Strontium and aragonite-calcite precipitation

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Alternating layers of calcite and aragonite, precipitated from mineral spring in fracture zones of serpentine mass, occur at Kashio, Oosika mura, Nagano Prefecture, Japan. Element mapping by means of Micro-area X-ray Fluorescence (MXRF) conclusively demonstrated that strontium concentrates more in aragonite layer, and not in calcite layer. Other elements including magnesium show no positive correlation with aragonite precipitation. MXRF analyses of aragonite samples from other localities and origins also indicated concentration of Sr as major impurity component, demonstrating that Sr plays essential role in metastable nucleation of aragonite in the precipitation of CaCO₃ polymorphs from aqueous solution. This can be understood on the basis of modifications of surface energy term in CaCO₃ nucleation in the presence of Sr. Temperature changes trigger to increase the Sr concentration in mineral spring, leading to metastable nucleation of aragonite.

Keywords: Calcite-aragonite, Carbonate precipitation in aqueous solution, Metastable nucleation, Strontium, Ostwald rule

INTRODUCTION

Precipitation and stability of calcite and aragonite, two representative CaCO₃ polymorphs, in aqueous solution have been one of the long-holding subjects in earth and biological sciences. Thermodynamics tells that calcite is a stable phase at lower pressure and aragonite at higher pressure than 5 kb at ordinary temperature. Yet aragonite is the major constituent of shells, pearls and other biominerals, indicating its metastable formation in aqueous solutions under 1 atmospheric pressure. This is a problem of metastable nucleation, i.e., nucleation and growth of thermodynamically unexpected phase. Why and how metastable nucleation can occur is a subject of general interest. CVD (Chemical Vapor Deposition) growth of diamond at 1 atmospheric pressure is another representative example of metastable nucleation. The so-called Ostwald step rule (Ostwald, 1900), saying that thermodynamically unexpected phases often nucleate prior to the nucleation of stable phase, is a classical, empirical rule concerning this problem. This rule, together with another rule called Ostwald ripening, has been well known in the field of crystal growth and synthesis for more than a century, and even now an important subject for investigation (e.g., Threlfall, 2003; Sear, 2005).

The role of minor elements or of strain field associated with lattice defects has been suggested as possible reasons for metastable nucleation to take place in aqueous solution or in solid state phase transition. Magnesium has been suggested to play a significant role in aragonite-calcite solid state phase transition, as well as in precipitation of aragonite from aqueous solution at ordinary pressure condition (Yoshida, 1987; Putnis, 1992; Berndt and Seyfried, Jr., 1999; Zhou and Zheng, 2000; Tsukamoto et al., 2001). Strontium has also been suspected of playing a significant role in biomineralogical precipitation of aragonite (Villers et al., 1994; Allison et al., 2001).

It has been known in some hot or mineral springs that alternating layers of calcite and aragonite occur as precipitates showing banded texture. These are usually called “travertine” (Flinn and Pentecost, 1995; Renaut and Jones, 1997), and occur exclusively as precipitations in mineral springs formed under lower pressure condition than 5 kb. Such a sample provides with useful information relating to metastable nucleation of aragonite in aqueous solution system. We applied MXRF (Micro-area X-ray Fluorescence) method to such a sample to see elemental distribution in layers of calcite and aragonite. The sample occurs as precipitations in mineral springs in fissures or a net–works developed in fractured zone of serpentinite mass. The results have demonstrated a clear correlation between concentration of Sr and precipitation of aragonite.
layer. The correlation between Sr and aragonite precipitation has been further confirmed by other samples of aragonite from different localities. This paper aims at demonstrating the correlation between Sr and precipitation of aragonite. Why and how Sr plays an important role in metastable nucleation of aragonite in aqueous solution will be discussed on the basis of modification of interface structure in the presence of Sr ions and its effect upon surface energy term in nucleation.

SAMPLES AND METHODS OF INVESTIGATION

Samples

Carbonate precipitates consisting of alternating layers of aragonite and calcite occur in a form of vein or net-work in fractured zones in a serpentine mass, outcropping on the eastern side close to the Median Tectonic Line of Japan, at Kashio (K1), Ooshika-mura, Shimoina-gun, Nagano Prefecture, Japan. The carbonates are considered to have been precipitated from mineral spring circulating in fracture zones of the serpentine mass, and not in the depth, judging from the mode of occurrence of “travertine” all over the world. There is a nearby locality (K2) with similar mode of occurrence, where only aragonite occurs.

