

## Formation Mechanism of Aragonite by Substitute of $Mg^{2+}$ Ions

Kyung-Sun Choi, Jin-Koo Park, Ji-Whan Ahn,<sup>†</sup> and Hwan Kim\*

Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, Korea

\*School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea

(Received November 11, 2004; Accepted December 16, 2004)

### ABSTRACT

Acicular type aragonite precipitated calcium carbonate was synthesized by carbonation reaction of  $Ca(OH)_2$  slurry and  $CO_2$  gas. As increasing the initial concentration of  $Mg^{2+}$  ion, calcite crystal phase substantially decreased while that of aragonite crystal phase increased. According to XRD and EDS analysis, it was found that the addition of  $MgCl_2$  induced the  $Mg^{2+}$  ion to substitute in  $Ca^{2+}$  ion site of calcite lattice then the unstabled calcite structure be resolved, consequently the growth of calcite structure is interrupted while the growth of aragonite structure is expedited.

**Key words :** Precipitated calcium carbonate, Aragonite, Carbonation process, Magnesium ion

### 1. Introduction

Crystal phases, morphology and particle size of Precipitated Calcium Carbonate (PCC) vary depending on the reaction conditions including the ingredients of the solution, pH, temperature, supersaturation, agitation speed and addition of ions or crystal seeds.<sup>1,2)</sup> Calcium carbonate has three polymorphs, which are calcite, aragonite and vaterite. Calcite is thermodynamically stable under ambient temperature and pressure, and tends to easily precipitate in the natural conditions, while the others are unstable. Aragonite has an acicular shape with a very large aspect ratio, and is attracting attention as a high functional inorganic material that can enhance strength and whiteness, and adjust opacity when used as fillers for rubber, plastics and paints as well as a pigment for the paper industry. Especially, because this material features excellent impact resistance, and it is possible to raise its oil absorption, we can expect to increase strength in shape control of thermoplastic resins and polypropylene resins by adding it as fillers. However aragonite is a metastable substance under atmospheric pressure and due to its rapid transfer to more stable calcite state, it is very difficult to synthesize aragonite. Thus studies to overcome such problems have been under way.<sup>3-7)</sup>

According to the results of researches that have been performed for synthesis of aragonite by carbonation process in recent years. Tanaka *et al.*<sup>8)</sup> reported that the effect of pH, temperature, flow rate of  $CO_2$  gas and reaction time on the synthesis of acicular type aragonite. Ota *et al.*<sup>9)</sup> reported that the initial pH value of reaction mixture solution deter-

mined the formation of aragonite. And, Sasaki *et al.*<sup>10)</sup> asserted that the  $Mg^{2+}$  ions are the most effective for synthesis mono phasic aragonite and reported that the effect of  $MgCl_2/CaO$  mole ratio, flow rate of  $CO_2$  gas and reaction time on the synthesis of aragonite. However, these results are applicable to a certain system or condition, and consideration of the effect of various reaction factors, especially, formation mechanism of aragonite was not available.

In this study, we inquired into the influence of  $Mg^{2+}$  ion on the structural change of calcite and the formation of aragonite while precipitated calcium carbonate is synthesized by carbonation reaction.

### 2. Experiment Procedures

We changed the initial pH value of the mixed solution from 12 to 7 by gradually adding the prepared 2.5 M  $MgCl_2$  aqueous solution (Junsei Co., purity > 98%) to 0.2 M  $Ca(OH)_2$  slurry (Sigma Co., purity > 95%). Maintaining the fixed reaction temperature of 80°C, we injected  $CO_2$  gas at the flow rate of 100  $cm^3/min$  to the mixed solution, and the pH value fell. When pH stabilized in the range of 5.5 to 6.0, we maintained this condition for about 30 minutes. After vacuum-filtering the precipitate, and was dried at 60°C in a drying oven. During the reaction, we maintained an agitation speed of 250 rpm.

