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Synthesis of protodolomite from coral reef sand

Hiroyuki Fujimura [a,b], Tamotsu Oomori [a], Shigeru Kochi [b],
Tomas A. Prolla [c], Shinichi Someya [b,*]

[a] Chemistry, Biology and Marine Science, Faculty of Science, University of the Ryukyus, 1 Senbaru, Nishihara, Okinawa 903-0213, Japan
[b] Marine Bioscience Laboratory, Marine Bio Co. Ltd., 7F Ikeda Building, 1 Kitanorimono-cho, Kanda, Chiyoda-ku, Tokyo 101-0036, Japan
[c] Departments of Genetics and Medical Genetics, University of Wisconsin, 445 Henry Mall, Madison, WI, United States

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Abstract

Protodolomite (calcium carbonate, PD) is widely used in calcium (Ca) and magnesium (Mg) nutritional supplements because it is rich in Ca (>20%) and Mg (>10%). Synthesis of PD usually involves the use of a NaCl solution with Ca^{2+} and Mg^{2+}. In this study, we synthesized PD from coral reef sand (CRS) and magnesium chloride ($MgCl_2$). First, CRS was dissolved in hydrogen chloride (HCl). $MgCl_2$ was then added to the solution and the concentrations of Ca^{2+} and Mg^{2+} in the solution were adjusted to 150 and 350 mM, respectively. The solution was mixed with sodium carbonate ($Na_2CO_3 = 156$ mM) and incubated at 40 °C for 2 days in order to precipitate PD. The precipitate was identified as PD by X-ray diffraction analysis and atomic absorption analysis. This is the first study to synthesize PD from CRS, providing a new source of PD for the food industry.

Keywords: Protodolomite; Coral reef sand; Dolomite; Calcium; Magnesium

1. Introduction

Protodolomite (PD) is a calcium magnesium carbonate which has a chemical composition of $Ca_{1-x}Mg_xCO_3$ ($x = 0.4$–0.5) (Ohde & Kitano, 1981). It is structurally and compositionally similar to dolomite ($Ca_{0.5}Mg_{0.5}CO_3$), and is defined as dolomite with disordered Ca and Mg in the crystal (Goldsmith, Graf, & Heard, 1961). PD, as found in nature, is formed from highly saline solutions containing Ca and Mg. Ohde and Kitano (1978) reported that PD could be synthesized from a NaCl solution, using Ca^{2+}, Mg^{2+}, and $NaHCO_3$. PD has also been synthesized from concentrated seawater by adding 400 mM Na_2CO_3 to seawater (Oomori, Kaneshima, Taira, & Kitano, 1983; Oomori, Kaneshima, & Kitano, 1988). In these reports, PD was synthesized in aqueous solutions under normal temperature (<100 °C) and pressure (1 atm) conditions. As for hydrothermal synthesis, PD was synthesized from calcite ($CaCO_3$) crystals in a $MgCl_2$ solution under high temperature (>150 °C) and pressure (>1 atm) conditions (Katz & Matthews, 1977; Lumsden, Morrison, & Lloyd, 1995; Sibley, 1990). Mitsusio, Nishizawa, and Matsuoka (1983) also synthesized PD in an aqueous phase by hydrothermal synthesis at 100 °C. These reports focussed on the mineralization mechanism of PD in the natural environment, and hence were not relevant for production in the food industry.

Since Ca and Mg are important nutrients for human health, PD is an ideal compound for the food industry. D is widely used in Ca and Mg supplements because it is rich in Ca (>20%) and Mg (>10%). Currently, only PD derived from natural mineral sources has been used in mineral supplements. However, a new method for synthesis of PD should be developed for the food

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[*] Corresponding author. Tel.: +81 3 3252 6351; fax: +81 3 3252 6355.

E-mail address: shin-s@marine-bio.co.jp (S. Someya).

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industry because the natural mineral sources for PD are limited. CRS contains >30% Ca and is widely used as a natural calcium source for mineral supplements. Thus, CRS is suitable as a natural and safe calcium source for synthesis of PD. In this study, we synthesize PD from CRS in order to provide chemically-derived PD of good quality for the food industry.

2. Materials and methods

2.1. Materials

CRS (Marine Bio Co. Ltd.), which contains >30% Ca, was used as a calcium source for the synthesis of PD. The chemical composition of the CRS is 97% of $CaCO_3$, 2% of $MgCO_3$ and 1% of residues such as SiO_2. Magnesium chloride ($MgCl_2 \cdot 6H_2O$) and sodium carbonate (Na_2CO_3) were purchased from Kanto Chemical Co., Inc (Tokyo, Japan). These reagents were all of analytical grade.