About 1 km west of the locality, there is a mineral spring called Kashio, which has been known as NaCl rich mineral spring, where salt making in mountain region far remote from the sea was actually done in older times. The mineral spring water contains 10.60 g/l of Na⁺ (10.77 g/l in sea water), 0.16 g/l of Ca²⁺ (0.40 g/l, sea water), 0.07 g/l of Mg²⁺ (1.29 g/l, sea water), 0.36 g/l of K⁺ (0.41 g/l, sea water), 19.30 g/l of Cl⁻ (19.35 g/l, sea water), but does not contain detectable amount of Sr²⁺ (Analysis by Investigation Center, Nagano Association for Pharmacists). The chemical composition of the mineral spring is very close to that of sea water, except lower contents of Ca and Mg ions. The source of this mineral spring water is still unknown, but it is certain that there is a contribution from underground water circulating in the serpentine mass. Only a little amount of carbonate precipitation is known at present in Kashio mineral spring.

From the mode of occurrence, it is anticipated that both precipitates consisting of alternating aragonite and calcite layers at K1 and of aragonite only at K2 were deposited from mineral spring with similar chemical composition as that of mineral spring at Kashio, which circulated through fracture zones of serpentine.

Optical microscopic observation shows alternating aragonite and calcite layers. Chemical analyses and element mapping by means of MRXRF were principally done on a sample from Kashio (K1). To confirm the results obtained on this sample, similar MXRF analyses were made on aragonite crystals from another site (K2) in Kashio, Ooshika-mura (single crystals occurring in a vein in serpentine mass, with no association of calcite), Shiraki, Toba-shi (single crystal, occurring in vein form in serpentine), Nagasaki-hana, Choshi-shi (polycrystalline aggregate occurring as an amygdaloidal mineral in basalt), and Morocco (transparent single crystal, locality and mode of occurrence unknown).

Methods of investigation

Element mapping was made by means of MXRF with beam diameters of 100 μm and 10 μm on a sample having alternating layers of aragonite and calcite, in square areas whose optical images and transmission X-ray images are recorded. Through this procedure, element distribution in calcite and aragonite layers were well correlated.

Quantitative MXRF analyses of aragonite and calcite from Kashio (K1) were made at two points respectively, with beam diameter of 100 μm, and scan time 100 s. For aragonite from other localities, only cation concentrations were analyzed by the similar method. No standard was used, and quantitative correction method was adopted.

RESULTS

Optical observation

Figure 1 is a macro-photograph of a sample showing banded texture consisting of alternating calcite and aragonite layers. Wavy banding is in concordant with the surface of substrate serpentine. Also noticed are narrowly spaced black to brownish black thin stripes parallel to the banding.

Figure 2 is a transmission photomicrograph, taken...
under polarized light, of a section from the substrate serpentine to the end of a carbonate precipitate in a sample from Kashio (K1). Within a total thickness of ca. 11 mm of the carbonate precipitate, two aragonite layers of 2.2 mm (A1) and 2.3 to 3.0 mm (A2) in thickness, and two calcite layers of 2.7 mm (C2) and 3.0 mm (C3) in thickness are seen. There are also thinner layers of calcite (C1) in the substrate serpentine. The innermost calcite layer (C4), precipitated at the latest stage, shows a somewhat perturbed texture from other layers.

Both aragonite (A1, A2) and calcite (C2, C3) layers consist of sheaf-like bundles of needle crystals of respective minerals, elongating nearly perpendicularly to the boundary. The length of individual single crystals (identified to be single under polarizing microscope) constituting a sheaf is longer in calcite layer (1.5 mm to 2.5 mm) than in aragonite layer (< 1.0 mm to 1.75 mm), and wider in calcite layer (3 μm to 0.2 mm) than in aragonite layer (6 μm to 10 μm).

Sizes, forms and orientations of individual single crystals vary systematically and similarly in both calcite and aragonite layers. In respective layers, crystal are small and short, and their orientations are random at the onset of precipitation, i.e. adjacent to the boundary with the...
Figure 4. Optical photomicrograph (a), transmission X-ray image (b), distribution of Sr (c), Mg (d), Fe (e) and other elements (Si, Ti, Al, Se) in total (f) of an area shown in (a). (C) calcite and (A) aragonite in (a). Scale in (a). Bar 1.0 mm.
Along the boundary between earlier formed underlying aragonite layer and later calcite precipitate at Kashio, K1. The result of quantitative analysis of this sample is given in Table 2 (a).