We observed the shape and size of the precipitate by an SEM (JSM 6400 made by Jeol Co.) and analyzed the crystalline phase with an XRD (X'Pert made by Philips Co.). We analyzed the concentration of  $Ca^{2+}$  and  $Mg^{2+}$  ions before and during the reaction with an ICP (ICPS-7500 made by Shimatsu Co.) and the XRD, and conducted EDS (Series II made by Noran Co.) analysis to check the  $Mg^{2+}$  ion in the calcite and aragonite lattices of synthesized calcium carbonate.

<sup>†</sup>Corresponding author : Ji-Whan Ahn

E-mail : ahnjw@kigam.re.kr

Tel : +82-42-868-3578 Fax : +82-42-861-3990

**Table 1.** Changes of pH, Ions Concentrations and Crystal Phases of Each Precipitate with the Addition of MgCl<sub>2</sub> Solution at 80°C

Batch no.	Starting materials (mole)		pH	Ion concentration (mole/L)		Phase of precipitates
	Ca(OH) <sub>2</sub>	MgCl <sub>2</sub>		C <sub>Ca</sub>	C <sub>Mg</sub>	
(a)	0.2	0	11.7	0.015	0	Calcite
(b)	0.2	0.15	10.0	0.150	0.00016	Calcite ≈ Aragonite
(c)	0.2	0.17	9.0	0.140	0.0051	Calcite ≈ Aragonite
(d)	0.2	0.25	8.1	0.124	0.045	Calcite ≈ Aragonite
(e)	0.2	0.4	7.8	0.124	0.155	Calcite ≈ Aragonite
(f)	0.2	0.5	7.6	0.121	0.201	Calcite ≈ Aragonite
(g)	0.2	0.6	7.5	0.118	0.250	Aragonite
(h)	0.2	0.8	7.3	0.118	0.450	Aragonite

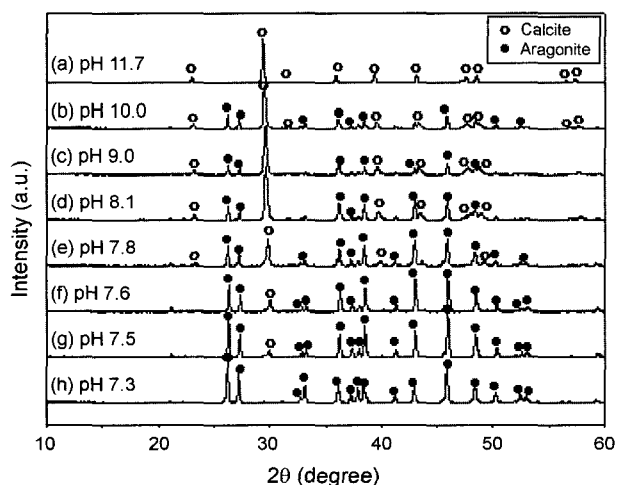
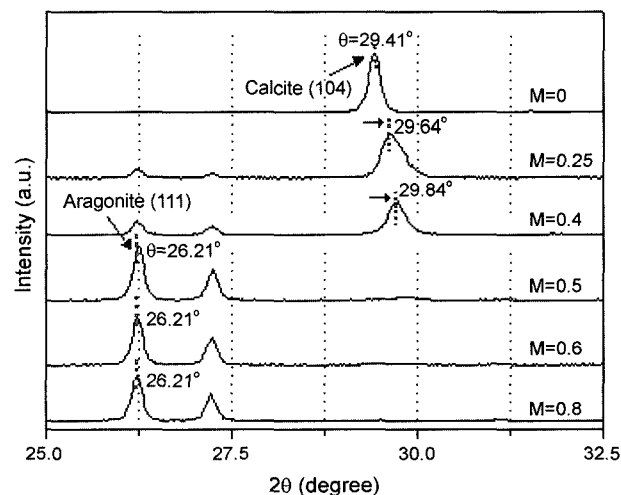
### 3. Results and Discussion