2.2. Synthesis

The synthesis of PD from CRS was carried out as shown in Fig. 1. First, CRS (10 g) was dissolved by 2 N HCl (120 ml) and the solution was filtered through a membrane filter (0.45 μm, ADVANTEC) to remove the residues. The filtrate was adjusted to pH 4 with 2 N NaOH. This solution was used as an original calcium solution, and the concentration of Ca^{2+} of this solution was determined to be 500 mM. To test effects of differing calcium concentrations on the formation of PD, seven calcium solutions were prepared from the original calcium solution: the concentration of Ca^{2+}, for each calcium solution, was adjusted to 15, 35, 70, 140, 200, 280 and 500 mM by diluting the original calcium solution with Milli-Q water. The concentration of Mg^{2+}, for each calcium solution, was fixed at 350 mM by adding $MgCl_2 \cdot 6H_2O$. These calcium solutions were defined as parent solutions. Then, 16 ml of 400 mM Na_2CO_3 solution were added to each parent solution to prepare final solutions.

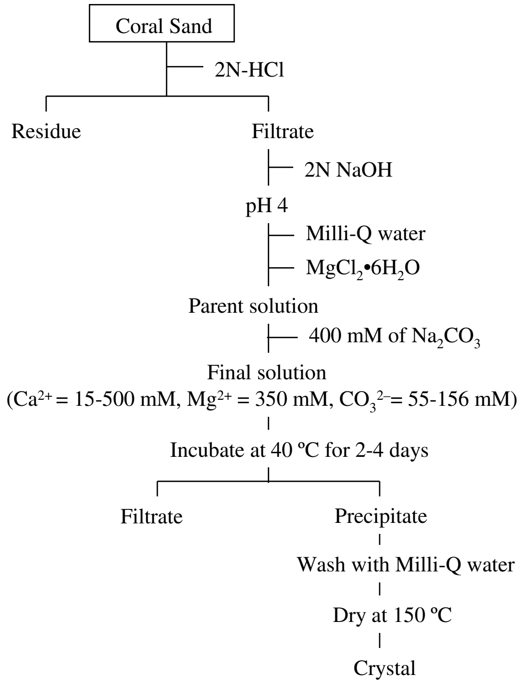

Fig. 1. Synthesis of protodolomite from coral reef sand.

To test effects of differing concentrations of Na_2CO_3 on the formation of PD, three different amounts of Na_2CO_3 solutions (4, 8 and 16 ml) were added to each parent solution (15–500 mM Ca^{2+}) to give final concentrations of 55, 97 and 156 mM Na_2CO_3. These final solutions were incubated at 40 °C for two days to precipitate PD. Finally, the precipitates were separated by filtration, washed with Milli-Q water, and dried at 150 °C for 24 h for isolating PD.

2.3. Analysis

The precipitate was analyzed for the identification of PD by X-ray diffraction analysis (ADP-1/7(53-120))(Rigaku) and atomic absorption analysis (Solaar969) (Thermo Elemental). X-ray diffraction analysis was carried out under Cu Kα and 30 KV–15 mA conditions. Concentrations of Ca^{2+} and Mg^{2+} were measured by atomic absorption, after dissolving 40 mg of the precipitate with 1 N HNO_3 (2 ml).

3. Results and discussion

In order to find optimal concentrations of Ca^{2+} for the synthesis of PD, we fixed the concentrations of Mg^{2+} and Na_2CO_3 at 350 and 156 mM, respectively. Effects of Ca^{2+} on the mole fractions of $MgCO_3$ were studied to find the optimal concentration of Ca^{2+} in the parent solution. The mole fraction of $MgCO_3$, which responds to x of $Ca_{1-x}Mg_xCO_3$, is a proportion of Mg compared to Ca in the carbonate crystal. In order to achieve synthesis of PD, mole fractions of $MgCO_3$ in the precipitates should be between 0.4 and 0.5 (Ohde & Kitano, 1981; Oomori et al., 1983). Mole fractions of $MgCO_3$ in the precipitates decreased exponentially as the concentration of Ca^{2+} increased in the parent solution (Fig. 2). $MgCO_3$ contents can be expressed by a simple exponential equation, which was derived from Fig. 2:

$$y = e^{-0.0052x}.$$

From this equation, the concentration of Ca^{2+} needed to form 0.4–0.5 mole fractions of $MgCO_3$ in the precipitate was calculated. The optimal range of Ca^{2+} concentration was calculated to be 130–180 mM