Figure 4 shows an optical photomicrograph (a), a transmission X-ray image (b), and element distribution (c, d, e and f) of an area consisting of calcite and aragonite layers. Although element mapping was done for Ca, Si, Sr, Fe, Ti, Mg and other elements (Al, Se), only those showing heterogeneous distribution are shown in Figure 4. Clear correlation with aragonite layer is confirmed only for Sr (Fig. 4c). Mg (Fig. 4d) shows a weak negative, almost negligible correlation with aragonite layer. Fe (Fig. 4e) and other elements in total (Si, Ti, Al, Se) (Fig. 4f) do not show any significant correlation with aragonite layer. Fe distributes in both along grain boundaries of calcite and aragonite crystals in sheaf-like bundles and in a form of stripes parallel to the aragonite and calcite layers. Fe concentration can be correlated to black thin strips observed under optical microscope. Other elements in total also show preferable concentration along grain boundaries of crystals in sheaf-like bundles. From the element mapping, we see that only Sr has one-to-one correlation with precipitation of aragonite layer, and no other elements including Mg show such a clear correlation.

Figure 5 shows a MXRF chart of a representative aragonite layer. The quantitative analytical results of aragonite layer (2 points) and of calcite layer (2 points) of sample from Kashio (K1) shown in Figures 2 and 4 are given in Table 1, with analytical errors 2σ. Sr concentrates in aragonite layer more than 7 times higher than in calcite layer, with 2σ lower than 0.12%, whereas Mg concentrates more in calcite layer than in aragonite layer, although 2σ for Mg is much higher. The data clearly confirm positive correlation of Sr and negative correlation of Mg with precipitation of aragonite layer seen in Figure 4. Table 1 also indicates that there is a certain critical value
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Table 1. MRXF analyses of aragonite and calcite layers in a sample from Kashio (1), shown in Figures 2 and 4

<table>
<thead>
<tr>
<th></th>
<th>A1</th>
<th>A2</th>
<th>C1</th>
<th>C2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>70.81 (1.44)</td>
<td>69.67 (4.65)</td>
<td>69.60 (5.31)</td>
<td>70.07 (4.58)</td>
</tr>
<tr>
<td>Sr</td>
<td>0.71 (0.12)</td>
<td>0.70 (0.13)</td>
<td>0.10 (0.06)</td>
<td>0.12 (0.07)</td>
</tr>
<tr>
<td>Mg</td>
<td>0.05 (1.22)</td>
<td>1.02 (3.96)</td>
<td>1.50 (4.48)</td>
<td>1.10 (3.87)</td>
</tr>
<tr>
<td>CaO</td>
<td>99.08</td>
<td>97.49</td>
<td>97.39</td>
<td>98.04</td>
</tr>
<tr>
<td>SrO</td>
<td>0.84</td>
<td>0.83</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>MgO</td>
<td>0.08</td>
<td>1.69</td>
<td>2.49</td>
<td>1.82</td>
</tr>
</tbody>
</table>

A1 and A2, aragonite layer; C1 and C2, calcite layer. Error bar (2σ) are indicated in parentheses.

Table 2. MRXF analyses of aragonite from several localities

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
<td>1.32 (Al)</td>
</tr>
<tr>
<td>Ca</td>
<td>70.40</td>
<td>99.18</td>
<td>96.99</td>
<td>83.33</td>
<td>96.95</td>
</tr>
<tr>
<td>Ti</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.01</td>
<td></td>
<td></td>
<td>4.86</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>0.64</td>
<td>0.82</td>
<td>2.63</td>
<td>4.50</td>
<td>1.10</td>
</tr>
<tr>
<td>Ag</td>
<td>0.38</td>
<td></td>
<td>0.00</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td></td>
<td></td>
<td>7.31</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>28.61</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

(a) Aragonite in aragonite–calcite layers, Kashio (K1).
(b) Aragonite occurring in the same mode of occurrence as (a) but with no association of calcite (K2).
(c) Aragonite from Shiraki, Toba–shi (vein in serpentinite).
(d) Aragonite from Naganaki–hama, Choshi–shi (amygdaloidal in basalt).
(e) Aragonite from Morocco (locality and mode of occurrence unknown).
(a) Full analysis except carbon. (b) to (e) only cation analysis.

in Sr contents above which metastable aragonite is formed and below which stable calcite is formed. In Table 2, analytical data of aragonite occurring without calcite in the same mode of occurrence at another point close to Kashio (K2), as well as of aragonite crystals from other localities are also given. In all aragonite samples analyzed, Sr concentrations ranging from 0.64 to 4.50 wt% in Sr content are noted (calculated total to 100 wt%, by quantitative correction method). Sr is universally noted in all aragonites analyzed. It is therefore safely concluded that Sr should have played an essential role in the precipitation of aragonite in aqueous solution.

