, a Sigma Aldrich Ni standard was processed through the whole chemical separation procedure together with every set of experimental samples to verify that no fractionation occurred during the Ni separation process. Also, to confirm the suitability of this procedure to separate Ni from a calcium carbonate matrix, a test was performed in which some Sigma Aldrich Ni standard was added to an originally Ni-free calcite saturated 0.2 M NaCl aqueous solution, representative of the experimental matrix, and to the calcite seed. They were then processed through the chemical separation steps in the same way the samples were processed. No isotope fractionation was observed for the processed standards relative to the corresponding original standards, confirming the quality of the chemical separation procedure. Blanks of the ion exchange chromatography were checked for every set of samples processed. They were measured using an Agilent 7700 quadrupole ICP-MS, with an associated analytical uncertainty estimated to be $\pm 5\%$. The measured blanks vary between 0.85 and 1.93 ng of Ni, which is negligible compared to the amount of Ni in the samples (at least 600 ng).

Isotope compositions in this paper are presented in delta notation, $\delta^{60}\text{Ni}$, corresponding to the ratio of ^{60}Ni relative to ^{58}Ni normalized to the Aldrich ICP standard. This standard was used rather than the certified SRM986 standard as it is the in-house standard for which we have a well-defined value and long-term reproducibility. The results of this study are not affected by the identity of the standard used, as we are interested in difference in the Ni isotope composition of the solid versus the fluid ($\Delta^{60}\text{Ni}_{\text{solid-fluid}}$) rather than absolute value of these isotopic compositions. This isotopic offset between Ni in the solid and the fluid phase is defined by

$$\Delta^{60}\text{Ni}_{\text{solid-fluid}} = \delta^{60}\text{Ni}_{\text{solid}} - \delta^{60}\text{Ni}_{\text{fluid}} \quad (4)$$

where $\delta^{60}\text{Ni}_{\text{solid}}$ and $\delta^{60}\text{Ni}_{\text{fluid}}$ refer to the measured nickel isotopic composition of the subscripted phase corresponding to the ratio of ^{60}Ni relative to ^{58}Ni normalized to the in-house standard.

3. RESULTS

3.1 Mineralogy and chemical composition of the precipitated phases

X-ray diffraction (XRD) patterns of the solids recovered from the reactors after all experiments appear identical to the original calcite seeds. Some representative Scanning Electron

Microscope (SEM) images of these post-experiment solids are shown in Fig. 2. The post-experiment solids maintained the characteristic calcite rhombic morphology. No aragonite needles were detected by this analysis.

Figure 2 SEM images of the initial calcite seed material (left) and of the calcite recovered after experiment C17 (right). The scales of the images are provided in the figure.

3.2 Chemical composition of the reactive fluids

A total of 12 coprecipitation experiments were performed in this study. A summary of the experimental conditions and the steady state reactive fluid compositions of all experiments is provided in Table 1. Steady-state aqueous Ca concentrations and alkalinities were usually achieved within 3 days after the start of each experiment. A significantly longer time (up to 21 days), however, was required to attain steady-state aqueous Ni concentrations. The time to reach steady state depends on the Ca and Ni concentrations in the inlet fluids and on the inlet fluid flow rate. Figure 3 shows a representative plot of the temporal evolution of aqueous fluid compositions during one of the flow experiments performed in this study. In this experiment, Ni was not initially present in the reactor. The reactive fluid reaches a steady state Ni composition of 11.25×10^{-6} mol/kg after approximately 5 days. The calcium concentration is relatively stable

throughout the experiment and has a steady state value of 0.014 mol/kg. The alkalinity also remained almost unchanged and has a steady state concentration of 0.027 mol/kg. Note the initial fluids in the reactor were pre-equilibrated with calcite, which fixed the fluid Ca concentration and alkalinity at the start of the experiment (see above).

Figure 3 Reactive fluid Ni and Ca concentrations, and alkalinity during experiment C15. These results illustrate a typical reactor fluid evolution during a flow experiment performed in this study. The black diamonds show the temporal evolution of calcium, while alkalinity is shown by the open squares. Both are consistent with the right scale. Nickel concentrations are represented by the grey circles and its scale is shown on the left. Analytical uncertainty is included in symbol size.

3.3 Mineralogy and composition of the precipitated phases

The mole fraction of nickel, X_{Ni} , in the precipitated calcite was calculated from the steady state reactive fluid compositions using eq. 2. The mole fraction of Ni in calcite is plotted as a function of the corresponding aqueous $[\text{Ni}^{2+}]$ to $[\text{Ca}^{2+}]$ ratio in Figure 4.