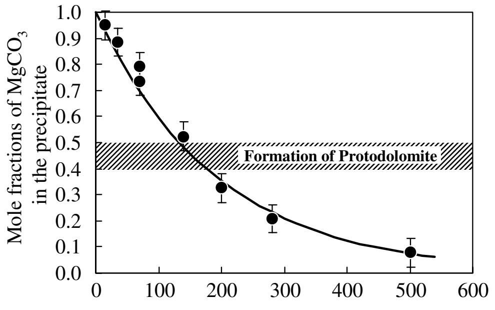

Fig. 2. Effects of Ca^{2+} on the mole fractions of $MgCO_3$ in the precipitates. The precipitates were obtained from 25 ml of parent solutions containing 350 mM Mg^{2+} at various concentration of Ca^{2+}. The concentration of Na_2CO_3 was 156 mM. The gray area indicates 0.4–0.5 mole fractions of $MgCO_3$.

at 156 mM of Na_2CO_3. In order to confirm this result, we carried out an experiment to synthesize PD in a parent solution containing 150 mM of Ca^{2+}. By atomic absorption analysis, the precipitate was found to contain 12.4% of Mg and 24.9% of Ca, which corresponded to 0.45 and 0.55 mole fractions of $MgCO_3$ and $CaCO_3$, respectively. These data were consistent with the results from the calculation. Thus, the optimal concentration of Ca^{2+} for synthesis is likely to be near or at 150 mM.

In order to find optimal concentrations of Na_2CO_3, the effects of Na_2CO_3 on the mole fractions of $MgCO_3$ were studied (Fig. 3). Mole fractions of $MgCO_3$ increased as the concentrations of Na_2CO_3 increased. Mole fractions of $MgCO_3$ eventually reached the saturation point at a concentration of 15 mM Ca^{2+}. Mole fractions of $MgCO_3$ decreased as the concentration of Ca^{2+} increased. At 140 mM Ca, which is in the range of optimum Ca concentration, the concentration of Na_2CO_3 is 120–156 mM, where the line is intersecting with the gray zone of PD production. From these results, the optimal concentration of Na_2CO_3 was found to be 120–156 mM in order to form 0.4–0.5 mole fractions of $MgCO_3$ when the concentration of Ca^{2+} was 140 mM.

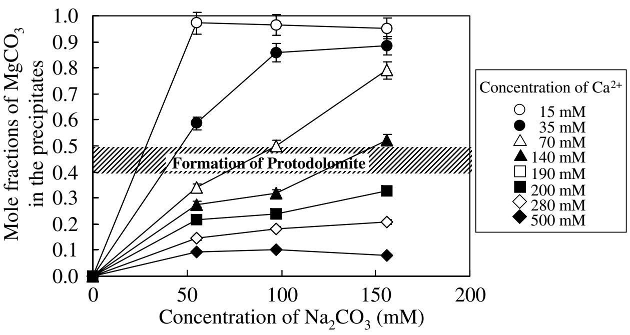

Fig. 3. Effects of Na_2CO_3 on the mole fractions of $MgCO_3$ in the precipitates. The precipitates were obtained from 25 ml of parent solutions containing 15–500 mM of Ca^{2+} and 350 mM of Mg^{2+} at various concentrations of Na_2CO_3. The gray area indicates 0.4–0.5 mole fractions of $MgCO_3$.

In order to find whether the precipitate identified was PD, we conducted X-ray analysis. The results of X-ray diffraction analysis using a precipitate obtained from 150 mM Ca^{2+} and 156 mM Na_2CO_2 solution, are shown in Fig. 4. Three main diffraction peaks of 2θ (Cu Kα) were observed: 30.75° ($d = 2.91$ Å), 40.95° ($d = 2.20$ Å), and 50.75° ($d = 1.80$ Å). These results were consistent with those observed with the standard natural protodolomite taken from Taketomi island (Okinawa, Japan) : 30.8° ($d = 2.91$ Å), 41.0° (2.20 Å), and 50.8° (1.80 Å). The main diffraction peaks of 2θ (Cu Kα) for calcite ($CaCO_3$) and magnesite ($MgCO_3$) are 29.4° and 32.7°, respectively. Our X-ray analysis results revealed that those two peaks were not observed, showing that the precipitate contains $CaCO_3$–$MgCO_3$, but not as $CaCO_3$ or $MgCO_3$. These results also indicate that Ca and Mg were contained in the carbonate lattice in the precipitate. The atomic absorption analysis results revealed that the precipitate contained 22.7% of Ca and 11.9% of Mg. These results were consistent with those of the standard natural protodolomite: 24.0% of Ca and 11.5% of Mg (Ohde & Kitano, 1981). Therefore, we conclude that the precipitate was identified as PD.