DISCUSSION

The present observations have conclusively demonstrated that only in the presence of Sr higher than a certain critical value, carbonate precipitates as aragonite, otherwise as calcite, in mineral or hot spring. Aragonite precipitation is positively correlated only to Sr and not to other ions, including Mg. Although Mg has been suggested as a most probable ion to enhance nucleation of aragonite, e.g., Yoshida (1987), Putnis (1992), Sabbides and Koutsoukos (1993), Flinn and Pentecost (1995), the present data indicate that this is not the case at least in an aqueous solution system of Kashio.

It is also noticed that carbonate precipitation and its intermission repeat through (1) nucleation of one phase on the surface of substrate or of underlying layer, (2) geometrical selection, formation of sheaf–like bundles, and (3) cessation of precipitation. This sequence forms one cycle. Another point to be noted is the presence of thin mixed layer of aragonite and calcite along the surface of underlying aragonite layer. Such thin mixed layer is not present in the boundary between underlying calcite layer and overlying aragonite layer (Fig. 3). This difference indicates that metastably formed aragonite becomes unstable and is partly dissolved or replaced by calcite when stable calcite appears, whereas stable calcite is not affected when metastable aragonite is formed.

Aragonite precipitation in aqueous solution is a problem of metastable nucleation. In nucleation of any phase, an energy barrier to create a cluster bigger than a critical size has to be overcome. The nucleation energy is a sum of surface energy term (plus) and volume energy term (minus). The activation energy for nucleation can be expressed as \( A_N = \gamma^3 / \Delta \mu^2 \), and so the nucleation energy is determined by a competition between surface energy term \( \gamma \) and driving force term \( \Delta \mu^2 \) (Sunagawa, 1992). Depending on competition between the two terms, it is possible that metastable phase becomes energetically favourable to nucleate prior to the nucleation of stable phase under a certain condition. Before the appearance of stable phase in the system, prior formed metastable phase can grow as if it is a stable phase, but once stable phase appears in the system, the metastable phase starts to dissolve or is replaced by the stable phase. This is because the appearance of stable phase decreases the concentration of dissolved substance in the solution, and the solution becomes undersaturated with metastable phase but saturated with stable phase. The process of prior appearance and steady growth of metastable phase and its dissolution or replacement followed by the appearance of stable phase was observed in situ on silicate minerals in high temperature solution system (Sunagawa, 1992). The observation of the presence
of mixed zone along the boundary between underlying aragonite and overlying calcite layers and the sharp boundary between underlying calcite and overlying aragonite layers indicate such a stability relation between metastably nucleated aragonite and stable calcite layers. Once metastable nucleation takes place and the condition is maintained (to suppress the nucleation of stable phase or to encourage the nucleation of metastable phase), the metastable phase can grow steadily.

In the present case, it is highly probable that Sr plays an essential role in modifying surface energy term to enable metastable aragonite to nucleate. In CVD diamond, presence of hydrogen in the vapor plays the same role to enable metastable diamond to nucleate. Changes of surface energy term by coverage of hydrogen on diamond crystals were shown by a computer simulation work (Zhang and Chen, 1995). Hydrogen also plays a role to destroying stable sp³ covalent bond and surviving metastable sp² bond (Sunagawa, 2005).

Why and how does Sr play an essential role in the precipitation of thermodynamically unexpected phase (aragonite) from an aqueous solution? This is related to the coordination number of Sr. Coordination number of Ca²⁺ is 9 in aragonite and 6 in calcite. Ca²⁺ distribution in calcite structure may be approximated to cubic close-packing, while in aragonite it is approximately hexagonal close-packing (Putnis, 1992). Because the ionic radius of Sr²⁺ (1.13Å for VI and 1.25Å for VIII) is larger than the ionic radius of Ca²⁺ (1.00Å for VI and 1.12Å for VIII), Sr²⁺ attract more CO₃⁻ to form 9 coordination, which is more than 6 coordination around Ca²⁺. This modifies packing from cubic to hexagonal in structure formation, or gives an effect to surface energy term to enable metastable aragonite to nucleate.

Strontianite SrCO₃ has aragonite structure with orthorhombic system, mmm. If we assume formation of strontianite structure as a precursor of the following growth of aragonite, higher concentration of Sr is required than the observed data. Casey et al. (1996) indicated that composition of aragonite or strontianite with even a few% are unstable and will unmix to form a mechanical mixture of Ca-rich strontianite and Sr-rich aragonite. The limit of miscible compositions of CaₓSr₁₋ₓCO₃ at Earth surface condition must have x < 0.01 or x > 0.99 at thermodynamic equilibrium. Parkman et al. (1998) indicated that Sr uptake on calcite surface occurs mainly by ion exchange for concentration < 0.3 μmoles/ml. Taking these into consideration, formation of strontianite of critical size is not likely as a precursor of aragonite formation.

It is more likely that the presence of Sr modifies interface energy term in nucleation energy, changing the competitive relation between surface energy and volume energy terms. This enables metastable nucleation of aragonite to take place. Once aragonite nucleates metastably the subsequent growth will be controlled by this structure, and aragonite growth proceeds so far as the condition (both temperature and Sr concentration) are kept unchanged. If the condition changes and Sr diminishes below a certain critical content, stable phase, calcite nucleates and grows. As the present observations indicate, there is a distinct stage of growth of one phase and its cessation, followed by precipitation of another phase, in association of Sr concentration, above a critical value. Such events should correspond to conditional change, either or both in Sr concentration or temperature. Metastably nucleated aragonite continues its growth so far as Sr is present above a critical value in the system, but as soon as Sr diminishes below this value, calcite precipitates. Conditional change is also noticed within calcite or aragonite layers, which is probably associated with temperature change, but unless Sr is present above a critical value in the system, aragonite layer is not formed.

Temperature is another factor to influence driving force term in nucleation energy. According to a Japanese patent (1990), aragonite (and not calcite) needle crystals can be synthesized industrially by applying forced increase of temperature at a rate of 0.5 to 10 °C/min to lime milk formed by introducing carbon dioxide into lime reaction system. Forced increase of temperature is the key point of this patent to industrially synthesizing aragonite instead of calcite.

Considering the mode of occurrence of alternating calcite and aragonite layer at Kashio (K1), it is anticipated that both temperature and Sr concentration in mineral spring changed alternately, since mineral spring is a mixture of original hydrothermal solution whose origin is unknown and underground water circulating in serpentinite mass. Sr may be derived from the circulating underground water through serpentinite mass. The reason for that Mg distributes more in calcite layers and does not play any significant role in aragonite precipitation in this system may be inferred to much smaller ionic radius of Mg (0.66 Å for IV, 0.97Å for VIII) than Ca and Sr. Mg ionic size is not big enough to form 9 coordination with CO₃²⁻, but easily incorporated into calcite structure. However, in the case of solid-state transformation from aragonite to calcite, Mg may play a significant role, since its presence in aragonite structure influences the strain state. Fe also seems not to have any significant role for aragonite formation due to the same reason. Thin strips of Fe appear due to accumulation of Fe on the growing interface of calcite or aragonite crystal, since the effective distribution coefficient of Fe both in calcite and aragonite is smaller than unity.
As can be seen from papers reporting Sr association in biogenic aragonite (e.g., Villiers et al. (1994), Allison et al. (2001) and many other older papers), Sr has been suggested to play an important role in biogenic crystallization of aragonite. The Sr contents in pearls have been used even for discriminating between sea water and fresh water pearls. The present observations seem to confirm this relation.

CONCLUSION

By correlating element distributions and precipitation of alternating aragonite and calcite layers in mineral spring in serpentine mass at Kashio, Nagano Prefecture, it has been clearly shown that only Sr plays an essential role in metastable nucleation of aragonite in the precipitation of carbonate polymorphs from aqueous solution. Chemical analyses of aragonite from other localities also support an intimate relation between Sr and aragonite precipitation. In the presence of Sr in aqueous solution, the surface energy term in nucleation is modified, leading to metastable nucleation of aragonite possible.

REFERENCES


Color version of Figures 1–4 is linked to the online version of the paper at http://www.jstage.jst.go.jp/browse/jmps

Manuscript received March 27, 2006
Manuscript accepted November 10, 2006
Published online January 25, 2007
Manuscript handled by Koichiro Fujimoto