Enrichment of lanthanides in aragonite

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Abstract: Using the constant addition technique, the coprecipitation of lanthanum, gadolinium, and lutetium with aragonite in seawater was experimentally investigated at 25 °C. Their concentrations in aragonite overgrowths were determined by inductive coupled plasma mass spectrometer. All these lanthanides were strongly enriched in aragonite overgrowths. The amount of lanthanum, gadolinium, and lutetium incorporated into aragonite accounted for 57%–99%, 50%–89%, and 40%–91% of their initial total amount, respectively. With the increase of aragonite precipitation rate, more lanthanides were incorporated into aragonite while their relative fraction in aragonite overgrowths decreased consistently. It indicated that the coprecipitation of lanthanides with aragonite was controlled by the kinetics of aragonite precipitation.

Keywords: lanthanide; aragonite; enrichment; coprecipitation; precipitation; rare earths

In ocean system, aragonite (molecular formula: CaCO3) is a very important species of carbonate minerals. It is the major constituent of many biomineralization products (e.g., shells, coral skeletons, and pearls) and widely distributed in tropic marine sediments. Most recently, the incorporation of lanthanides (Ln) into aragonite have generated growing interests. Many researchers have proposed coral Ln/Ca ratios as proxies for seawater chemistry\[1–4\]. They interpreted that lanthanides can not be enriched in aragonite. However, some other researchers have reported that lanthanides are strongly enriched in aragonite during sedimentation or diagenesis\[5–7\] processes. Experimental studies on the enrichment of lanthanides in aragonite are thereby of particular importance for relative researches\[8\].

1 Experimental

1.1 Materials

The seawater used in the experiments was artificially prepared by dissolving analytical grade reagents in distilled water\[9\]. Thereafter, the initial solutions were prepared by sequential addition of lanthanide stock solutions, 0.1 mol/L NaOH solutions and NaHCO3 solids into filtered artificial seawater. Three members of lanthanides, La, Gd, and Lu, were investigated in this study and their concentrations in initial solutions were set at 5 ng/g. Aragonite powders used as seed materials were synthesized in the laboratory by ultra pure Sigma® calcite\[10,11\]. Their specific surface area was determined to be 0.771 m2/g by Kr-BET method\[12\].

1.2 Method

Constant addition system\[13\] is shown in Fig. 1. The whole system was placed in a bio-culturing box to maintain the temperature at a steady level (25±0.5 °C). At the beginning of each experiment, about 0.6 g aragonite powders were carefully introduced into the reactor to induce precipitation of aragonite. During the experiment, CO2/N2 gas mixture ($p_{CO2}=0.0030\times10^5$ Pa) was continuously introduced into the reactor from the bottom with two purposes: (1) maintaining $p_{CO2}$ of the solution at a constant level, and (2) serving as a

![Fig. 1 Schedule diagram of the constant addition system](image_url)
stirrer. Once the designed duration was reached, samples were immediately collected for analyses: those of the initial solution were directly collected from the reservoir, while those of the steady solution and solid (seed materials+overgrowths) were separated by filtration through 0.45 μm cellulose acetate membranes. After careful salt washing and 48 h freeze-drying, solid samples were sealed in plastic bottles to keep out of moisture.

### 1.3 Analyses and calculations

The total alkalinity and Ca\(^{2+}\) concentrations of collected liquid samples were determined by titration\(^{[13]}\) on Metrohm® 798 titrator. Their relative errors were restricted within ±0.25% and ±0.5%, respectively. According to the difference in the total alkalinity (\(\Delta A_t, \text{μmol/kg}\)) between initial solution and reacting solution, the mass of aragonite overgrowths (\(W_{\text{overg}}, g\)) was calculated as

\[
W_{\text{overg}} = W_{\text{soln}} \times \frac{\Delta A_t}{20000}
\]

where \(W_{\text{soln}}\) refers to the mass of reacting solutions in gram. Thereafter, the precipitation rate of aragonite (\(R, \text{μmol/(m}^2\text{h)}\)) was calculated as

\[
R = \frac{W_{\text{overg}}}{10^5} \frac{W_{\text{soln}} \times \Delta A_t}{2T \times S}
\]

where \(T\) is the duration in hour and \(S (\text{m}^2)\) is the total surface area of seed materials. The values of ‘\(S\)’ are products of the mass of seed materials (\(W_{\text{seed}}, g\)) and the specific surface area.