Table 1 shows the changes of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions concentrations and pH values in the mixed 0.2 M Ca(OH)<sub>2</sub> slurry with 2.5 M MgCl<sub>2</sub> aqueous solution before the carbonation reaction. And, also the crystalline phases of the product after the completion of carbonation reaction are indicated, respectively. As more MgCl<sub>2</sub> is added, the pH of the mixed solution fell rapidly from 11.7 to 8.1, but it can be seen that, after a certain quantity of MgCl<sub>2</sub>, the rate of change become slow to the range of 7.8 to 7.3. Accordingly, most of the Mg<sup>2+</sup> ions react with OH<sup>-</sup> ions that have been formed and are used to create Mg(OH)<sub>2</sub>, only an extremely small quantity of Mg<sup>2+</sup> remains in ion condition and participates in the reaction, and the more MgCl<sub>2</sub> is added, the higher becomes the concentration of Mg<sup>2+</sup> in the solution.

Fig. 1 is a result of XRD analysis on the educed precipitates according to each condition shown in Table 1. In accordance with the added quantity of MgCl<sub>2</sub>, the formed phase was primarily calcite with an extremely small amount of aragonite in the pH range of 10 to 8.1. However, as more MgCl<sub>2</sub> was added, pH fell to 7.8 and the education of aragonite increased significantly up to the level of calcite. On the

other hand, we observed that, the concentration of Mg<sup>2+</sup> ion was extremely low (0.00016 to 0.04500 M) until the addition of MgCl<sub>2</sub> reached 0.25 mole and confirmed that the product was calcite at this time. However, when the addition of MgCl<sub>2</sub> was 0.4 mole and the concentration of Mg<sup>2+</sup> ion increased to 0.155 M, near that of Ca<sup>2+</sup>, the formation ratio of aragonite exceeded that of calcite. As the concentration of Mg<sup>2+</sup> ion grew, the education of aragonite continued to increase, and when there existed more than 0.250 M of Mg<sup>2+</sup> ion, aragonite was educed in a mono phase.

Fig. 2, the result of XRD analysis on precipitates with varying quantity of MgCl<sub>2</sub> added, shows that the more MgCl<sub>2</sub> is added, that is, the higher the initial concentration of Mg<sup>2+</sup> ion in the solution, the main peak of educed calcite (104) was shifted toward higher angle. While 2θ=29.41° at the main peak of calcite (104) with no MgCl<sub>2</sub> added at all, 2θ=29.64° with 0.25 mole MgCl<sub>2</sub> and 2θ=29.84° with 0.4 mole MgCl<sub>2</sub>. However, at the main peak of aragonite (111), the value of 2θ remains nearly constant regardless of the quantity of MgCl<sub>2</sub> added. This means that Mg<sup>2+</sup> ion is taken into the place of Ca<sup>2+</sup> in calcite lattices and forms (Ca,Mg)CO<sub>3</sub> (magnesian calcite) solid solution. And, it can be assumed that the more Mg<sup>2+</sup> ion is dissolved into calcite lat-

**Fig. 1.** XRD patterns of precipitate with the pH values at the reaction temperature of 80°C.**Fig. 2.** XRD patterns of precipitate with the addition of MgCl<sub>2</sub> solution (M= mole of MgCl<sub>2</sub>).

**Table 2.** The Quantity of  $Mg^{2+}$  Ions Substituted in Calcite Lattice

Reaction conditions			$d_{104}$	$Mg^{2+}$ mole% (ideal)	$Mg^{2+}$ mole% (EDS observation)
$Ca(OH)_2$ (mole/L)	Temperature ( $^{\circ}C$ )	$MgCl_2$ (mole)			
0.2	80	0	3.034	0	0
0.2	80	0.25	3.010	7.921	7.59
0.2	80	0.4	2.999	11.784	9.59
0.2	80	0.5	2.991	14.702	12.93

tices, the closer the value of  $d_{104}$  moves toward  $MgCO_3$ . Therefore it is possible to calculate the quantity of  $Mg^{2+}$  ion dissolved into calcite lattices by calculating the shift of the calcite main peak (104) toward a higher angle. Since the  $d_{104}$  value of  $MgCO_3$  in JCPDS phase is 2.724 and that in calcite phase is 3.304, we can calculate the quantity of  $Mg^{2+}$  ion dissolved in lattice theoretically assuming that there exists a linear relationship between the quantity of  $Mg^{2+}$  ion dissolved in lattice and the  $d_{104}$  value.

