

琉球大学学術リポジトリ

Catalytic Effect of Magnesium Ions on Polymorphic Crystallization of Calcium Carbonate

メタデータ	言語: 出版者: 琉球大学理学部 公開日: 2009-08-28 キーワード (Ja): キーワード (En): 作成者: 大森, 保 メールアドレス: 所属:
URL	http://hdl.handle.net/20.500.12000/12170

Catalytic Effect of Magnesium Ions on Polymorphic Crystallization of Calcium Carbonate

Tamotsu OOMORI* and Yasushi KITANO**

Abstract

The effect of Mg^{2+} ions on the polymorphic crystallization of calcium carbonate has been studied by precipitating carbonate minerals from $Ca(HCO_3)_2$ (Ca^{2+} , 400 mg/l) solutions containing various amount of Mg^{2+} ions (0 to 2000 mg/l) at the temperature of 2 to 80°C. The concentration of Mg^{2+} ions and temperature in a parent solution affect remarkably the aragonite formation. The precipitating fields of calcite and/or aragonite are systematically represented on $\log[Mg^{2+}]$ vs. $1/T$ diagram. Energetic effect of Mg^{2+} ions on aragonite formation is estimated from an Arrhenius type relationship between required concentration of Mg^{2+} ions and absolute temperature to form aragonite; $[Mg^{2+}] = A \cdot \exp(-E/RT)$, where $E = 13$ Kcal/mol, which will be needed to form aragonite nucleus from solution.

The presence of calcite seeds favors the calcite formation in the presence of Mg^{2+} ions lower than 400 mg/l.

1. Introduction

It is important to reveal the role of Mg^{2+} ions and of the other divalent cations, anions and dissolved organic materials in parent solutions on the carbonate formation for the understanding of inorganic and biological precipitation of calcium carbonates. The biologically formed marine carbonate skeletons are composed of low Mg-calcite, high Mg-calcite and aragonite, where low Mg-calcite is thermodynamically stable under natural conditions (Jamieson¹, Macdonald²). The controlling factors of the polymorphic formation in marine carbonate skeletons are biological species, temperature, and salinity in the water environments (Lowenstam³, Chave⁴, Dodd⁵, Kitano et al.⁶, Milliman⁷).

It is evident that Mg^{2+} ions in a parent solution favor aragonite precipitation in marine environments (Kitano and Hood⁸, Simkiss⁹, Groot and Duyvis¹⁰). Mg^{2+} ions act as an inhibitor for nucleation and/or growth of calcite (Mclester et al.¹¹, Bischoff¹², Bischoff and Fyfe¹³, Pytkowicz¹⁴, Berner^{15,16}). Katz¹⁷ and Mucci and Morse¹⁸ studied the incorporation of magnesium to calcite. Incorporation of magnesium makes calcite unstable thermodynamically (Kitano and Frutsu¹⁹, Jensen and Kitano²⁰, Winland²¹, Plummer and Mackenzie²²). And the incorporation of magnesium to carbonate decreases the surface tension of calcite (Mg poor and Mg rich) and aragonite, and decreases the nucleation energy of these minerals. The decrease in the nucleation energy is larger for aragonite than that for calcite (Möller and Lajacopalan²³).

Received: October 31, 1984

*Department of Chemistry, College of Science, University of the Ryukyus, Nishihara, Okinawa, 903-01.

**Water Research Institute, Nagoya University.

The purpose of this paper is to clarify the role of Mg^{2+} ions in a parent solution on the crystallization of calcium carbonates.

2. Experimental Procedure

Effects of Mg^{2+} ions and temperature in a parent solution on the formation of calcium carbonate polymorphs have been studied by precipitating carbonates from calcium bicarbonate solution containing various amounts of Mg^{2+} ions at various temperatures. The calcium bicarbonate solution was prepared by bubbling CO_2 gas to calcium carbonate suspension and filtering with Toyo filter paper (No. 2). Then CO_2 gas was bubbled again. Various amounts of $MgCl_2$ solution were added to 1000 ml of the $Ca(HCO_3)_2$ solution. The solution were stirred continuously at 2, 10, 22, 40, 60 and 80°C. Also, sea water was used to have informations about carbonate polymorphism formed from it. The calcium and magnesium contents of solutions and precipitates were determined by EDTA titration and atomic absorption.