Figure 4 Mole fraction of Ni in calcite, X_{Ni} , as a function of the molar $[Ni^{2+}]$ to $[Ca^{2+}]$ ratio of the reactor fluid at steady state in all experiments performed in this study. The uncertainty associated with these measurements is included within the symbol size.

3.4 Ni partitioning between calcite and fluid D_{Ni}

The nickel partition coefficient, D_{Ni} , was calculated from measured concentrations of Ni in the reactor fluid and solid after steady state was attained, using eq. 1. The measured Ni partition coefficients range from 0.73 to 1.29 with an average value of 1.09 ± 0.36 . The corresponding calcite growth rates, determined using eq. 3, varied from 1.22×10^7 to 2.72×10^9 mol $m^2 s^{-1}$. No effect of the calcite growth rate on the partition coefficient is evident (see Fig. 5).

Figure 5 Measured nickel partition coefficients, D_{Ni} , as a function of the logarithm of the calcite growth rate R_p . The analytical uncertainty associated with these measurements is included within the symbol size.

Table 1 Summary of the calculated calcite growth rates, reactor fluid compositions and partition coefficients generated in the present study. The values of $[Ca]_{inlet}$ and $[Ni]_{inlet}$ refer to the indicated elemental concentration of the combined two injection fluids.

Expt.	$\text{Log } R_p$ $\text{mol m}^{-2} \text{s}^{-1}$	$[Ca]_{inlet}$ mol/kg	$[Ni]_{inlet}$ mol/kg $\times 10^4$	Initial seed Mass, g	pH	Alkalinity Mol/kg	$[Ni]_{ss}^a$ mol/kg $\times 10^5$	$[Ca]_{ss}^a$ mol/kg	X_{Ni} (mol %) $\times 10^3$	D_{Ni}
C15	-7.23	0.21	1.75	1.5	6.00	0.027	1.13	0.014	0.84	1.23
C16	-7.23	0.21	1.75	1.5	5.99	0.028	1.24	0.014	0.83	0.93
C17	-6.92	0.21	1.75	0.75	6.10	0.031	7.16	0.011	0.84	1.24
C18	-7.53	0.21	1.75	3.0	6.05	0.028	8.26	0.013	0.84	1.29
C19	-8.01	0.06	0.82	1.5	6.08	0.028	2.20	0.015	1.33	0.89
C23	-7.10	0.21	4.77	3.0	6.07	0.027	6.15	0.022	2.21	0.81
C26	-7.38	0.20	1.70	2.0	6.12	0.029	0.84	0.012	0.88	1.25
C27	-7.91	0.10	1.21	2.0	6.34	0.037	2.57	0.024	1.27	1.20
C29	-8.20	0.06	0.82	2.6	6.44	0.029	1.47	0.013	1.43	1.26
C31	-8.29	0.06	0.81	2.0	6.17	0.030	2.96	0.019	1.29	0.84
C36	-7.68	0.07	0.68	2.2	6.11	0.032	0.98	0.011	1.00	1.16
C37	-7.37	0.20	1.70	4.0	6.01	0.030	1.03	0.011	0.85	0.92

a) the subscript ss refers to the indicated concentration reactor fluid concentration at steady state

3.5 Ni isotope fractionation during calcite growth

The isotopic compositions of reactor fluids and precipitated solids at steady state are compiled in Table 2. These values were used to calculate the $\Delta^{60}\text{Ni}_{\text{calcite-fluid}}$ values depicted as a function of calcite growth rate in Fig. 6. The negative values of $\Delta^{60}\text{Ni}_{\text{calcite-fluid}}$ reflect the preferential incorporation of light Ni isotopes in the precipitated calcite. The values of the Ni fractionation range from -0.13 to -0.93 ‰. The extent of Ni isotope fractionation during Ni incorporation into calcite decreased with increasing carbonate growth rates.

Figure 6 Ni isotope fractionation between precipitated Ni bearing calcite and the reactor fluid as a function of the calcite growth rate. The error bars represent 2 standard deviations. The dotted line shows a linear regression of the data.

Table 2 Results of isotopic analysis of fluids and solids recovered from the coprecipitation experiments and the associated fractionation.

