NOTE

Differential dissolution technique for the geochemical separation of the calcite and dolomite of dolomitic limestones

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Trace element geochemistry for dolomitic limestones was carried out by chemical separation of the constituent calcite and dolomite. A five-minute treatment for fine-grained dolomitic limestone with 0.5 M acetic acid differentially dissolves the calcite, but 82–90% of dolomite remained undissolved. The fraction of dissolved dolomite contributed 2–17% to the calcite fraction, depending on the calcite/dolomite ratios of the samples. The residue of the acetic acid treatment was treated with 0.5 M HCl and an almost pure dolomite fraction was obtained. Comparison of the trace element concentrations in the calcite and dolomite fractions for four dolomitic limestones revealed that the REE abundances in both the fractions were similar, while the Fe, Mn, P, and Al concentrations in the dolomite fractions were higher than those in the calcite fractions. The method developed in this study can be used for trace element studies of dolomitic limestones.

Keywords: limestone, calcite, dolomite, differential dissolution technique, trace element

INTRODUCTION

Some limestones contain dolomite, but there are no clear modern depositional analogs for many types of dolomitic limestones, except for depositional settings such as sabkhas and Coorong-type lagoons (e.g., Shin et al., 1965; Von Der Borch, 1976). Thus, the conversion of calcite into dolomite with time, which is called dolomitization, has been proposed (e.g., Badiozamani, 1973). In order to understand the genesis of dolomite, identifying the trace element characteristics of calcite and dolomite in dolomitic limestones is important, for which a separation technique is required.

For this purpose, the differential dissolution technique has been attempted as follows. Petersen and Chesters (1966) showed that a five-minute treatment of dolomitic limestones with the citrate-NH4OH buffer solution of pH 5.85 dissolved calcite completely, and then the residual dolomite was dissolved in 3 M HCl. Zhao et al. (2009) dissolved the calcite from dolomitic limestones using a 0.5 M acetic acid for 4 hours, and then treated the residual dolomite with 3.4 M acetic acid at 60°C for 24 hours. El Hefnawi et al. (2012) applied the 0.2 M acetic acid and 0.2 M sodium acetate buffer solution (pH 4) to the powder dolomitic limestones to dissolve calcite differentially, and the remaining dolomite was dissolved in 1 M HCl.

These investigations have shown the effectiveness of the differential dissolution technique. However, the chemical separation process of the calcite and dolomite fractions for the dolomitic limestones can be further improved. Since the purification of citrate and sodium acetate used in the previous studies are difficult, acetic acid is more appropriate for trace element studies because it can easily be purified by distillation. Therefore, we aimed to improve the separation process of calcite and dolomite for dolomitic limestones by differential dissolution in acetic acid. This technique was used for some dolomitic limestones.

SAMPLES AND EXPERIMENTAL METHODS

The individual dissolution characteristics of pure calcite, aragonite, and dolomite crystals were identified. Samples of four dolomitic limestones found in Japan (SO-1, FB-1, KZ-1, and KZ-2) were used to test the effectiveness of our procedure. The ages, formations, and locations of the limestone samples are listed in Supplementary Table S1, and their thin section micrographs are shown in Supplementary Fig. S1. The pure minerals were crushed using an agate mortar. The dolomitic limestone
samples were crushed using a jaw-crusher and an agate ball mill. The particle-sized samples (10–20 μm in size) sorted by nylon mesh sieves were used for every experiment.

The pure mineral particles were treated with 40 mL of 0.5 M acetic acid at 25°C. After an appropriate reaction time, the remaining minerals were collected by centrifuge, dried and weighed with an electrical balance in a dry box. Moreover, in order to check the plausibility of the procedure, the mixtures of calcite (0.25 g) and dolomite (0.25 g) particles were treated with 0.5 M acetic acid (40 mL) for 5 minutes. The solutions were immediately filtered using a 0.20-μm membrane filter, and were analyzed for Ca and Mg concentrations.