In order to get informations about the characterization of magnesium effect, the experiments on the effect of the presence of calcite seeds were also carried out in the presence of Mg^{2+} ions in a parent solution. The solution containing calcite seeds was prepared as follows: 2000 ml of calcium bicarbonate solution was stirred until $CaCO_3$ separation started to come out. The formed precipitates were filtered off with Toyo filter paper (No. 2) during the presence of suspended carbonate in the solution, that is, before the formed carbonate deposited and the solution became transparent*. The prepared filtrates contain calcite seeds. Concentration of the seeds in a parent solution is around 5 mg/l or less. The various volumes of $MgCl_2$ solution, saturated with calcite at $P_{CO_2} = 1$ atm., were added to the filtrates containing calcite seeds. When $MgCl_2$ solutions not saturated with calcite were added, the seeds did not work. These solutions saturated with calcite were stirred for about 20 minutes and then kept still at 25°C. Carbonate precipitates appeared like snow fall after one day. For the complete precipitation, the solution was kept standing still further for one week at 25°C. The floating carbonates suspended in the surface were discarded carefully and the precipitates on the bottoms of the beakers were tested by X-ray diffraction, because the mineral composition of carbonates floating in the surface of the solution was usually complex.

*When the solution is filtered after the solution became transparent, the presence of seeds in the solution is negligible.

3. Results and Discussion

Crystallizing fields of calcium carbonate polymorphs are shown in Fig. 1. It is evident that the presence of Mg^{2+} ions and the high temperature in the parent solution favor the aragonite formation. The experimental result shows that only aragonite is precipitated from sea water under ordinary conditions.

The boundary of the precipitating fields of aragonite and calcite is shown by the strait line in the $\log[Mg^{2+}]$ vs. $1/T$ diagram, whereas the boundary line between calcite and calcite + aragonite deviates down from a straight line in a high temperature range (see Fig. 1). This may be caused by the mixing of complex carbonate formed in the surface of the solution at high temperatures. The boundary of the precipitating fields is considered to be expressed by an Arrhenius type relationship between

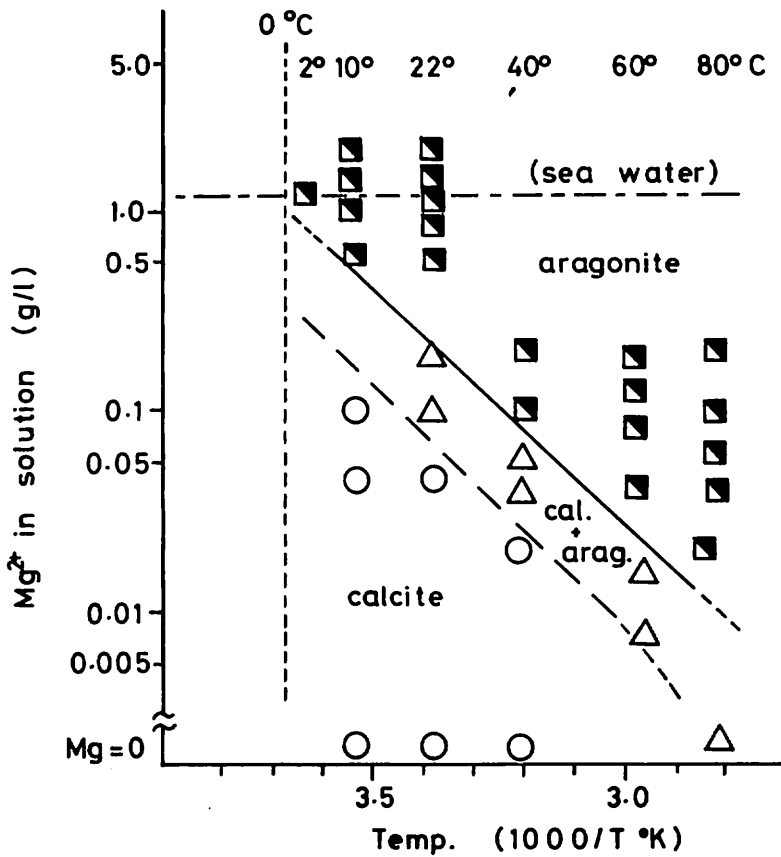


Fig. 1. Precipitating fields of calcite and/or aragonite.

required concentration of Mg^{2+} ions and temperature to form aragonite;

$$[Mg^{2+}] = A \exp(Q/T),$$

where A and Q are constant, and Q contains an energy term. The above equation is rewritten;

$$[Mg^{2+}] = A \exp(-E/RT),$$

where A is constant and R is gas constant. Mg^{2+} ions in solution control the rate of calcium carbonate crystallization (Pytkowicz¹⁴, Berner¹⁶). So, E is an energy term such as activation energy for aragonite formation from solution. From the experimental results shown in Fig. 1, the energetic effect of Mg^{2+} ions is estimated to be shown as $E = 13$ Kcal/mol. Activation energies for calcite growth from solution without Mg^{2+} ions and for transformation of aragonite to calcite were reported to be 11.0 Kcal/mol (Nancollas and Reddy²⁴) and 57.4 Kcal/mol (Bischoff²⁵), respectively. It seems that activation energy for calcite growth from Mg^{2+} containing solution is larger than that from solutions without Mg^{2+} ions.