Label	Log R_p	$\delta^{60}\text{Ni}_{\text{fluid}}$ ‰	2σ	$\delta^{60}\text{Ni}_{\text{calcite}}$ ‰	2σ	$\Delta^{60}\text{Ni}_{\text{calcite-fluid}}$ ‰	2σ
inlet		-0.438	0.016				
C15	-7.23	-0.364	0.032	-0.681	0.070	-0.317	0.077
C16	-7.23	-0.264	0.116	-0.652	0.144	-0.388	0.185
C17	-6.92	-0.319	0.134	-0.675	0.026	-0.356	0.136
C18	-7.53	-0.189	0.038	-0.724	0.016	-0.535	0.041
C19	-8.01	-0.333	0.052	-1.206	0.027	-0.873	0.059
C23	-7.10	0.107	0.125	-0.021	0.110	-0.128	0.167
C26	-7.38	-0.457	0.054	-0.728	0.049	-0.271	0.073
C27	-7.91	-0.211	0.068	-1.041	0.131	-0.830	0.148
C29	-8.20	-0.203	0.125	-1.134	0.188	-0.931	0.226
C31	-8.29	-0.179	0.024	-1.108	0.084	-0.929	0.087
C36	-7.68	0.054	0.096	-0.504	0.061	-0.558	0.114
C37	-7.37	-0.124	0.104	-0.692	0.125	-0.568	0.163

4. DISCUSSION

4.1 Ni distribution coefficient between calcite and the aqueous fluid

The Ni mole fraction (X_{Ni} , Fig. 4) in the precipitated calcite at the end of all experiments displays a positive correlation with the Ni^{2+} to Ca^{2+} concentration ratio with a partition coefficient of 1.09 ± 0.36 . This behavior is similar to that reported in literature. The partition coefficient of Ni has also been experimentally determined during its incorporation into foraminiferal calcite, where D_{Ni} values ranged from 0.4 to 2 with an average of 1 ± 0.5 (Munsel et al. 2010). Also, several studies report partition coefficients from studies performed on abiogenic calcite. For dilute solid solutions ($X_{\text{Ni}} < 0.001$), the Ni partition coefficient D_{Ni} , was reported to be about 3.5 by Wang and Xu (2001) and between 0.1 and 6 by Curti (1999). Carlson and Aalto (1997) reported this partition coefficient to be about 2 using liquid scintillation counting. Lakshatanov and Stipp (2007) measured the partition coefficient of Ni between an aqueous fluid and calcite at various carbonate growth rates. These authors used synthetic calcite seeds and worked at ionic strengths between 0.06 and 0.84. They reported a partition coefficient value equal to 1.04 ± 0.11 that is in excellent agreement with the value determined in this study.

The partition coefficient, D_{Ni} , measured in this study can be compared to the values of the equilibrium partition coefficient, D_{Ni} , derived from the thermodynamics of solid solutions and the solubility products of the two end-members, $CaCO_3$ and $NiCO_3$ generated from (see the appendix),

$$D_{Ni} = \frac{K_{Calcite}}{K_{NiCO_3}} \quad (5)$$

where $K_{Calcite}$ and K_{NiCO_3} refer to the equilibrium constants for the calcite and $NiCO_3$ hydrolysis.

Using $K_{Calcite} = 8.48$ (Minteqv4 data base; Parkhurst and Appelo, 2013) and $pK_{NiCO_3} = 11.01$ (for gaspeite as reported by Gamsjäger et al., 2001 and corrected for the CO_2 dissolution reaction using data from the Minteqv4 database), Eq. 5 yields a D_{Ni} value of 360, which is much higher than that reported in the present study. Similarly, using the semi-empirical relation proposed by Rimstidt et al. (1998; see the appendix),

$$D_{Ni} = 1.6 \left(\frac{K_{CaCO_3}}{K_{NiCO_3}} \right)^{0.37} \quad (6)$$

yields a value equal to 46. However, assuming that the end-member of the solid solution is $NiCO_3(6H_2O)$ ($pK_{NiCO_3(6H_2O)} = 7.55$; Gamsjäger et al, 2001) instead of $NiCO_3$ yields for D_{Ni} a value of 0.14 and 0.52 using Eq. 5 and 6, respectively. These values are in good agreement with the experimental values of this study and of Lakshtanov and Stipp (2007), which strongly suggests, in accord with Ni isotope data, that the nickel incorporated in calcite during our experiments is solvated.