The dolomitic limestone samples were treated for 5 minutes with 0.5 M acetic acid (0.5M-AcA) in polyethylene bottles. The solutions were immediately filtered, and the residual solids were dried and weighed. These residues (mostly dolomite) were dissolved in 0.5 M HCl for 24 hours. The residues (mostly silicate) of the 0.5 M HCl treatment were dried and weighed.

The Ca and Mg concentrations were determined by atomic absorption spectrometry using Sr as the interference suppressor. The concentrations of Fe, Mn, Al, and P were measured by standard addition method using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Prior to ICP-AES analyses, the acetic acid solutions were evaporated to dryness to expel the acetic acid, and were dissolved in 0.5 M HCl. The rare earth elements (REEs) were measured by an isotope dilution method using a thermal ionization mass spectrometer, and its uncertainties were usually less than 5%. The chemical procedures were similar to those in Toyama and Terakado (2014). The x-ray powder diffraction (XRD) method was used for mineral identification. The MgCO3 mole fraction in calcite was calculated using XRD peak shift (Chave, 1952; Wada et al., 1993).

RESULTS

Dissolution characteristics of pure minerals

As for the pure calcite, aragonite, and dolomite crystal samples, changes of the dissolution rates with time are illustrated in Fig. 1. The calcite and aragonite were dissolved within 3 and 5 minutes, respectively, while it took about 300 minutes for complete dissolution of dolomite, which indicates that the differential dissolution method is effective.

As for the mixture of pure calcite and dolomite, the dissolved amounts of calcite and dolomite were calculated from the Ca and Mg concentrations in the solutions, using a Ca/Mg molar ratio of 1.18 obtained from the Ca and Mg concentrations in the dolomite. The calcite dissolved completely, while only 4% dissolution of dolomite was achieved, which would be a good separation between calcite and dolomite.

Natural dolomitic limestones

The Ca and Mg concentrations in the 0.5M-AcA and 0.5 M HCl solutions are listed in Table S1. To calculate the trace element abundances in the dissolved solids (i.e., calcite and dolomite), the amount of dissolved solid for each treatment was calculated using the Ca and Mg concentrations in the solutions, and the assumption that the Ca and Mg concentrations in 0.5 M HCl solution were attributed to dolomite only. The concentrations of Al, Mn, Fe, and P in the solids for the 0.5M-AcA treatment are lower than those for the 0.5 M HCl (Table S1 and Fig. 2). The REE patterns of the 0.5M-AcA and the 0.5 M HCl are similar, and show obvious negative Ce anomalies and lack of Eu anomalies. The residues of the 0.5M-AcA treatments were composed of dolomite with 1–2% calcite, and those of the 0.5 M HCl ones were quartz with small amounts of plagioclase.

DISCUSSIONS

Effectiveness of the differential dissolution technique

In order to examine the effectiveness of the differential dissolution technique for the dolomitic limestones, undesired dolomite dissolution in the calcite fraction (i.e., the 0.5M-AcA) was evaluated as follows (the contribution of dolomite dissolution to the calcite fraction):

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\text{Dissolved dolomite amount} = \frac{\text{Dissolved calcite amount} + \text{Dissolved dolomite amount}}{100(\%)}
\]
“Dissolved calcite amount” and “Dissolved dolomite amount” were calculated using the Ca and Mg concentrations in calcite fraction, molar fraction of Mg in calcite, solution amount, and the assumption that the Mg/Ca molar ratio of dolomite is similar to that of the dolomite fraction treated with 0.5 M HCl. In order to examine these values for the previous studies, it was assumed that the Ca/Mg molar ratio of dolomite was unity and that the Mg in calcite fraction was derived from dolomite. The values are plotted against the dolomite/(calcite+dolomite) weight ratios in the whole rock analyses (the calculation from calcite and dolomite amounts dissolved by acid treatments) in Fig. 3. The contributions of the dolomite dissolution to the calcite fractions for SO-1, FB-1, KZ-1, and KZ-2 were 2, 6, 17, and 13%, respectively.