Besides, it is possible to confirm the  $Mg^{2+}$  ion in calcite lattices through EDS analysis. Table 2 shows the results of theoretical calculation on  $Mg^{2+}$  ion dissolved in calcite lattices and the average actual values measured by EDS analysis. According to Table 2, even though some difference exists between the theoretical calculation and the EDS measurement, the increasing trend of  $Mg^{2+}$  ion dissolved in calcite lattices in response to a higher value of  $MgCl_2$  added is apparent.

Fig. 3 shows the results of SEM and EDS analysis on cubic calcite (a) and acicular aragonite (b) when 0.4 mole and 0.6 mole  $MgCl_2$  was added, respectively. Fig. 3(a) is calcite phase with cubic shapes about 1  $\mu m$ , and EDS analysis shows a  $Ca^{2+}$  peak and an extremely small  $Mg^{2+}$  peak. On the other hand, Fig. 3(b) is aragonite phase with acicular shapes about 20 to 30  $\mu m$ , and EDS analysis detected a  $Ca^{2+}$  peak only. Consequently we confirmed that  $Mg^{2+}$  ion is dissolved in calcite lattices and forms  $(Ca,Mg)CO_3$  solid solution, but it is not dissolved in aragonite lattices. We can explain that, because  $MgCO_3$  has a calcite-type structure,  $Mg^{2+}$  ion can be easily contained in calcite lattices and forming magnesian calcite, but it is not dissolved in aragonite

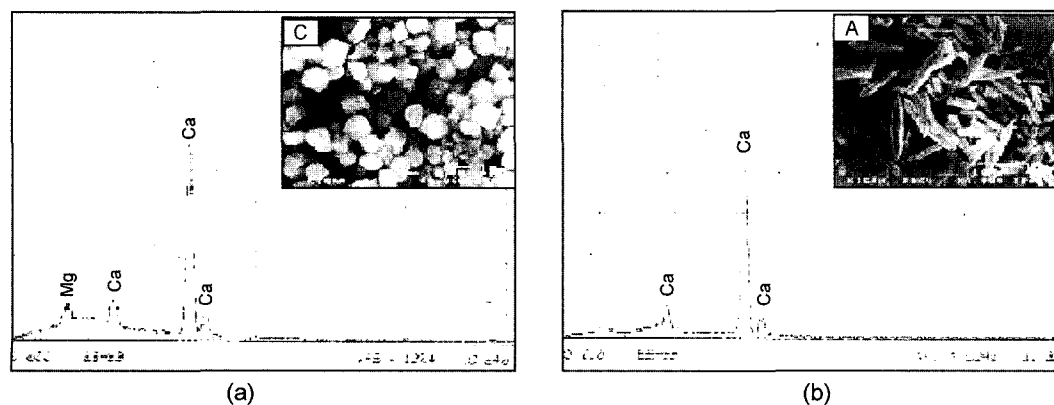
lattices.

Many researchers investigated the influence of various ions in kinetic studies on the phase transfer of thermodynamically unstable aragonite.<sup>11</sup> Among the ions that have been investigated,  $Mg^{2+}$  ion is known to be the most effective in suppressing the formation of calcite nuclei and crystal growth. As mechanisms for the suppression of calcite, the suppression of forming nuclei, adsorption to the location of growth, the distortion of calcite lattices, and the kinetic problem of cation dewatering have been presented,<sup>12</sup> but no clear interpretation is yet available.

However, from the results of this study, the suppression of calcite formation and the mechanism of aragonite eduction can be interpreted as follows.  $Mg^{2+}$  ion, whose radius is smaller than that of  $Ca^{2+}$  is substituted  $Ca^{2+}$  ion site, and distortion in the lattices of magnesian calcite takes place. Thus, it can be explained that, as the re-dissolution of magnesian calcite lattice due to an unstable structure is increased, the formation of calcite is suppressed and the eduction of aragonite proceeds relatively faster.