Our data exhibit no systematic variation of D_{Ni} as a function of the calcite growth rate. This observation together with $D_{Ni} = 1$ is consistent with identical incorporation rates of Ni and Ca into the growing calcite crystal (Rimstidt et al., 1998) and an equal affinity of Ni^{2+} for the fluid and calcite lattice. This observation also indicates the Ni concentration in calcite bulk crystal is the same as this concentration and in the distorted/hydrated thin layer present at the crystal surface, in accord with Watson's (2004) growth entrapment model. This behavior contrasts with that of i) the alkaline earth metals (Mg, Sr, Ba), which exhibit a greater affinity for the fluid than the crystal ($D < 1$) and whose partition coefficients increase with increasing calcite growth rate and ii) the divalent transition metals (Cd, Mn, Zn, Co), whose greater affinity for the crystal than the fluid ($D > 1$) leads to a decrease of their partition coefficients with increasing calcite growth rate (Watson, 2004; Mavromatis et al., 2013).

Partition coefficients in nature are similar to those found in this study. For example, the Ni concentration in carbonates from the Peru margin range from 2.2 to 3.9 ppm (Ciscato et al. 2018). Combining these values with the average seawater concentrations of Ni (0.8 nmol/kg; Sohrin and Bruland, 2011) and Ca (0.01 mol/kg; Dickson and Goyet, 1994), leads to a D_{Ni} value ranging from 4.83 to 8.56, which is relatively close to that measured in this study

The greater the equilibrium partition coefficient, the more affinity an element has for the solid. The partition coefficients calculated for Ni in the present study indicate that its incorporation into calcite is moderate. Out of the divalent metals, Be, Mg and Ba have lower partition coefficients and thus a lower affinity for calcite (Pingitore and Eastman 1984; Tesoriero and Pankow 1996; Rimstidt et al. 1998; Saulnier et al. 2012) than Ni. On the other hand, Mn, Fe, Cu and Zn have higher partition coefficients than Ni, and thus a higher affinity for calcite (Kitano et al. 1980; Lorens 1981; Dromgoole and Walter 1990; Marchitto 2011). In contrast, rare earth elements incorporate more strongly into calcite, with partition coefficient values of up to 4000 (Zhong and Mucci 1995; Webb and Kamber 2000; Voigt et al. 2017). This likely results from the sixfold coordination of most REEs in the calcite calcium site (Elzinga et al., 2002) with an ionic radii close to that of Ca^{2+} ($r_{\text{io}} \sim 1.0 \text{ \AA}$), unlike that of Ni^{2+} ($r_{\text{io}} = 0.69 \text{ \AA}$). Note, however, that the incorporation of REE^{3+} ions into the calcite structure, unlike that of divalent metals, does not proceed via a simple Ca^{2+} - REE^{3+} exchange reaction but requires the associated incorporation of a monovalent cation (i.e. Na^+ in NaCl or seawater solutions, Marques Fernandes et al., 2008; Voigt et al., 2017).

4.2 Controls on Ni isotope compositions in calcite

Why are lighter Ni isotopes are preferentially incorporated into calcite?

Equilibrium isotope fractionation was not achieved during our experiments. The dependence of $\Delta^{60}\text{Ni}_{\text{calcite.-fluid}}$ on calcite growth rate shown in Fig. 6, however, shows that $\Delta^{60}\text{Ni}_{\text{calcite.-fluid}}$ decreases with decreasing growth rate and suggests that the equilibrium $\Delta^{60}\text{Ni}_{\text{calcite.-fluid}}$ is likely $\leq -1.0 \text{ ‰}$, lower than that observed for the lowest calcite growth rate of this study ($10^{-8.3} \text{ mol/cm}^2 \text{ s}$). The observed enrichment in calcite of light Ni isotopes is likely due to differences in the Ni structural environment, notably the Ni-O bond length in the Ni aquo ion compared to that in Ni-bearing calcite. Nickel is in octahedral coordination in its aquo ion, in gaspeite (NiCO_3) and when incorporated as a trace metal in calcite (Varadwaj et al., 2008; Pertlik, 1986; Zavarin and Doner,

