NOTE

Dolomitization of limestone with MgCl_2 solution at 150°C: Preserved original signatures of rare earth elements and yttrium as marine limestone

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We have studied the mobility of rare earth elements (REE) and yttrium during dolomitization of marine limestone in reaction with MgCl_2 solution at 150°C for 10 and 20 days. On the experiment using the pulverized limestone of 7.5 g and 25 ml of 2 M MgCl_2 solution, 90% of the calcite transformed into dolomite at 150°C within 20 days. The dolomitized products showed that there is no significant change of REE abundances of original marine limestone. This is experimental evidence for the field observation that dolostones sometimes preserve the REE and Y signatures of limestone precursors.

INTRODUCTION

It has been reported that dolostones often preserve the REE characteristics of precursor limestones in the studies of marine carbonates of Lower Carboniferous Burlington and Keokuk Formation, the midcontinental region of USA (Banner *et al.*, 1988) and the Middle Devonian Western Canada Sedimentary Basin (Qing and Mountjoy, 1994). Our recent REE study of the Middle Permian Kuzuu limestone-Dolostone complex (the Nabeyama Formation), central Japan, also revealed that there is no significant difference in the REE and Y abundance pattern between the Upper Limestone and Middle Dolostone (Miura *et al.*, 1999). The field observation suggests that REE and Y patterns are preserved during dolomitization of marine limestone. However, this has not been confirmed experimentally yet.

Laboratory dolomitization of calcite in reaction with MgCl_2 solutions is very sluggish at normal temperatures, but calcite transforms completely into dolomite within 100 hours at hydro-

thermal conditions of 200–300°C (Katz and Matthews, 1977; Sibley *et al.*, 1987). This paper reports our preliminary experimental study on mobility of REE and Y during dolomitization of marine limestone in reaction with MgCl_2 solution at 150°C.

EXPERIMENTAL

A marine limestone sample from the Upper Limestone Member of Middle Permian Kuzuu Limestone-Dolostone complex, central Japan, was pulverized and used as the starting material. This limestone sample (TKC-10 in Miura *et al.*, 1999) scarcely contains non-carbonate impurities. No dolomite was detected in it by X-ray diffraction analysis (XRD). Aliquots of the powdered limestone were reacted with 2 M MgCl_2 solution, 2 M MgCl_2 + 0.5 M NaCl solution and 2 M MgCl_2 + 0.5 M KCl solution at 150°C. In the first series of runs, aliquots (10 g) of limestone powder and 25 ml of the respective 2 M MgCl_2 solutions were taken in Teflon sealed vessels (internal volume of

Table 1. Ca, Mg, REEs and Y concentrations in the starting material of limestone and the experimental solid products, along with experimental conditions^{*1}

Run No.	1-1	1-2	1-3	2-1	2-2	2-3
Weight of limestone (g)	10.0	10.0	10.0	7.5	7.5	7.5
Volume of solution (ml)	25.0	25.0	25.0	25.0	25.0	25.0
Temp. (°C)	150	150	150	150	150	150
Reaction time (days)	10	10	10	20	20	20
Starting material (Limestone) ^{*2}						
Composition of initial solutions						
MgCl ₂ (M)	2.0	2.0	2.0	2.0	2.0	2.0
NaCl (M)	—	0.5	—	—	0.5	—
KCl (M)	—	—	0.5	—	—	0.5
Analyses of solid products						
Ca (wt. %)	33.2	27.9	27.4	22.0	22.3	21.4
Mg (wt. %)	3.29	6.99	7.00	11.2	10.5	10.8
Dol. (molar ratio (%)) ^{*3}	28	59	59	91	88	91
REE (ppm)						
La	8.64	8.85	8.41	9.50	8.92	8.93
Ce	1.92	1.95	1.85	2.04	1.91	1.92
Pr	1.17	1.19	1.13	1.26	1.18	1.19
Nd	5.04	5.18	4.94	5.49	5.13	5.16
Sm	0.805	0.829	0.797	0.873	0.814	0.820
Eu	0.182	0.188	0.181	0.200	0.185	0.187
Gd	1.04	1.08	1.05	1.15	1.06	1.07
Tb	0.140	0.147	0.142	0.154	0.142	0.143
Dy	0.896	0.933	0.910	0.995	0.920	0.923
Ho	0.206	0.213	0.207	0.228	0.211	0.212
Er	0.575	0.605	0.586	0.632	0.584	0.584
Tm	0.072	0.075	0.072	0.076	0.071	0.071
Yb	0.376	0.397	0.387	0.413	0.382	0.385
Lu	0.055	0.058	0.056	0.057	0.053	0.053
Y	11.9	11.3	11.7	13.2	12.6	12.6
A (ICP-AES) A (ICP-MS) B (ICP-AES) Averaged ^{*4}						
	37.1	8.21	8.03	8.96	8.54	
	0.263	1.77	1.77	1.93	1.85	
		1.12	1.07	1.19	1.14	
		4.59	4.61	5.12	4.86	
		0.752	0.733	0.795	0.769	
		0.177	0.166	0.185	0.178	
		1.00	0.94	1.06	1.02	
		0.142	0.126	0.147	0.140	
		0.838	0.812	0.925	0.875	
		0.203	0.185	0.206	0.200	
		0.541	0.525	0.586	0.559	
		0.067	0.065	0.073	0.069	
		0.340	0.341	0.379	0.360	
		0.048	0.050	0.054	0.051	
		11.6	13.1	12.5	12.4	