#### 4. Conclusions

When the synthesis of precipitated calcium carbonate by carbonation reaction of  $Ca(OH)_2$  slurry and  $CO_2$  gas at  $80^{\circ}C$  mono phasic calcite crystal phase obtained, however, as increasing the addition of  $MgCl_2$ , calcite crystal phase gradually decreased while aragonite crystal phase increased. At the condition of the same concentration of  $Mg^{2+}$  and  $Ca^{2+}$  ions in the solution, formation yield of aragonite prior to calcite and mono phasic aragonite was formed with the exceed



**Fig. 3.** SEM and EDS analysis on calcite and aragonite particles (C : calcite, A : aragonite).

Mg<sup>2+</sup> ion concentration. As a result of measuring the quantity of dissolved Mg<sup>2+</sup> ion in the calcite and aragonite lattice which are educted with mixing phases, with increasing the addition of MgCl<sub>2</sub> quantity of Mg<sup>2+</sup> ions dissolved in calcite lattice was increased but it was not affected to aragonite lattice. So, we could find that Mg<sup>2+</sup> ions were substituted to Ca<sup>2+</sup> ions site of calcite lattice and formed magnesian calcite. So, distorted calcite structure resolved and the crystal growth of aragonite is expedited.

## REFERENCES

1. O. Sohnle and J. W. Mullin, "Precipitation of Calcium Carbonate," *J. Crystal Growth*, **60** 239-50 (1982).
2. J. L. Wray and F. Daniels, "Precipitation of Calcite and Aragonite," *J. Am. Chem. Soc.*, **79** 2031-34 (1957).
3. F. Lippmann, "Sedimentary Carbonate Minerals," Springer-verlag (1973).
4. Y. Kojima and A. Sadotomo, "Control of Crystal Shape and Modification of Calcium Carbonate Prepared by Precipitation from Calcium Hydrogencarbonate Solution," *J. Ceram. Soc. Jpn. Int.*, **100** 1128-35 (1992).
5. J. L. Bischoff, "Kinetics of Calcite Nucleation : Magnesium Ion Inhibition and Ionic- Strength Catalysis," *J. Geophys. Res.*, **73** 3315-22 (1968).
6. R. L. Folk, "The National History of Crystalline Calcium Carbonate : Effect of Magnesium Content and Salinity," *J. Sedi. Petrol.*, **44** [1] 40-53 (1974).
7. W. A. House, M. R. Howson, and A. D. Pethybridge, "Crystallization Kinetics of Calcite in the Presence of Magnesium Ions," *J. Chem. Soc., Faraday Trans*, **1** **84** [8] 2723-34 (1988).
8. H. Tanaka, H. Horiuchi, and T. Ohkubo, "Synthesis of Whisker Aragonite CaCO<sub>3</sub>," *Gypsum & Lime*, **216** 314-21 (1988).
9. Y. Ota, S. Inui, T. Iwashita, and Y. Abe, "Preparation of Aragonite Whiskers," *J. Am. Ceram. Soc.*, **78** [7] 1983-84 (1995).
10. K. Sasaki, M. Hongo, and M. Tsunekawa, "Synthesis of Aragonite-Type of Calcium Carbonate from Calcined Scallop Shell (3rd Report)," *Shigen-to-Sozai*, **114** 715-20 (1998).
11. A. Gutjahr and H. Dabringhaus, "Studies of the Growth and Dissolution Kinetics of the CaCO<sub>3</sub> Polymorphs Calcite and Aragonite : I. Growth and Dissolution Rates in Water," *J. Crystal Growth*, **158** 296-309 (1996).
12. G. H. Nancollas and K. Sawada, "Formation of Scales of Calcium Carbonate Polymorphs : The Influence of Magnesium Ion and Inhibitors," *Soc. Petro. Eng. AIME*, 645-52 (1982).