1999). Reported Ni-O bond lengths of the Ni aquo ion range from 2.05 to 2.07 Å (Caminiti et al., 1977; Sandstrom, 1979; Magini et al., 1982; Fujii et al., 2011). There has been, however, no direct measurements of the Ni-O bond length in calcite. The Ni-O bond length in gaspeite has been reported to be 2.076 Å (Pertlik 1986). Because the Ca-O bond length in calcite (2.36 Å; Reeder 1990) is significantly longer than the Ni-O bond length in gaspeite, it seems likely the Ni-O bond in Ni-bearing calcite is larger than that in gaspeite. Although there is no published data on the Ni-O bond length in Ni²⁺-doped calcite, an analogy can be made based on zinc and cobalt bearing calcite. The Zn-O and Co-O bond lengths in the pure zinc and cobalt carbonates, smithsonite and spherocobaltite, are identical and equal to 2.11 Å (Reeder et al. 1999), whereas these bond lengths in Zn- and Co-doped calcites are 2.15 Å and 2.16 Å, respectively (Reeder et al., 1999). It seems reasonable, therefore, that the Ni-O bond length in calcite is approximately equal to 2.11 Å or ~0.05 Å larger than that in the nickel aquo complex. As longer bond distances favor lighter isotopes (Criss, 1999; Schauble, 2004), this difference is likely a major factor in the Ni isotope fractionation between aqueous Ni and Ni in the calcite structure observed in this study. It should be pointed out that the substitution of Ca ions in the calcite lattice by partially solvated Ni instead of anhydrous Ni with the subsequent protonation of oxygens does not lead to a sufficient change in Ni-O bond length to reverse the preferential enrichment of the solid phase in light Ni isotopes.

Note that nickel adsorbed at the calcite-fluid interface was found to have a $\Delta^{60}\text{Ni}_{\text{calcite-fluid}} = -0.49 \text{ ‰}$ (Castillo Alvarez et al., 2020), an isotope fractionation significantly smaller in magnitude than the equilibrium fractionation value of $\Delta^{60}\text{Ni}_{\text{calcite-fluid}} \leq -1.0 \text{ ‰}$ observed in this study for coprecipitation of Ni incorporated into the calcite lattice. These differences likely reflect a larger Ni-O bond length of Ni incorporated in the crystal lattice compared to that present in Ni complexes on the calcite surface. Note that Ni adsorbed on calcite at the onset of co-precipitation experiments accounts for only a negligible fraction of the total Ni incorporated in calcite. Using a value of the Ni partition coefficient during Ni adsorption on calcite, $K_d = 0.011$ at pH 8.3 (Castillo Alvarez et al., 2020) it is found that the mass of Ni adsorbed on calcite surfaces at the onset of a co-precipitation experiment never exceeded $7.8 \times 10^{-8} \text{ g}$ (note the value of K_d at the 6.0-6.4 pH of the experiments should be at least 3 times less than at pH 8.3, see Fig. 5 in Castillo Alvarez et al., 2020). In comparison the mass of Ni incorporated in calcite during the coprecipitation experiments of this study ranged between 5.2×10^{-4} and $1 \times 10^{-3} \text{ g}$, thus about 4 orders of magnitude higher. As a result the Ni isotope composition of Ni co-precipitated with calcite will not be affected by Ni sorbed on calcite at the onset of co-precipitation experiments.

Aqueous Ni complexation with the ligands present in our experimental solution was insufficient to significantly impact $\text{Ni}^{2+}(\text{aq})$ isotope composition and calcite Ni isotope composition. At the conditions of our experiments ($\text{pH} \leq 6.4$, $\text{Alk.} \leq 0.037 \text{ N}$, $\text{Cl}^- = 0.2 \text{ N}$), NiHCO_3^+ was the only significant Ni aqueous complex present in solution, with a fraction of total dissolved Ni that never exceeded 11.3 %, and $\text{Ni}^{2+}(\text{aq})$ accounted for at least 88 % of dissolved nickel. Using the values of the reduced partition functions for the $^{60}\text{Ni}/^{58}\text{Ni}$ isotope pairs of $\text{Ni}^{2+}(\text{aq})$ and NiHCO_3^+ reported by Fujii et al. (2011), it can be concluded that Ni- HCO_3^- complexation led to an enrichment of $\text{Ni}^{2+}(\text{aq})$ in ^{58}Ni of no more than 0.05 ‰, a value less than the uncertainty attached to our measurements.

Why does the magnitude of Ni isotope fractionation decreases with increasing calcite growth rate?