On the other hand, lanthanide concentration in collected solid samples (\(X_{\text{Ln(solid)}}, \text{μg/g}\)) were determined by inductively coupled plasma mass spectrometry (ICP-MS, Thermo® X series) after direct dissolution and dilution (~0.02 g solids to 20 g 1.5% HNO₃). Thereafter, the relative fraction of lanthanides in aragonite overgrowths (\(X_{\text{Ln(overg)}}, \text{μg/g}\)) were calculated by \(X_{\text{Ln(solid)}}\) as

\[
X_{\text{Ln(overg)}} = X_{\text{Ln(solid)}} \times \frac{W_{\text{seed}} + W_{\text{overg}}}{W_{\text{overg}}}
\]

### 2 Results

#### 2.1 Precipitation of aragonite

Eleven independent experiments were conducted at 25 °C and their primary parameters are briefly listed in Table 1. In order to identify the mineral species of CaCO₃ overgrowths, X-ray diffraction (XRD) analyses were executed to solid samples before and after reactions. All these solids were confirmed to be pure aragonite (Fig. 2). The kinetics of aragonite precipitation in seawater, as summarized by Morse and Mackenzie (1990)\(^{[14]}\), can be expressed as

\[
\log R = n \log (\Omega - 1) + \log k
\]

where \(\Omega\) is the saturation state; ‘\(n\)’ and ‘\(k\)’ are constants. As shown in Fig. 3, the relation between ‘\(R\)’ and ‘\(\Omega\)’ in our experiment can also be well expressed by classic formula. Moreover, it shows no difference to that obtained under normal conditions (no Ln). The precipitation of aragonite was not affected by the presence of lanthanides.

### Table 1 Primary parameters of experiments

<table>
<thead>
<tr>
<th>No.</th>
<th>(W_{\text{seed}}, g)</th>
<th>(W_{\text{soln}}, g)</th>
<th>Duration (\text{h})</th>
<th>pH</th>
<th>(W_{\text{overg}}, g)</th>
<th>(\Omega)</th>
<th>(R, (\text{μmol/(m}^2\text{h)}))</th>
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<td>0.6011</td>
<td>404.5</td>
<td>33.0</td>
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<td>0.0104</td>
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<td>0.0013</td>
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<td>0.0028</td>
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<td>0.0070</td>
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Fig. 2 XRD patterns of solids before and after reactions

(1) Raw seed materials of calcite; (2) Calcite+overgrowths (~100:1); (3) Raw seed materials of aragonite; (4) Aragonite+overgrowths (~10:1)

Fig. 3 Comparison between kinetic expressions of aragonite precipitation
2.2 Enrichment of lanthanides in aragonite

The enrichment of individual lanthanides in aragonite can be directly expressed by the ratio of its absolute amount in aragonite overgrowths (\( \text{Ln}_{\text{overg.}} \)) to its total amount in initial solutions (\( \text{Ln}_{\text{total}} \)), i.e. \( \text{Ln}_{\text{overg.}} / \text{Ln}_{\text{total}} \). The values of \( \text{Ln}_{\text{overg.}} \) and \( \text{Ln}_{\text{total}} \) were calculated as

\[
\text{Ln}_{\text{overg.}} = \frac{X_{\text{Ln(overg.)}} \times W_{\text{overg.}}}{6} \quad (5)
\]
and

\[
\text{Ln}_{\text{total}} = [\text{Ln}]_{\text{init.}} \times W_{\text{sol'n}}. \quad (6)
\]

