NOTE

Magnesian calcite synthesis from calcium bicarbonate solution containing magnesium and barium ions

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The present authors have studied the influence of barium and magnesium ions, which are contained together in a calcium bicarbonate parent solution, on the crystal form of carbonate formed from the parent solution. Magnesium ions in a parent solution inhibit calcite formation and favor aragonite formation, whereas barium ions inhibit aragonite formation and favor calcite formation. The degree of these influences is affected by the concentrations of these ions in the parent solution. When the influence of barium ions is stronger than that of magnesium ions, magnesian calcite is formed and the MgCO\(_3\) content of the magnesian calcite increases with increasing concentration of magnesium ions in a parent solution. From the calcium bicarbonate solutions containing both more than 35 ppm of barium ions and 1,200 ppm of magnesium ions monohydrocalcite is formed. Monohydrocalcite does not incorporate both MgCO\(_3\) and BaCO\(_3\) in its crystal lattice.

The distribution coefficients of magnesium and barium have been measured when magnesian calcite is precipitated.

The distribution coefficient of magnesium or barium for magnesian calcite tends to increase with increasing barium carbonate content or magnesium carbonate content of the formed magnesian calcite, respectively.

INTRODUCTION

The skeletal parts of calcareous marine organisms are composed of the minerals, calcite, aragonite and magnesian calcite (CHAVE, 1952, 1954; LOWENSTAM, 1954; KITANO and KANAMORI, 1966; KITANO et al., 1969). The study on the distribution of trace metals for these minerals is important for the understanding of the geochemical behaviors of trace metals on the earth's surface. And a number of studies have been carried out on the measurement of the distribution coefficients of trace metals between solution and carbonate precipitate; Sr (HOLLAND et al., 1963, 1964; BODINE et al., 1965; KINSMAN and HOLLAND, 1969; KITANO et al., 1971, 1973, KATZ et al., 1972), Zn (TSUSUE and HOLLAND, 1966; CROCKET and WINCHESTER, 1966; KITANO et al., 1969), Cu (KITANO et al., 1968), UO\(_2\) (KITANO and OOMORI, 1971), Mn (BODINE et al., 1965; RAISWELL and BRIMBLECOMBE, 1977), Ba (KITANO et al., 1971), Mg (KITANO and KANAMORI, 1966; KATZ, 1973; KITANO et al., 1976), Cd (KITANO et al., 1978). Magnesium carbonate in skeletal calcite is present as a solid solution between calcite and magnesite or dolomite (CHAVE, 1952; GOLDSMITH et al., 1955; KITANO and FURUTSU, 1959; KITANO and KANAMORI, 1966). And magnesian calcite and aragonite are unstable, relative to Mg-poor calcite at ordinary temperature and pressure (GARRELS et al., 1960; CHAVE et al., 1962; JANSEN and KITANO, 1963; PLUMMER and MACKENZIE, 1974; DE BOER, 1977). There are few reports on the measurement of the distribution coefficients of chemical elements for magnesian calcite. For the partition study, it is necessary to synthesize magnesian calcite from aquatic solution at normal temperature and pressure.

Laboratory syntheses of magnesian calcite were accomplished at high temperatures and pressures (HARKER and TUTTLE, 1955; GRAF and GOLDSMITH, 1956; GOLDSMITH and HEARD, 1961), and recently at normal temperature and pressure from aqueous solutions (KITANO and KANAMORI, 1966; GLOVER and SIPPLE, 1966; GOLDSMITH and HEARD, 1961), and recently at normal temperature and pressure from aqueous solutions (KITANO and KANAMORI, 1966; GLOVER and SIPPLE, 1966; KITANO et al., 1976; OHDE and KITANO, 1978). A parent solution must contain magnesium, calcium and carbonate ions for the precipitation of magnesian calcite having a calcitic lattice configuration.
Kitano (1962) showed that magnesium ions in a parent solution favor the precipitation of aragonite, which does not capture magnesium in its lattice. The presence of magnesium ions in a parent solution inhibits magnesian calcite very strongly. Kitano (1962) also reported that barium ions in a parent solution favor the precipitation of calcite, which does not capture barium in its lattice. Thus when sufficient amounts of barium ions are contained in parent solutions containing magnesium ions even in large amounts, magnesian calcite formation is expected from the solutions. The synthesis experiment based on this idea was tried previously, but magnesian calcite was not formed (Kitano et al., 1976). In order to disclose the reason, detailed experiments on the crystal formation of carbonates have been made, and it has been confirmed that magnesian calcite is formed from calcium bicarbonate solutions containing certain amounts of both barium and magnesium ions.

EXPERIMENTAL

Procedure for carbonate formation to study effects of magnesium and barium ions in parent solution on crystal form of carbonate precipitate Magnesium chloride and barium chloride in various proportions were placed in beakers (51) containing calcium bicarbonate solution (Ca\(^{2+}\), 320 – 370 ppm). Carbon dioxide gas gradually escaped from the parent solution, and carbonate was precipitated. The formed carbonate precipitate was filtered off and washed with distilled water until the precipitate was free from the parent solution. After it had been dried in an air bath at 60°C, a fraction of the precipitate was used for the determination of magnesium and barium contents, while another fraction was used for identification of the crystal form by X-ray diffractometer and also optical microscope. Calcium and magnesium in the formed carbonate were determined by atomic absorption spectrometer, and barium by flame emission spectrometer after calcium and magnesium ions had been removed with ion exchange resin.