When minerals precipitate from aqueous fluids at high growth rates the system is not likely at isotopic equilibrium. Such non-equilibrium effects have been reported in a number of systems (Lemarchand et al. 2004; Fantle and DePaolo 2007; Tang et al. 2008; Böhm et al. 2012; Mavromatis et al. 2013). Ions in aqueous solution need to dehydrate before they can be incorporated into the calcite crystal lattice (e.g. Marriott et al., 2004; Raiteri and Gale, 2010) and water molecules have shorter residence times in the solvation shells around lighter isotopes (Hofmann et al. 2012). For metals like Ca and Sr, the ion desolvation rate has been suggested to be the primary mechanism responsible for the enrichment of light metal isotopes in the calcite crystal (Hofmann et al. 2012). Indeed, Lammers et al. (2020) showed, based on molecular simulations that the preferential dehydration of light Ca isotopes at the calcite surface only occurs at kink sites during classical spiral growth. This should lead to the preferential attachment of light metal isotopes to advancing steps on calcite surfaces and to an increasing extent of fractionation with increasing growth rates, such as seem in Fig. 7. Also shown in this figure are the measured isotopic fractionation between calcite and aqueous fluids for Ni, Mg, and Sr as a function of the calcite growth rate. The behavior for Ni is similar to that observed for Mg, but contrasts to that observed for Ca, Sr and Ba in calcite (Böhm et al. 2012; Mavromatis et al. 2013, 2020; AlKhatib and Eisenhauer 2017).

Figure 7 Isotope fractionation factor between calcite and aqueous fluids for Ni, Mg, Sr, and Ca plotted as a function of the logarithm of the calcite growth rate $\log R_p$. The data plotted for Mg, Sr, and Ca was originally reported by Mavromatis et. al. (2013, black squares), Alkhatib and Eisenhauer (2017, triangles), and Bohm et. al. (2012, diamonds).

These observations are consistent with the relative rate of H_2O exchange in the aqueous metal coordination sphere compared to that of Ca. Strontium, barium and calcium have similar water exchange rates ($10^{-8.9}$, $10^{-9.2}$ and $10^{-8.8} \text{ s}^{-1}$, respectively) and exhibit similar isotope fractionation trends. In contrast Ni and Mg have water exchange rates of $10^{-4.3}$ and $10^{-5.4} \text{ s}^{-1}$ respectively, and show the opposite isotope fractionation trend as a function of calcite growth rate. As Ca^{2+} desolvation is the rate limiting step for calcite growth, it is unlikely that Ni, which desolvates at rates 5 orders of magnitude slower than Ca, completely desolvates as it incorporates into the calcite structure except at very slow calcite growth rates (Watkins et al., 2017). As a result there is, at rapid calcite growth rates, less isotope fractionation between calcite and the Ni aquo ion. It has been shown that the high hydration energy of aqueous metals like $\text{Ni}^{2+}(\text{aq})$ slows their dehydration on the calcite surface and within its surface layer (Mavromatis et al., 2013). Nickel attached to the calcite surface remains partly hydrated even after its incorporation into the calcite structure, as suggested by the value of Ni partition coefficient measured in this study (see above). This relatively slow desolvation rate relative to Ca^{2+} results in a kinetic isotope fractionation involving dehydration of ions, which prevails over the preferential attachment of light Ni isotopes to kink sites during the classical growth mechanism operating in our experiments

Can Ni isotopes in calcite track past seawater Ni isotopic compositions?

The deviations of Ni isotope fractionations from equilibrium fractionation can be used to gather information on geochemical processes and paleoenvironments. Given the correlation that exists between the isotope fractionation of Ni and the calcite growth rate, Ni isotopic compositions of primary calcite have the potential to record information of the seawater composition at the time of deposition. Notably, the use of Ni isotope compositions to determine the growth rates and thereby the saturation state of calcite during its time of formation can provide an independent test for paleoenvironmental reconstructions when used together with other marine calcite proxies. It should be pointed out that Ni^{2+} complexation with the main dissolved inorganic ligands of modern seawater (SO_4^{2-} , CO_3^{2-} , HCO_3^- , Cl^-) should not significantly impact the isotopic composition of the Ni^{2+} incorporated in calcite lattice. Indeed, at pH 8.2, dissolved nickel is predominately in the form of the Ni^{2+} aquo ion ($\sim 77\%$) and the formation of NiSO_4° (19.1 %), NiCO_3° (2.1 %), NiHCO_3^+ (0.4 %) and NiCl^+ (0.2 %) leads, according to the reduced partition functions for the isotope pairs of aqueous Ni species reported by Fujii et al. (2011), to an enrichment of $\text{Ni}^{2+}(\text{aq})$ of only 0.1 ‰ in ^{58}Ni .