^{*1} Analytical data for REEs and Y in solid products by ICP-MS and those for Ca and Mg by ICP-AES are listed.

^{*2} Kuzuu limestone of the Upper Limestone Member of Nabeyama Formation (the sample number TKC-10 in Miura et al. (1999) was used as starting material. The data sets of A (ICP-AES) and B (ICP-MS) were obtained by using the same aliquot (A). The data set of B (ICP-AES) is for another aliquot (B).

^{*3} The dolomite content (molar ratio (%)) of each solid product is calculated as $[2\text{Mg}/(\text{Mg} + \text{Ca})] \times 100$.

^{*4} We calculated the average values from the mean values for aliquot (A) by two techniques and the data for aliquot (B).

37 ml) with stainless-steel jackets. They had been placed in an electric oven at 150°C for 10 days. In the second series of runs, aliquots (7.5 g) of the limestone powder and 25 ml of the respective 2 M MgCl₂ solutions had been held similarly at 150°C for 20 days.

Solid products were separated from the respective experimental solutions by filtration with cellulose nitrate membrane filter (pore size of 0.45 μ m), and were dried at 50°C. Their carbonate minerals were identified by XRD. Each run product was dissolved in HCl. The REE and Y in the solution were separated from matrix elements by the method of coprecipitation with Fe(III) oxyhydroxide and cation-exchange chromatography described elsewhere (Kawabe *et al.*, 1991, 1994). Finally they were analyzed by ICP atomic emission spectrometry (ICP-AES) and ICP mass spectrometry (ICP-MS). REE and Y in the starting material have also been determined in the same way. Calcium and Mg contents in the solid products were estimated from the Ca and Mg concentrations in the initial solution and filtrates determined by ICP-AES. The Ca and Mg contents of the starting material were determined by ICP-AES. Analytical results of REEs, Y, Ca and Mg for the experimental run products and starting material are summarized in Table 1, together with experimental conditions. Analytical uncertainties for REE data by ICP-AES are 5% or less (Kawabe *et al.*, 1994, 1998), and those by ICP-MS are 3% or less. Therefore only the REE and Y data by ICP-MS for run products are listed in Table 1.

RESULTS AND DISCUSSION

REE and Y abundances in the starting material of marine limestone

Figure 1 shows the REE and Y abundance pattern for the starting material of marine limestone normalized by C1 chondrite (Anders and Grevesse, 1989). Three analytical data sets are plotted: two sets of ICP-AES and ICP-MS analyses for an aliquot (A) and a set of ICP-AES analyses for another aliquot (B). The REE and Y pattern has a concave tetrad effect, a large negative

Fig. 1. The REE and Y abundance pattern for starting material of the marine limestone. ICP-AES and ICP-MS data for an aliquot (A) and ICP-AES for another aliquot (B) are normalized by C1 Chondrite (Anders and Grevesse, 1989).