In order to get informations about the characterization of magnesium role on the polymorphic crystallization of $CaCO_3$, the experiments on calcite seeds were carried out. The results are shown in

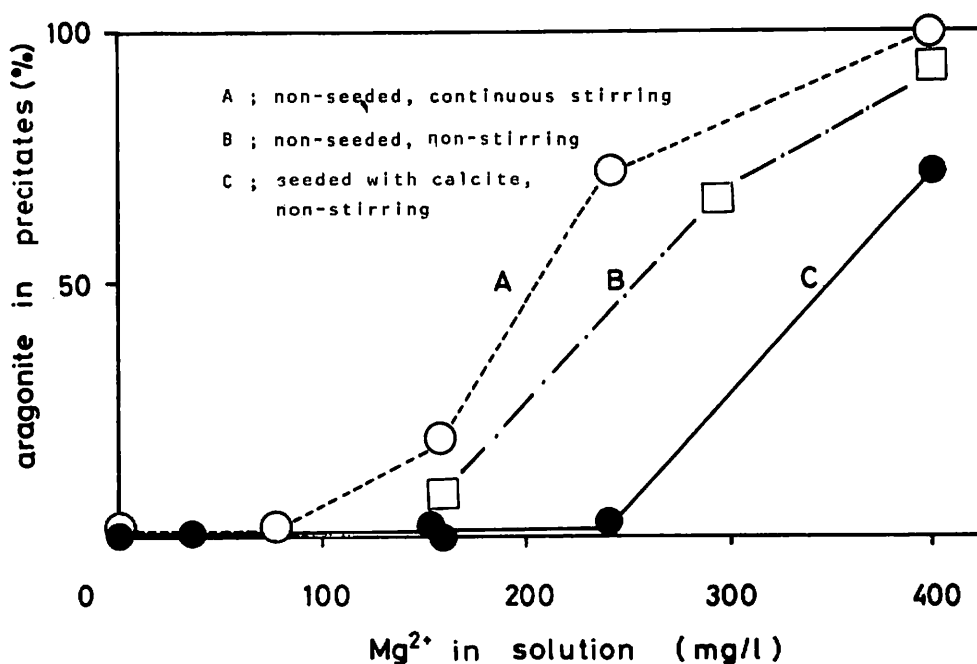


Fig. 2. Aragonite proportion of precipitates vs. added amount of Mg²⁺ ions in solution.

Fig. 2 with the experimental results without the seeds. It is apparent that the presence of calcite seeds favor the calcite formation in the presence of Mg²⁺ ions of lower than 400 mg/l. Aragonite is a dominant precipitates, when the parent solutions containing Mg²⁺ ions of more than 200 mg/l without calcite seed were stirred at 25°C. But, aragonite was not formed from calcite seeded and non-stirred solution containing 240 mg/l of Mg²⁺ ions. The seeds seem to exceed magnesium ions in the effect at moderate Mg²⁺ concentration in a parent solution. The microscopic observations in the seed experiments recognized the growth of oolitic aragonite on the surface of calcite crystals. Magnesium ions may promote the formation of aragonite nucleous on the surface of calcite crystals. Nucleation stage is important for the formation of carbonate polymorphism. The energy estimated above is considered to be the energy needed to form aragonite nucleous from solutions. Kitano et al.²⁶ showed that the ions in a parent solution favorable for aragonite formation, such as copper and zinc, were much incorporated in carbonate precipitate at earlier stage of carbonate crystallization than at later stage, although the crystal form of those metal carbonate is not aragonitic but calcitic. Incorporation of magnesium to carbonate lattice sometimes causes the thermodynamical instabilization and the enhanced solubility of calcite (Berner¹⁶, Plummer and Mackenzie²²). From the study on the kinetics for calcium carbonate formation from supersaturated solutions containing Mg²⁺ ions, Möller and Lajacopalan²³ reported that the incorporation of magnesium to carbonate decreases the surface tension of carbonate minerals, and lowers the nucleation energy of calcite (Mg poor and Mg rich) and aragonite. The decrease in the nucleation energy for aragonite is maximum in the highly supersaturated solution having larger than 4 of Mg²⁺/Ca²⁺ molar ratio. The incorporation of magnesium may lower the energy needed for aragonite nucleous formation.