The Mg/Ca molar ratio in a parent solution is important for the formation of PD. Oomori et al. (1983) suggested that a Mg/Ca ratio of 17.7 is appropriate for forming dolomite when the parent solution of seawater was concentrated to 6 times its original volume by

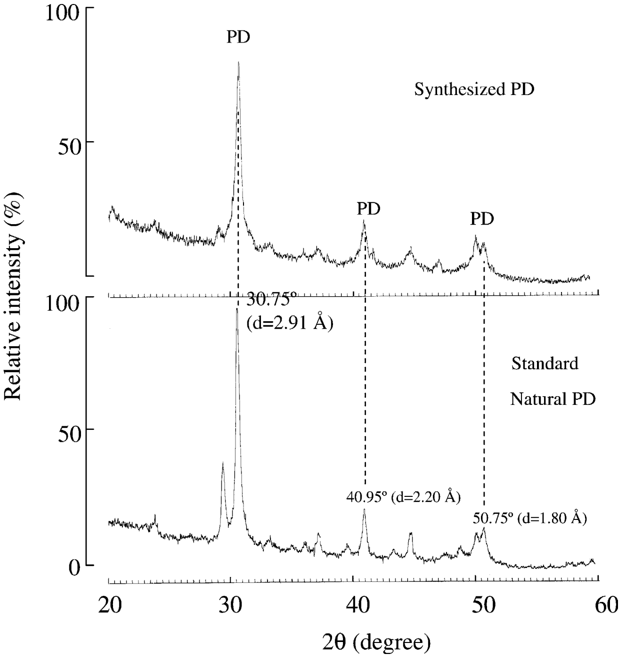

Fig. 4. X-ray diffraction patterns of synthesized precipitate and natural PD as standard. The X-ray diffraction chart was obtained under Cu Kα radiation and 30 KV–15 mA instrumental conditions. The synthesized precipitate was obtained from the solution containing 150 mM Ca^{2+}.

evaporation. Ohde and Kitano (1978) obtained a PD at Mg = 2100 mM and Ca = 50 mM (Mg/Ca = 42) from various combinations of Mg (0–2100 mM) and Ca (1–50 mM), and found that a higher Mg/Ca ratio was favourable for the PD formation. Oomori et al. (1983) also described the importance of the carbonate ion concentration for PD formation, although they only tested up to 55 mM Na_2CO_3. We obtained PD from a low Mg/Ca ratio (=1) in the parent solution. This might be due to the difference of CO_3^{2-} concentration. Our CO_3^{2-} concentration was three times higher than that in the reports of PD formation under natural environmental conditions (cf. Oomori et al., 1983).

In conclusion, for the synthesis of PD from CRS, the optimal concentration of Ca^{2+} was found to be 130–180 mM, and the optimal concentration of Na_2CO_3 was found to be 120–156 mM. PD is widely used in Ca and Mg nutritional supplements because it is rich in Ca (>20%) and Mg (>10%). Using this method, PD can now be synthesized from CRS and used as Ca and Mg supplements for the food industry. This approach can be helpful for obtaining an alternate source of limited natural PD minerals.

References

Goldsmith, J. P., Graf, D. L., & Heard, H. C. (1961). Lattice constants of the calcium ~ magnesium carbonates. *The American Mineralogist, 46*, 453–457.

Katz, A., & Matthews, A. (1977). The dolomitization of $CaCO_3$: an experimental study at 252–295 °C. *Geochimica et Cosmochimica Acta, 41*, 297–308.

Lumsden, D. N., Morrison, J. W., & Lloyd, R. V. (1995). The role of iron and Mg/Ca ratio in dolomite synthesis at 192 °C. *The Journal of Geology, 103*, 51–61.

Mitsusio, H., Nishizawa, H., & Matsuoka, K. (1983). Hydrothermal synthesis of dolomite, part 3. *Research Report of Kochi University Natural science (in Japanese), 32*, 327–334.

Ohde, S., & Kitano, Y. (1978). Synthesis of protodolomite from aqueous solution at normal temperature and pressure. *Geochemical Journal, 12*, 115–119.

Ohde, S., & Kitano, Y. (1981). Protodolomite in Daito-jima, Okinawa. *Geochemical Journal, 15*, 199–207.

Oomori, T., Kaneshima, K., & Kitano, Y. (1988). Solubilities of calcite, aragonite and protodolomite in supratidal Brines of Minamidaito-jima Island, Okinawa, Japan. *Marine Chemistry, 25*, 57–74.

Oomori, T., Kaneshima, K., Taira, T., & Kitano, Y. (1983). Synthetic study of protodolomite from brine water. *Geochemical Journal, 17*, 147–152.

Sibley, D. F. (1990). Unstable to stable transformations during dolomitization. *The Journal of Geology, 98*, 739–748.