Ce anomaly, a small negative Eu anomaly and a high Y/Ho ratio. These are the typical characteristics of REE and Y patterns for marine limestones (Kawabe *et al.*, 1991; Miura *et al.*, 1999).

The same sample solution of aliquot (A) was used in the measurements for both ICP-AES and ICP-MS determinations. The two sets of data represent analytical biases between the two techniques. The differences in REE and Y analyses between aliquot (A) and (B) may suggest heterogeneity of REE and Y abundances in the starting material. We calculated the average values from the mean values for aliquot (A) by the two techniques and the data for aliquot (B) as "the averaged values for starting material" (Table 1). We use this data set for discussion of REE and Y abundances.

Dolomitization of limestone by MgCl₂ solution and mobility of REE and Y

Dolomite was detected in every run product by XRD. The dolomite content (molar ratio (%)) of each solid run product has been calculated as $[2\text{Mg}/(\text{Mg} + \text{Ca})] \times 100$ (Table 1). In the first series of runs at 150°C for 10 days, only 28% of calcite transformed into dolomite in reaction with 2 M MgCl₂ solution without NaCl or KCl. However, 59% of calcite were altered into dolomite

when 0.5 M NaCl or KCl was involved in the MgCl_2 solution. In the second series of runs for 20 days at 150°C , about 90% of calcite were dolomitized by 2 M MgCl_2 solution irrespective of the presence of 0.5 M NaCl or 0.5 M KCl in the MgCl_2 solution. It appears that NaCl or KCl in the MgCl_2 solution makes the reaction rate of the earlier stage of dolomitization faster in the present experimental condition.

The REE and Y patterns normalized by C1 chondrite for dolomitized run products are shown in Figs. 2(a) and (b), in which the solid curve corresponds to "the averaged values for starting material". The REE and Y abundance patterns for dolomitized run products are approximately the same as that for the original marine limestone. The weight of solid carbonate decreases as calcite is altered to dolomite: the decrease in weight amounts to 8% when calcite transforms completely into dolomite. Because of this decrease in weight, REE and Y contents of the solid run products increase with increasing dolomite content if REE and Y in the original limestone are perfectly preserved in the dolomitized products. In Fig. 2(b) for the run products dolomitized by about 90%, all the REE data points of run products seems to be displaced by about 10% upwards from those of the original limestone, whereas such a shift cannot be recognized in Fig. 2(a) for the run products with lower dolomite contents.

Our experimental results appear to support the field observation that dolostones sometimes preserve the REE and Y signatures of limestone precursors as in the Middle Permian Kuzuu Limestone-Dolostone sequence, central Japan (Miura *et al.*, 1999), the Mississippian Burlington and Keokuk Formation, the midcontinental region of USA (Banner *et al.*, 1988), and the Middle Devonian Western Canada Sedimentary Basin (Qing and Mountjoy, 1994). Many natural dolomites must have been formed under much lower temperatures than the present experimental temperature of 150°C . Mass ratios of limestone to solution, chemical compositions of Mg-bearing solutions, and other parameters in natural dolomite formations are not well-known. However, if

Fig. 2. (a) Chondrite-normalized REE and Y patterns for dolomitized run products in the first series of runs at 150°C for 10 days. The solid curve represents the averaged analyses for the starting material of original limestone listed in Table 1. (b) Chondrite-normalized REE and Y patterns for dolomitized run products in the second series of runs at 150°C for 20 days. The solid curve represents the averaged analyses for the starting material of original limestone listed in Table 1.

dolomitization is essentially the cation-exchange reaction between Ca^{2+} in calcite and Mg^{2+} in aqueous solution, $\text{Mg}^{2+}_{(\text{aq})} + 2\text{CaCO}_{3(\text{c})} = \text{CaMg}(\text{CO}_3)_2(\text{c}) + \text{Ca}^{2+}_{(\text{aq})}$, our experimental results may be important to consider the reason why the REE and Y characteristics of dolostones resemble those of the marine limestones associated intimately with them.

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