Theoretically, the contribution of dolomite dissolution to the calcite fraction was calculated as a function of the dolomite/(calcite+dolomite) weight ratio in the whole rock analysis, assuming that calcite was dissolved completely and dolomite was partly dissolved based on the dolomite dissolution rate. Two examples corresponding to the dolomite dissolution rates of 10% and 18% are shown in Fig. 3. The contribution of the dolomite dissolution to calcite fraction increases with the increasing dolomite/(calcite+dolomite) weight ratio in the whole rock analyses.

The data points of SO-1, FB-1, KZ-1, and KZ-2 almost fall on the 18% line. However, the dissolution rate of dolomite is higher than the value obtained from the mixtures of pure calcite and dolomite crystals in Subsection “Dissolution characteristics of pure minerals”. Such a discrepancy may be attributed to the dissolution of the smaller-sized dolomite particles dispersed in calcite grains, which is consistent with the thin section observations (Fig. S1).

The contribution of dolomite dissolution to the calcite fraction for the data of Petersen and Chesters (1966) is about 10% for the sample having the dolomite/(calcite+dolomite) weight ratio in the whole rock of about 0.18. This value of 10% is considerably higher than the estimated value of our method. As for the data of El Hefnawi et al. (2012), most data points are plotted above the 18% line, even though their data points are scattered as shown in Fig. 3. As for Zhao et al. (2009), the data...
points are plotted much above the 18% line. Therefore, the separation of calcite in the present study has been more efficient than those of the previous ones.

The contributions of the undesired calcite to the dolomite fractions for the previous studies were calculated using the Ca and Mg concentrations in the dolomite fractions and assuming the Ca/Mg molar ratio to be 1 in dolomite. The undesired contribution of calcite to the dolomite fraction as reported by Petersen and Chesters (1966) is about 6%. As suggested by Zhao et al. (2009), such contributions were 4 to 5% or 70 to 99% for the whole rock dolomite/(calcite+dolomite) weight ratios of 0.5–0.6 or 0.01–0.07, respectively. According to El Hefnawi et al. (2012), the average contribution was about 47% for the dolomite/(calcite+dolomite) weight ratios of 0.1 to 0.6. The undesired calcite contribution in the dolomite fractions of the present study is 1 to 2% (see Subsection “Natural dolomitic limestones”), which is smaller than those obtained in the previous studies.

Thus, the separation method used in this study is more efficient not only for calcite but also for dolomite as compared to the previous studies, and further refinement seems possible. Meanwhile, we would like to suggest a shorter reaction period (such as one or two minutes) for the 0.5M-AcA treatment to reduce the undesired dolomite dissolution, because the calcite was almost dissolved in less than two minutes (Fig. 1).

Trace element abundances in calcite and dolomite

The discrepancies of Fe concentrations between the calcite and dolomite fractions are conspicuous (Fig. 2), which may literally reflect the concentration differences between calcite and dolomite. Alternatively, it can be considered that the particulate Fe compounds, such as Fe oxides dispersed in the samples, were not dissolved by the short-duration treatment with 0.5M-AcA, but could be dissolved by long-duration treatment with 0.5 M HCl. Similarly, the P concentrations in the dolomite fractions are higher than those in the calcite fractions. It is known that apatite cannot be dissolved easily in 6 M acetic acid, but can be dissolved in 2 M HCl (Akaiwa and Aizawa, 1979). Therefore, it is possible that apatite was not dissolved in the 0.5M-AcA, but was dissolved in the 0.5 M HCl. This suggests that the Fe and P concentration differences between calcite and dolomite fractions are an experimental artifact reflecting the acidic strength and/or the reaction time. If such factors are effective, higher REE abundances in the dolomite fractions are expected because REEs tend to be incorporated in Fe-oxide and apatite. However, the REE abundances in the dolomite and calcite fractions are similar, which indicates that the participation of Fe oxide and/or apatite is minimal; but further investigations are necessary. Finally, despite the limited number of applications, these results prove the effectiveness of the present method, and we would like to recommend this method for geochemical studies of dolomitic limestones.

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REFERENCES


Chave, K. E. (1952) A solid solution between calcite and dolomite. J. Geology 60, 190–192.


SUPPLEMENTARY MATERIALS

URL (http://www.terrapub.co.jp/journals/GJ/archives/data/49/MS378.pdf)

Figure S1

Table S1