4.3 Resolving the Ni isotope imbalance in the ocean

A number of previous studies concluded that our current understanding of the Ni isotopic balance in the oceans is not well constrained. The nickel isotope composition of seawater has been reported to be between $\delta^{60}\text{Ni} = 1.20$ and 1.74% (Cameron and Vance 2014; Takano et al. 2017; Archer et al. 2020) while rivers, the main input of Ni into the ocean, are substantially lighter with an annual $\delta^{60}\text{Ni}$ average of $+0.80\%$ (Cameron and Vance 2014). This difference in the isotopic composition of the ocean compared to rivers requires the existence of either another source of isotopically heavy Ni or an additional sink of isotopically light Ni.

Various processes have been suggested as the possible light Ni sink from the oceans including the adsorption of Ni on Fe-Mn oxides, the incorporation of Ni into sulfide-rich sediments, Ni uptake into organic matter and biological uptake (Gall et al. 2013; Gueguen et al. 2013; Wasylenki et al. 2015; Vance et al. 2016, 2017; Ciscato et al. 2018; Archer et al. 2020; Little et al., 2020), yet ambiguities remain (Cameron and Vance 2014; Ciscato et al. 2018). Castillo Alvarez et al. (2020) showed that light Ni isotopes are preferentially adsorbed onto calcite with a $\Delta^{60}\text{Ni}_{\text{calcite-fluid}} = -0.49 \pm 0.16\%$. The present study demonstrates that light Ni is also

preferentially co-precipitated with calcite with $\Delta^{60}\text{Ni}_{\text{calcite-fluid}}$ of -1.0 ‰ or larger. These results suggest that Ni adsorption onto calcite surfaces and Ni coprecipitation into calcite may contribute to resolving the imbalance in the global marine Ni budget given the large mass of calcite precipitated in the oceans.

The quantification of the amount of Ni in marine carbonates and its isotopic composition is necessary to accurately estimate the contribution of Ni uptake in calcite to the Ni marine isotope budget. The annual output flux of Ni from the oceans via carbonate precipitation is challenging to constrain and current estimates have substantial uncertainties. Ciscato et al. (2018) suggested that the Ni buried with CaCO_3 accounts for only about 1 to 2 % of the total Ni sink from the oceans. This estimate does not, however, account for carbonates precipitated in a number of environments such as deltaic sediments, representing roughly 45 % of the carbonates buried, and that buried along the continental shelves and slopes (Hedges and Keil 1995). An alternate estimate could be made by recalling that the removal of CaCO_3 from seawater has been estimated to be between 3.2 and 14.7×10^{13} mol of carbonate per year (Hedges and Keil, 1995; Milliman and Droxler, 1996; Milliman et al., 1999; Schneider et al., 2000; Berelson et al., 2007). This CaCO_3 contains between 1.52 and 12.92 ppm of Ni (Zhao and Zheng 2014) with an average of ~ 2.69 ppm of Ni. Multiplying the annual mass of CaCO_3 removed from seawater by this average Ni concentration would results in the removal of 1.5 to 6.7×10^8 moles of Ni by carbonate minerals each year. This compares to an estimated global riverine input of Ni to the oceans of 3.6×10^8 mol/year (Cameron and Vance, 2014) and an estimated flux of Ni from the oceans of 7.2 to 17×10^8 mol/year. It has been argued, however, that these latter estimates present a mass balance problem as they are 2–5 times the quantified input (Ciscato et al., 2018). The mass of Ni estimated here to be removed from the ocean via carbonate precipitation ranges from 40 to 180 % of that estimated to be added to oceans by global rivers. Although such estimates are highly uncertain, the observation that the measured Ni fractionation into calcite during its coprecipitation ranges up to at least – 1.0 ‰, the removal of Ni by its incorporation into CaCO_3 exported from the ocean could change notably the Ni isotope composition of seawater. As such this process could help to bridge the gap between the Ni isotope composition of sources and sinks in the ocean.

5. CONCLUSIONS

Experiments were performed to determine the effect of the calcite growth rate on the degree of Ni isotope fractionation during its coprecipitation at 25°C, a pH of 6.2, and a pCO₂ of 1 atm. The major results of this study include:

- 1) Lighter Ni isotopes were preferentially incorporated into precipitated calcite. This is likely the result of the change in Ni coordination environment occurring during the incorporation process. Nickel does not change its coordination number as it incorporates into calcite from aqueous fluids. The Ni-O interatomic distance, however, is significantly longer for Ni incorporated in calcite than it is for aqueous Ni(H₂O)₆²⁺. The value of Ni equilibrium fractionation, $\Delta^{60}\text{Ni}_{\text{calcite-fluid}}$, derived in this study is ≤ -1.0 ‰. This is more negative than the corresponding value for Ni sorption on calcite surface (-0.49 ‰). This difference likely reflects longer Ni-O bond lengths for the Ni incorporated into calcite than for the Ni species adsorbed at the calcite surface.
- 2) Nickel isotope fractionation between calcite and fluid depends on the calcite growth rate. The measured nickel isotope fractionation changes from -0.9 to -0.2 ‰ as the calcite growth rate increases from 10^{-8.3} to 10^{-6.9} mol m⁻² s⁻¹. The decrease in the extent of Ni isotope fractionation as the growth rate increases is attributed to the slow dehydration rate of aqueous Ni²⁺. This slow dehydration hinders the incorporation of dehydrated Ni²⁺ into calcite, a behavior similar to that observed for Mg, but contrasts to the behavior exhibited by Ca, Sr and Ba. These observations likely stem from the rate of exchange of H₂O of the aqueous metals in their coordination sphere compared to that of aqueous Ca²⁺.
- 3) The precipitation rate of marine carbonates is determined by the saturation state of the ocean with respect to these minerals. At the same time, the saturation state of carbonates is influenced by pH, pCO₂ and temperature. As Ni isotope fractionation in calcite depends on its growth rate, measured Ni isotope compositions have the potential to reveal information on past environmental conditions.
- 4) The preferred enrichment in light Ni isotopes on/in calcite from seawater during adsorption and precipitation likely contributes to solving the Ni isotope budget imbalance in the ocean given the large amount of Ni that gets incorporated into carbonate minerals globally.

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APPENDIX

Thermodynamic description of nickel partition coefficient between the fluid and calcite

According to the thermodynamics of solid solutions (i.e. Saxena, 1973), Ni distribution coefficients, D_{Ni} , in the aqueous calcite-Ni carbonate system can be defined as the equilibrium constant of the exchange reaction given by

where $i(ss)$ stands for the i th component of the solid solution. The law of mass action for Eq. (A-1) can be written

$$D_{Ni} = \frac{X_{NiCO_3(ss)} \gamma_{NiCO_3(ss)} a_{Ca^{2+}}}{X_{CaCO_3(ss)} \gamma_{CaCO_3(ss)} a_{Ni^{2+}}} \quad (A-2)$$

where X_i and γ_i represent the mole fraction and activity coefficient, respectively, of the i th component of the solid solution, and a_i denotes the activity coefficient of the i th aqueous ion. For a dilute solid solution $\gamma_{CaCO_3(ss)} \rightarrow 1$ and $\gamma_{NiCO_3(ss)} \rightarrow \text{const.} \neq 1$. This leads to the classical expression of the apparent distribution coefficient, $D_{Ni(ap)}$, given by

$$D_{Ni(ap)} = \frac{X_{NiCO_3(ss)} |Ca(aq)|}{X_{CaCO_3(ss)} |Ni(aq)|} \quad (A-3)$$

assuming no significant complexation of Ni(aq) and Ca(aq).

At equilibrium, the two constituents of the solid solution should be simultaneously in equilibrium with the two end-members of the solid solution, which provides two additional relations involving the calcite and $NiCO_3$ solubility products:

$$K_{calcite} = \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{X_{CaCO_3(ss)} \gamma_{CaCO_3(ss)}} \quad (A-4)$$

and

$$K_{NiCO_3} = \frac{a_{Ni^{2+}} a_{CO_3^{2-}}}{X_{NiCO_3(ss)} \gamma_{NiCO_3(ss)}}. \quad (A-5)$$

Combination of Eqs. A- 2, A-4 and A-5 provides the following expression for the partition coefficient

$$D_{Ni} = \frac{K_{\text{Calcite}}}{K_{\text{NiCO}_3}} \quad (\text{A-6})$$

which allows determination of D_{Ni} from the solubility products of the two end-members, calcite and NiCO_3 . Based on the McIntire model (McIntire, 1963) and correlations of partition coefficients for divalent metals that form rhombohedral carbonates, Rimstidt et al. (1998) proposed the following expression similar to Eq. A-6:

$$D_{Ni} = 1.6 \left(\frac{K_{\text{Calcite}}}{K_{\text{NiCO}_3}} \right)^{0.37} \quad (\text{A-7})$$

Eqs A-6 and A-7 have been used in this study to calculate the values of D_{Ni} considering two different Ni carbonate end-members, the anhydrous NiCO_3 (gaspeite) and $\text{NiCO}_3(6\text{H}_2\text{O})$ (hallyerite).

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