References

- 1) Jamieson, J.C. (1953) Phase equilibrium in the system calcite-aragonite. *Jour. Chem. Phys.* **21**, 1385-1390.
- 2) Macdonald, G.J.F. (1956) Experimental determination of calcite-aragonite equilibrium relations at elevated temperature and pressures. *Amer. Mineral.* **41**, 744-756.
- 3) Lowenstam, H.A. (1954) Factors affecting the aragonite; calcite ratios in carbonate secreting organisms. *J. Geol.* **62**, 284-322.
- 4) Chave, K.E. (1962) Factors influencing the mineralogy of carbonate sediments. *Limnol. Oceanogr.* **7**, 218-233.
- 5) Dodd, J.R. (1963) Paleocological implication of shell mineralogy in two pelecypod species. *J. Geol.* **71**, 1-11.
- 6) Kitano, Y., Kanamori, N., Tokuyama, A. (1969) Effect of organic matter on solubility and crystal form of carbonates. *Amer. Zoologist* **9**, 681-688.
- 7) Milliman, J.D. (1974) Recent sedimentary carbonate, part 1. *Marine carbonates*. Springer-Verlag.
- 8) Kitano, Y. and Hood, D.W. (1965) The influence of organic material on the polymorphic crystallization of calcium carbonate. *Geochim. Cosmochim. Acta* **29**, 29-41.
- 9) Simkiss, K. (1964) Variations in the crystalline form of calcium carbonate precipitated from artificial sea water. *Nature* **201**, 492-493.
- 10) Groot, K. De and Duyvis, E.M. (1966) Crystal form of precipitated calcium carbonate as influenced by adsorbed magnesium ions. *Nature* **212**, 183-184.
- 11) Mclester, M.E., Martin, D.F. and Taft, W.H. (1970) Effects of alkali-earth metal ions on the transformation of aragonite to calcite in aqueous solution. *J. Inorg. Nucl. Chem.* **32**, 391-399.
- 12) Bischoff, J.L. (1968) Catalysis, inhibition and the calcite-aragonite problem. II The vaterite-aragonite transformation. *Amer. J. Sci.* **266**, 80-90.
- 13) Bischoff, J.L. and Fyfe, W.S. (1968) Catalysis, inhibition and the calcite-aragonite problem. I The aragonite-calcite transformation. *Amer. J. Sci.* **266**, 65-79.
- 14) Pytkowicz, R.M. (1973) Calcium carbonate retention in super-saturated sea water. *Amer. J. Sci.* **273**, 515-522.
- 15) Berner, R.A. (1966) Diagenesis of carbonate sediments; Interaction of magnesium in sea water with mineral grains. *Science* **153**, 188-191.
- 16) Berner, R.A. (1975) The role of magnesium in the crystal growth of calcite and aragonite from sea water. *Geochim. Cosmochim. Acta* **39**, 489-504.
- 17) Katz, A. (1973) The interaction of magnesium with calcite during crystal growth at 25–90°C and one atmosphere. *Geochim. Cosmochim. Acta* **37**, 1563-1586.
- 18) Mucci, A. and Morse, J.W. (1983) The incorporation of Mg^{2+} and Sr^{2+} into calcite overgrowth: influences of growth rate and solution composition. *Geochim. Cosmochim. Acta* **47**, 217-233.
- 19) Kitano, Y. and Frutsu, T. (1959) The state of small amount of magnesium contained in calcareous shells. *Bull. Chem. Soc. Japan* **13**, 1-4.
- 20) Jensen, J.F. and Kitano, Y. (1963) The resistance of Recent marine carbonate sediments to solution. *J. Oceanogr. Soc. Japan* **18**, 208-219.
- 21) Winland, H.D. (1969) Stability of calcium carbonate polymorphs in warm, shallow sea water. *J. Sed. Petrol.* **39**, 1579-1587.

- 22) Plummer, L.N. and Mackenzie, F.T. (1974) Predicting mineral solubility from rate data. Application to the dissolution of magnesian calcites. *Amer. J. Sci.* **274**, 61-83.
- 23) Möller, P. and Rajacopalan, G. (1976) Changes of excess free energies in the crystal growth process of calcite and aragonite due to the presence of Mg^{2+} ions in solution. *Z. Physik. Chem. Neue Folge Bd.* **99**, S. 187-198.
- 24) Nancollas, G.H. and Reddy, M.M. (1971) The crystallization of calcium carbonate II. Calcite growth mechanism. *J. Colloid and Interface Sci.* **37**, 824-830.
- 25) Bischoff, J.L. (1969) Temperature controls on aragonite-calcite transformation in aqueous solution. *The Amer. Mineral.* **54**, 149-155.
- 26) Kitano, Y., Kanamori, N. and Oomori, T. (1971) Measurements of distribution coefficients of strontium and barium between carbonate precipitate and solution—Abnormally high values of distribution coefficients measured at early stage of carbonate formation. *Geochem. J.* **4**, 183-206.