Procedure for measurement of distribution coefficient Calcium bicarbonate solutions containing magnesium ions (0 – 1,200 ppm) and also barium ions (0 – 50 ppm) were prepared. The solutions in beakers (51) were stirred fairly vigorously with a magnetic stirrer at 25±2°C. The release of carbon dioxide gas from these solutions was followed by carbonate precipitation. During the lapse of time in the process of carbonate formation, the changes in pH value and the concentrations of calcium, magnesium and barium ions in a parent solution were measured. And the values of distribution coefficient were calculated with Doener Hoskin’s equation. The magnesium and barium contents of the precipitate were determined and the crystal form was identified.

RESULTS AND DISCUSSION

Effect of magnesium and barium ions in parent solution on crystal form of precipitate Figure 1 shows the relation between the initial concentrations of barium and magnesium ions in calcium bicarbonate parent solutions and the crystal forms of carbonates formed from the parent solutions at 25±2°C. The presence of magnesium ions in the parent solution inhibits the precipitation of calcite and favors the precipitation of aragonite. The presence of barium ions inhibits the precipitation of aragonite and favors the precipitation of calcite. Figure 1 indicates the chemical conditions of a parent solution for the formation of carbonate minerals. From Fig. 1, it is seen that magnesian calcite is formed, when the concentration ratio of barium ions to magnesium ions is larger than about 1/25 in an original solution. Figure 2 shows the magnesium content of the calcites formed from calcium bicarbonate solutions containing both magnesium and barium ions against
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Fig. 2. MgCO₃ contents of calcites formed from calcium bicarbonate solutions (Ca²⁺, 320 – 370 ppm) containing both magnesium (Mg²⁺, 300 – 2,000 ppm) and barium ions (Ba²⁺, 10 – 50 ppm).

The original concentration of magnesium ions in the calcium bicarbonate parent solutions. The formed carbonates in Fig. 2 have all calcite type crystal form. And the figure indicates that the magnesium carbonate content of the formed calcites increases with increasing concentration of magnesium ions within 1,000 ppm in the parent solution. But in the parent solution containing more than 1,200 ppm and 35 ppm of magnesium and barium ions respectively, the magnesium carbonate content of the formed calcites became extremely small (see Fig. 2), because the formed calcites were not magnesian calcite but monohydrocalcite. Monohydrocalcite does not contain magnesium in its lattice as aragonite.

The formation of monohydrocalcite, magnesian calcite or aragonite and also the magnesium carbonate content of formed carbonates in the solution system are governed by the concentrations of magnesium and barium ions in parent solutions.

Measurement of distribution coefficients of barium and magnesium between carbonate precipitate and solution

The distribution coefficients of magnesium (Dₑ₂₅) and barium (Dₑ₂₅) between solution and calcite have been calculated in the following system: Ca(HCO₃)₂ (Ca²⁺, 320 – 370 ppm) + MgCl₂ (Mg²⁺, 0 – 800 ppm) + BaCl₂ (Ba²⁺, 0 – 40 ppm) → Calcite (at 25± 2°C). Dₑ₂₅ is defined as (Xₑ/XₐCa)/(aₑ⁺²⁺/aₐCa⁺²⁺), where Xₑ and XₐCa denote the molar fractions of trace metal (Me) and calcium in carbonate precipitate respectively and aₑ⁺²⁺ and aₐCa⁺²⁺ denote the activities of metal ions (Me²⁺) and calcium ions in a parent solution respectively. It is noted that the ionic radii of magnesium and barium are smaller and larger, respectively, than that of calcium.

Figure 3 shows a plot of Dₑ₂₅ against the barium carbonate content of formed calcites. The figure indicates that the value of Dₑ₂₅ tends to increase slightly with increasing barium carbonate content of calcites. Figure 4 shows a

Fig. 3. Values of distribution coefficient of magnesium between calcite and calcium bicarbonate parent solution containing magnesium (Mg²⁺, 0 – 800 ppm) and barium (Ba²⁺, 0 – 40 ppm) ions, against barium carbonate content of carbonate precipitate.

Fig. 4. Values of distribution coefficient of barium between calcite and calcium bicarbonate parent solution containing magnesium (Mg²⁺, 0 – 800 ppm) and barium (Ba²⁺, 0 – 40 ppm) ions, against magnesium carbonate content of carbonate precipitate.
plot of \(D_{\text{Mg}}\) against the magnesium carbonate content of formed calcites. The value of \(D_{\text{Mg}}\) also increases with the magnesium carbonate content of calcites. These trends seem to have an analogy with the results observed by Ichikuni (1973) in the MnCO\(_3\) and SrCO\(_3\) contents of calcitic calcium carbonate.

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