As shown in Table 2, La, Gd, and Lu were all strongly enriched in aragonite overgrowths. About 57%–99% of initially doped La, 50%–89% of initially doped Gd, and 40%–91% of initially doped Lu were incorporated into aragonite. The enrichment of La in aragonite is systematically stronger than that of Gd and that of Lu, while there is no significant difference between Gd and Lu. With the increase of aragonite precipitation rate, more lanthanides were incorporated into aragonite (Fig. 4). However, their relative fraction in aragonite overgrowths (\( X_{\text{Ln(overg.)}} \), ng/g) consistently decreased with the increase of aragonite precipitation rate (Fig. 5). All these signs indicate that the enrichment of lanthanides in aragonite was kinetically controlled by the precipitation of aragonite.

3 Discussion

Theoretically, the incorporation of lanthanides into aragonite can be divided into two sub-processes: the first one is the migration of \( \text{Ln}^{3+} \) from the solution to the surface of aragonite (i.e. the adsorption), and the second one is the migration of \( \text{Ln}^{3+} \) from the surface of aragonite into the lattice of aragonite (i.e. the coordination)\(^{[15]} \). With the continuous and steady growth of aragonite, the above sub-processes were repeated again and again. Eventually, the allocation of

<table>
<thead>
<tr>
<th>No.</th>
<th>( \text{Ln}_{\text{total}} / \text{ng} )</th>
<th>( [\text{Ln}]_{\text{overg.}} / \text{ng} )</th>
<th>( X_{\text{Ln(overg.)}} % )</th>
<th>( \text{Ln}<em>{\text{overg.}} / \text{Ln}</em>{\text{total}} % )</th>
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<td>Exp. 11</td>
<td>2346</td>
<td>167</td>
<td>2326</td>
<td>99</td>
</tr>
</tbody>
</table>

\( \text{Ln}_{\text{total}} / \text{ng} \) | \( [\text{Ln}]_{\text{overg.}} / \text{ng} \) | \( X_{\text{Ln(overg.)}} \% \) | \( \text{Ln}_{\text{overg.}} / \text{Ln}_{\text{total}} \% \)

Fig. 4 Responses of \( \text{Ln}_{\text{overg.}} / \text{Ln}_{\text{total}} \) ratios to aragonite precipitation rates

Fig. 5 Responses of lanthanide relative fractions in aragonite overgrowths to aragonite precipitation rates
lanthanides in the solid-solution system (including the solution, the interface of solid-solution, and the solid) reached a dynamic balance. It should be noted that such a balance is variable with the growth rate (i.e. precipitation rate) of aragonite. With the increase of aragonite precipitation or growth rate, it is more difficult for the adsorption to offer sufficient supply of lanthanides to the coordination. As a result, it was observed in this study that $X_{\text{Ln(overg.)}}$ decreased with the increase of aragonite precipitation rates.

With respect to the remarkable enrichment of La, Gd, and Lu in aragonite, it is reasonable to assume that they are all incorporated into aragonite lattices by substituting Ca$^{2+}$. However, there is remarkable charge difference between Ln$^{3+}$ and Ca$^{2+}$, so the incorporation of Ln$^{3+}$ into aragonite should be accompanied with the relative charge compensation mechanism. It is widely accepted that there are two types of likelihood, one as $\text{Ln}^{3+} + 2\text{Na}^{+} \rightarrow 2\text{Ca}^{2+}$ and the other as $2\text{Ln}^{3+} \rightarrow 3\text{Ca}^{2+}$. 

The latter mechanism (Eq. 8) has been verified by experimental studies on the coprecipitation of Ln$^{3+}$ with calcite\cite{16}. In this study, all the experiments were conducted in artificial seawater with low lanthanide concentrations and high Na$^{+}$ concentrations. We argue that the latter one (Eq. 8) is much more convincible for the incorporation of Ln$^{3+}$ into aragonite. However, further evidence should be collected to support such assumption.

References:


