Partition coefficients of Ra and Ba in calcite

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Homogeneous partition coefficients (D) for Ra and Ba in calcite were determined from coprecipitation experiments using the Continuous Addition Method (CAM). The D -values derived for Ra and Ba are:

$$D_{\text{Ra}} = (1.5 \pm 0.6) \times 10^{-1} \quad \text{and} \quad D_{\text{Ba}} = (1.6 \pm 1.1) \times 10^{-2}.$$

Although these data were derived at low precipitation rates (R) for calcite ($R < 9 \text{ nmol mg}^{-1} \text{ min}^{-1}$), the solutions were significantly oversaturated in calcite. Values of D should, ideally, be derived at equilibrium and hence the effect of oversaturation should be examined. Therefore, a coprecipitation experiment using the Free Drift Method (FDM) with slow degassing was also carried out. This experiment occurs under conditions that are only slightly oversaturated and the rate of coprecipitation was confirmed to be slow compared to dissolution and precipitation at the calcite surface. The resultant heterogeneous partition coefficients showed good agreement with homogeneous partition coefficients derived by CAM. This indicates that the oversaturation in CAM did not affect partitioning of these metals in calcite and that the derived D -values represented equilibrium partitioning between the solution and the solid phase.

The derived value of D_{Ra} is one order of magnitude larger than that of D_{Ba} despite the larger ionic radius of Ra. This indicates that compatibility of ionic radius is not a dominant parameter for preferential incorporation of Ra and Ba in calcite.

Keywords: coprecipitation, calcite, Ra, Ba

INTRODUCTION

It has long been known that divalent metal ions (Me) may be incorporated into calcite through a coprecipitation reaction. A number of investigations show that the size and chemical properties of Me have a large effect on the extent and mechanisms of incorporation (Lorens, 1981; Mucci and Morse, 1983; Pingitore and Eastman, 1984; Terakado and Taniguchi, 2006; Tesoriero and Pankow, 1996). For Me with ionic radii less than that of Ca, the closer the Me radius is to that of Ca, the higher the rate of uptake. In contrast, for Me with radii greater than that of Ca, the dependence on the size of the Me radius is not clear. Tunusoglu *et al.* (2007) studied partitioning of Ba (radius larger than that of Ca) by coprecipitation when equilibrated with calcite under ambient conditions; however, incorporation mechanisms were not identified because no change was detected at low concentrations of

Ba (less than 500 ppm) and complications were introduced by precipitated BaCO_3 (witherrite) identified at high concentrations of Ba (above 1000 ppm). In particular, partitioning behavior of Me at equilibrium is difficult to study, since the kinetics of precipitation and dissolution of calcite influences the partition reaction due to very slow diffusion of Me into calcite. It is known that Me larger than Ca form orthorhombic carbonates while calcite is rhombohedral and therefore Me with larger ionic radii than Ca would be expected to show limited diffusion into the smaller lattice structure. Therefore, reliable data on partition reactions which exclude the influence of slow diffusion causing disequilibrium distribution of trace elements in calcite are difficult to derive.

Little data have been reported on the coprecipitation of Ra, which has the largest ionic radius in the family of alkaline earth metals. The present study aims at investigating Ra coprecipitation with calcite by the Continuous Addition Method (Tesoriero and Pankow, 1996) in order to provide reliable data on the partition coefficients. In addition, the same experimental method was used for Ba, to examine the effect of affinity within the alkaline earth group for different ionic radii.

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The results were evaluated by calculation of the homogeneous partition coefficient (D) (Curti, 1997). D is defined as:

$$D = \frac{X_{\text{MeCO}_3(\text{s})}/X_{\text{CaCO}_3(\text{calcite})}}{[\text{Me}]/[\text{Ca}]} \quad (1)$$

where $X_{\text{MeCO}_3(\text{solid,s})}$ and $X_{\text{CaCO}_3(\text{calcite})}$ are the mole fractions of $\text{MeCO}_3(\text{s})$ and $\text{CaCO}_3(\text{calcite})$ in the coprecipitated solid and $[\text{Me}]$ and $[\text{Ca}]$ are concentrations of Me and Ca in solution. This partition coefficient is known to be affected by the precipitation rate of calcite (R). R is here defined as the amount of precipitated calcite per unit weight of seed crystal and time ($\text{nmol mg}^{-1}\text{min}^{-1}$; Lorens, 1978). This rate can be converted into a more conventional area-based unit using the measured specific surface of the seed crystals $-0.45 \text{ m}^2\text{g}^{-1}$ (see also *Comparison with the dissolution and precipitation kinetics of calcite*). Values of D for Sr and Ba as a function of R have been measured by Lorens (1981), Tesoriero and Pankow (1996) and Terakado and Taniguchi (2006). These data are shown in Fig. 1. The values of D for Sr and Ba tend to increase with R . The changes in D versus R are interpreted by the authors as an effect of the precipitation kinetics; the D -values obtained at very low R are thought to represent Me partitioning at equilibrium. Tesoriero and Pankow (1996) indicated that, with this trend, D becomes effectively constant at R less than $30 \text{ nmol mg}^{-1}\text{min}^{-1}$ for Sr and $40 \text{ nmol mg}^{-1}\text{min}^{-1}$ for Ba.

However, we have some doubts that the low R used in the cited experiments represents equilibrium partitioning of Me. In previous studies, the techniques used to obtain the values of D for varying R were the pH-stat method (Lorens, 1981), the continuous addition method (Tesoriero and Pankow, 1996) and the evaporation method (Terakado and Taniguchi, 2006). Figure 1 shows that only the partition coefficients of Sr (Lorens, 1981) are reasonably constant at low precipitation rates (at $R < 10 \text{ nmol mg}^{-1}\text{min}^{-1}$). Other data sets do not exhibit a convincing linear trend at low R .

The values of D should become constant at sufficiently low R if kinetic effects depend solely on the precipitation rate of calcite. However, most data trends for D have non-zero slopes even at the lowest precipitation rates. A cause of this variation in the D -values could be strong oversaturation. In all the methods mentioned above, a specific level of oversaturation had to be maintained in order to keep the precipitation rate constant and hence reaction progresses with precipitation dominating. However, for equilibrium partitioning of Me to occur, there should be a balance between dissolution and precipitation. Lorens (1981) indicates that an increase in the partition coefficient of Sr is caused by the initial sorption of

Fig. 1. D for Sr, Ba and Ra as a function of precipitation rate of calcite.

Sr on newly precipitated calcite crystals, before sorption equilibrium is attained. Therefore, we argue that the derived D values may not reflect an equilibrium state.

The values of D representing partitioning of Me in an equilibrium state were derived from coprecipitation experiments. In the present study, the Free Drift Method (FDM) of Meece and Benninger (1993) was adopted. In this method, precipitation of calcite results from increased pH induced by degassing of $\text{CO}_2(\text{g})$, resulting in an increase in the saturation index. The initial solution was first equilibrated with calcite at 1 atm of $100\% \text{ CO}_2(\text{g})$. Trace amounts of Ra or Ba were then added to the solution and the reaction cells were sealed to delay degassing. Slow degassing leads to a gradual increase in pH, inducing precipitation due to decreased solubility, with consequent incorporation of Ra or Ba.

This experiment with very slow coprecipitation was planned to ensure equilibrium partitioning of Me. Because the concentrations of Ca and Ra change from initial to final state in the closed system during the experimental period, partition coefficients have been evaluated using the equation for heterogeneous partition coefficients (λ) (Curti, 1999) for a system in which only a small increment in the mass of the solid phase occurs:

$$\frac{d[\text{Me}]}{d[\text{Ca}]} = \lambda \frac{[\text{Me}]}{[\text{Ca}]} \quad (2)$$

where $[\text{Me}]$ and $[\text{Ca}]$ are molal concentrations of Me and

Table 1. Experimental conditions for the continuous addition method (CAM)

Case	Tracer	Duration (min)	Weight of seed crystals (mg)	Concentration of CaCl ₂ and Na ₂ CO ₃ (mol kg ⁻¹ water ⁻¹)
C1-1	Ba	60	400	0.5
C1-2	"	"	"	"
C1-3	"	"	"	"
C1-4	"	"	"	1.0
C1-5	"	"	"	"
C1-6	"	"	"	"
C1-7	"	240	"	0.5
C1-8	"	"	"	"
C1-9	"	"	"	"
C1-10	"	1440	"	"
C1-11	"	"	"	"
C1-12	"	"	"	"
C1-13	"	"	900	"
C1-14	"	"	"	"
C1-15	"	3960	"	"
C2-1	Ra	1440	400	"
C2-2	"	"	"	"
C2-3	"	"	"	"

Ca in solution. Although Eqs. (1) and (2) have slightly different forms, D and λ are comparable measures of partitioning, relating the mole ratio of the elements in the coprecipitated phase to the ratio in solution. The former is applied for constrained R /higher oversaturation and the latter unconstrained R /lower oversaturation conditions. For practical application, Eq. (2) can be integrated to yield:

$$\ln \frac{[Me]}{[Me]_0} = \lambda_{Me} \ln \frac{[Ca]}{[Ca]_0} \quad (3)$$

where $[Me]_0$ and $[Ca]_0$ are initial concentration of Me and Ca (termed the logarithmic distribution law).

EXPERIMENTAL METHODS

Continuous addition method

The experimental procedure used is the same as that described by Tesoriero and Pankow (1996). The experimental conditions are shown in Table 1.

The initial solution was filtered (MILLIPORE, 0.45 μ m) and equilibrated with calcite (KANTO CHEMICAL CO., INC., JIS Special grade reagent, >99.5%) at $P_{CO_2} = 1$ atm (>99.5%). Initially, 400 ml of the solution was poured into a reaction cell and bubbled with CO₂ gas at $P_{CO_2} = 1$ atm to maintain constant pH and carbonate concentration. Then, 400 mg or 900 mg of seed calcite were added to the solutions, depending on the case (see Table

1). Twenty ml of CaCl₂/Na₂CO₃ solution were added by a syringe pump to attain an oversaturated state and initiate calcite coprecipitation. The precipitation rate was adjusted by varying the amount of CaCl₂/Na₂CO₃ added. The concentrations of CaCl₂/Na₂CO₃ solutions were 0.5 and 1.0 molal (mol kg⁻¹). Experimental durations were 60, 240, 1440 and 3960 minutes and temperature was maintained at $25 \pm 2^\circ\text{C}$. Because a constant precipitation rate was attained within 60 minutes, RaCl₂ (AEA Technology) or BaCl₂ (KANTO CHEMICAL CO., INC., JIS Special grade reagent, >99.0%) solutions were added after 60 minutes. In the case of a high precipitation rate, however, they were added after 30 minutes to give an experimental duration of 60 minutes. The Ra and Ba were added in the reaction cell to give concentrations of 7.28×10^{-6} mol kg⁻¹ and 3.00×10^{-8} mol kg⁻¹, respectively. Sampling of the solution was carried out during the experiment. After the coprecipitation reaction was completed, the solid phase was filtered and dried and the concentrations of Ra or Ba and calcium were analyzed. Solids were also analyzed by XRD to confirm that the crystal system was rhombohedral, thus that of calcite.

The concentrations of Ca and Ba, if they were above about 7×10^{-6} mol kg⁻¹, were analyzed by ICP-AES (Perkin Elmer, OPTIMA 3300XL, detection limit is 2×10^{-7} for Ca or 7×10^{-8} mol kg⁻¹ for Ba, respectively. Concentrations of Ba less than 7×10^{-6} mol kg⁻¹, were analyzed by ICP-MS (Agilent Technologies, Agilent 7500, detection limit is 7×10^{-10} molal). The concentration of ²²⁶Ra was measured one month after sampling, to ensure

Table 2. Measured values of aqueous composition and Ba/Ca ratios in solid phases and calculated partition coefficients of Ba and precipitation rate using CAM

Case	Total Ca (mol kg ⁻¹) in solution	Total Ba (mol kg ⁻¹) in solution	Ba/Ca mol ratio in solid	Homogeneous partition coefficient (D)	Precipitation rate of calcite (nmol mg ⁻¹ min ⁻¹)
C1-1	$(1.51 \pm 0.02) \times 10^{-2}$	$(7.21 \pm 0.07) \times 10^{-6}$	$(3.40 \pm 0.33) \times 10^{-5}$	$(7.11 \pm 0.68) \times 10^{-2}$	106 ± 9
C1-2	$(1.75 \pm 0.02) \times 10^{-2}$	$(6.99 \pm 0.07) \times 10^{-6}$	$(7.08 \pm 2.14) \times 10^{-5}$	$(1.78 \pm 0.52) \times 10^{-1}$	91 ± 10
C1-3	$(1.75 \pm 0.02) \times 10^{-2}$	$(6.41 \pm 0.06) \times 10^{-6}$	$(2.57 \pm 0.23) \times 10^{-5}$	$(7.02 \pm 0.62) \times 10^{-2}$	119 ± 11
C1-4	$(2.75 \pm 0.04) \times 10^{-2}$	$(7.65 \pm 0.08) \times 10^{-6}$	$(4.45 \pm 0.30) \times 10^{-5}$	$(1.60 \pm 0.11) \times 10^{-1}$	224 ± 16
C1-5	$(2.16 \pm 0.03) \times 10^{-2}$	$(7.21 \pm 0.07) \times 10^{-6}$	$(2.96 \pm 0.13) \times 10^{-5}$	$(8.86 \pm 0.40) \times 10^{-2}$	393 ± 14
C1-6	$(2.49 \pm 0.03) \times 10^{-2}$	$(7.28 \pm 0.07) \times 10^{-6}$	$(3.56 \pm 0.17) \times 10^{-5}$	$(1.22 \pm 0.06) \times 10^{-1}$	302 ± 15
C1-7	$(1.34 \pm 0.02) \times 10^{-2}$	$(7.06 \pm 0.07) \times 10^{-6}$	$(2.13 \pm 0.14) \times 10^{-5}$	$(4.06 \pm 0.26) \times 10^{-2}$	50.9 ± 1.4
C1-8	$(1.40 \pm 0.02) \times 10^{-2}$	$(6.92 \pm 0.07) \times 10^{-6}$	$(2.57 \pm 0.16) \times 10^{-5}$	$(5.21 \pm 0.32) \times 10^{-2}$	51.5 ± 1.5
C1-9	$(1.26 \pm 0.02) \times 10^{-2}$	$(6.99 \pm 0.07) \times 10^{-6}$	$(2.16 \pm 0.15) \times 10^{-5}$	$(3.89 \pm 0.27) \times 10^{-2}$	55.6 ± 4.0
C1-10	$(1.09 \pm 0.01) \times 10^{-2}$	$(8.59 \pm 0.08) \times 10^{-6}$	$(9.94 \pm 0.56) \times 10^{-6}$	$(1.26 \pm 0.07) \times 10^{-2}$	7.9 ± 0.1
C1-11	$(1.06 \pm 0.01) \times 10^{-2}$	$(7.86 \pm 0.08) \times 10^{-6}$	$(1.10 \pm 0.06) \times 10^{-5}$	$(1.48 \pm 0.08) \times 10^{-2}$	8.2 ± 0.1
C1-12	$(1.08 \pm 0.01) \times 10^{-2}$	$(6.77 \pm 0.07) \times 10^{-6}$	$(1.65 \pm 0.11) \times 10^{-5}$	$(2.62 \pm 0.18) \times 10^{-2}$	8.6 ± 0.5
C1-13	$(1.16 \pm 0.02) \times 10^{-2}$	$(7.14 \pm 0.07) \times 10^{-6}$	$(8.17 \pm 0.73) \times 10^{-6}$	$(1.32 \pm 0.12) \times 10^{-2}$	3.7 ± 0.2
C1-14	$(1.03 \pm 0.01) \times 10^{-2}$	$(7.28 \pm 0.07) \times 10^{-6}$	$(9.72 \pm 0.76) \times 10^{-6}$	$(1.37 \pm 0.11) \times 10^{-2}$	3.5 ± 0.1
C1-15	$(1.10 \pm 0.01) \times 10^{-2}$	$(7.06 \pm 0.07) \times 10^{-6}$	$(8.40 \pm 0.72) \times 10^{-6}$	$(1.31 \pm 0.11) \times 10^{-2}$	1.3 ± 0.1

Table 3. Measured values of aqueous composition and Ra/Ca ratio in solid phases and calculated partition coefficient of Ra and precipitation rate with CAM

Case	Total Ca (mol kg ⁻¹) in solution	Total Ra (mol kg ⁻¹) in solution	Ra/Ca mol ratio in solid	Homogeneous partition coefficient (D)	Precipitation rate of calcite (nmol mg ⁻¹ min ⁻¹)
C2-1		$(1.97 \pm 0.02) \times 10^{-8}$	$(2.29 \pm 0.05) \times 10^{-7}$	$(1.25 \pm 0.05) \times 10^{-1}$	
C2-2	$(1.07 \pm 0.03) \times 10^{-2}$ *	$(1.93 \pm 0.02) \times 10^{-8}$	$(2.47 \pm 0.06) \times 10^{-7}$	$(1.37 \pm 0.05) \times 10^{-1}$	8.2 ± 0.7*
C2-3		$(1.95 \pm 0.02) \times 10^{-8}$	$(3.28 \pm 0.07) \times 10^{-7}$	$(1.80 \pm 0.07) \times 10^{-1}$	

*Average of C1-10, C1-11 and C1-12 in Table 2.

secular equilibrium with daughters had been attained (closed system assures no loss of Rn), using a liquid scintillation counter (PACKARD, TRI-CARB 2750TR/LL, detection limit 2×10^{-11} mol kg⁻¹).

Free drift method

Experiments were carried out at $25 \pm 1^\circ\text{C}$. The initial 500 ml solutions were prepared from a filtered solution (MILLIPORE, $0.45 \mu\text{m}$) equilibrated with calcite (KANTO CHEMICAL CO., INC., JIS Special grade reagent, >99.5%) at $P_{\text{CO}_2} = 1 \text{ atm}$ (>99.5%). Trace amounts of Ba and Ra needed for the initial solutions were prepared from BaCl₂ (KANTO CHEMICAL CO., INC., JIS Special grade reagent, >99.0%) and RaCl₂ (AEA Technology) and 0.02 g of seed calcite (KANTO CHEMICAL CO., INC., JIS Special grade reagent, >99.5%). The initial concentrations of Ba were 7.3×10^{-7} , 7.3×10^{-6} , 1.2×10^{-4} and 2.5×10^{-4} mol kg⁻¹ and the initial concentrations of Ra were set to 1.5×10^{-10} and 1.5×10^{-9} mol

kg⁻¹. After adding the solutions of Ba or Ra and the seed calcite, the reaction cell was closed. Due to slow CO₂(g) degassing in the closed cell, pH increased and consequently the solubility of the calcite gradually decreased. As a result, calcite coprecipitation with Ba or Ra was initiated.

The duration of the experiment was from 38 to 85 days and the temperature was maintained at $25 \pm 1^\circ\text{C}$. The duration depended on the chemical state of the solution in the reaction cell. The estimated pH in solution equilibrated with calcite under air is 8.25. The reaction cell was opened and sampled after pH had stabilized close to this value. After the coprecipitation reaction was complete, the solid phase was removed using a membrane filter (AMICON, YM100, nominal molecular weight limit 100,000). The concentrations of HCO₃⁻, Ba and Ra remaining in solution were then measured. After drying, the specific surface area was determined by the BET method with a particle size analyzer (QUANTASORB QS-

Fig. 2. Schematic diagram of the experimental apparatus. Temperature was maintained at $25 \pm 1^\circ\text{C}$.

18). For the Ba experiment, the precipitate was dissolved in acid and the concentrations of Ca and Ba were determined. Solids were also analyzed by XRD to confirm that the crystal system is rhombohedral and thus, that of calcite.

The procedures to measure concentrations of Ca, Ba and Ra are the same as specified in *Continuous addition method*. The concentration of total inorganic carbon was analyzed by a total organic carbon analyzer (SHIMADZU CO., TOC-5000, detection limit 1 ppm—approx. 10^{-4} mol kg^{-1}).

RESULTS AND DISCUSSION

Homogeneous partition coefficients of Ra and Ba from the continuous addition method

Measured experimental data are shown for Ba and Ra obtained in the coprecipitation experiments in Tables 2 and 3, respectively. Ba and Ca concentrations and their molar ratios in the solid phase were measured in Ba experiments. For the experiments with Ra, concentrations of Ca in solution could not be measured directly and hence, the average values were taken from the triplicate Ba experiments C1-10, C1-11 and C1-12, which had duration and seed weight the same as for the Ra case.

Partition coefficients (D) were derived using Eq. (1). The values of D for Ra and Ba at $R < 9 \text{ nmol mg}^{-1}\text{min}^{-1}$ were calculated to be $(1.5 \pm 0.6) \times 10^{-1}$ and $(1.6 \pm 1.1) \times 10^{-2}$, respectively. Errors were calculated from spread in measured values of partition coefficients (3 for Ra, 6 for Ba). The values for D_{Ba} are in good agreement with those of Tesoriero and Pankow (1996) and are about one third to one half of those of Taniguchi and Terakado (2006). For D_{Ra} , no comparison with other data is possible, since this is the first experimental determination of this parameter.

The extent of incorporation appears to be generally correlated with the size of the ionic radius. Ionic radii

Fig. 3. pH evolution in the coprecipitation experiments.

with sixfold coordination for Ba and Ra are 1.35×10^{-10} m (Shannon, 1976) and 1.39×10^{-10} m (estimated from eightfold and twelvefold radii in Shannon, 1976 by Sverjensky and Molling, 1992), respectively. Ra was previously assumed to be less well incorporated than Ba. However, D measured for Ra is one order of magnitude larger than that for Ba. Therefore, it is suggested that the mechanism for incorporation of Ba and Ra in calcite does not directly depend on the ionic radius.

Saturation state of solution in coprecipitation experiments using the Free Drift Method

Heterogeneous partition coefficients (λ) for Ra and Ba were measured by FDM with slow degassing to exclude (or, at least, minimize) the effect of oversaturation on partition coefficients.

A low saturation state was estimated by the variation in pH during the experiment. Figure 3 shows the measured pH values versus duration. It indicates that there was a slow increase in pH with time. Plots of each case show different slopes because the rate of CO_2 degassing from the solution surfaces was not controlled in the experiments. The pH at calcite equilibrium with air was estimated to be 8.25 by thermodynamic calculations using the database of Arthur *et al.* (1999). As seen, the measured pH approached this value. The duration of increasing pH varied from 30 to 80 days. High pH increase rates, in the range from 0.1 to 0.3 per day, were observed in the F1-1, F1-2, F1-3 and F1-6 cases. The precipitation rate of calcite (R) and the saturation index (Ω) were estimated

Table 4. Initial and final aqueous compositions and calculated Ba partition coefficients and precipitation rates with FDM

Case	pH	Initial Ca (mol kg ⁻¹) in solution	Final Ca (mol kg ⁻¹) in solution	Initial Ba (mol kg ⁻¹) in solution	Final Ba (mol kg ⁻¹) in solution	Final C (mol kg ⁻¹) in solution	Heterogeneous partition coefficient (λ)	Precipitation rate of calcite (nmol mg ⁻¹ min ⁻¹)	Ω^*
F1-1	8.35	$(9.17 \pm 0.12) \times 10^{-3}$	$(5.93 \pm 0.08) \times 10^{-4}$	$(7.92 \pm 0.11) \times 10^{-7}$	$(7.19 \pm 0.10) \times 10^{-7}$	$(1.03 \pm 0.26) \times 10^{-3}$	$(3.49 \pm 0.51) \times 10^{-2}$	3.12 ± 0.06	0.16 ± 0.13
F1-2	8.38	$(9.03 \pm 0.12) \times 10^{-3}$	$(5.76 \pm 0.08) \times 10^{-4}$	$(7.22 \pm 0.10) \times 10^{-6}$	$(6.90 \pm 0.09) \times 10^{-6}$	$(1.01 \pm 0.26) \times 10^{-3}$	$(1.65 \pm 0.51) \times 10^{-2}$	3.04 ± 0.06	0.17 ± 0.13
F1-3	8.35	$(8.67 \pm 0.12) \times 10^{-3}$	$(6.40 \pm 0.08) \times 10^{-4}$	$(2.49 \pm 0.03) \times 10^{-4}$	$(2.39 \pm 0.03) \times 10^{-4}$	$(1.09 \pm 0.27) \times 10^{-3}$	$(1.51 \pm 0.54) \times 10^{-2}$	3.00 ± 0.06	0.20 ± 0.13
F1-4	8.30	$(9.17 \pm 0.12) \times 10^{-3}$	$(6.07 \pm 0.08) \times 10^{-4}$	$(7.35 \pm 0.10) \times 10^{-7}$	$(7.11 \pm 0.09) \times 10^{-7}$	$(1.18 \pm 0.29) \times 10^{-3}$	$(1.22 \pm 0.52) \times 10^{-2}$	1.73 ± 0.02	0.18 ± 0.13
F1-5	8.23	$(8.92 \pm 0.12) \times 10^{-3}$	$(6.37 \pm 0.08) \times 10^{-4}$	$(7.54 \pm 0.10) \times 10^{-6}$	$(7.32 \pm 0.10) \times 10^{-6}$	$(1.24 \pm 0.31) \times 10^{-3}$	$(1.14 \pm 0.53) \times 10^{-2}$	1.42 ± 0.02	0.15 ± 0.13
F1-6	8.29	$(9.06 \pm 0.12) \times 10^{-3}$	$(6.48 \pm 0.09) \times 10^{-4}$	$(2.57 \pm 0.03) \times 10^{-4}$	$(2.40 \pm 0.03) \times 10^{-4}$	$(1.05 \pm 0.26) \times 10^{-3}$	$(2.56 \pm 0.53) \times 10^{-2}$	2.71 ± 0.04	0.13 ± 0.13
F1-7	8.29	$(8.48 \pm 0.11) \times 10^{-3}$	$(6.70 \pm 0.09) \times 10^{-4}$	$(8.32 \pm 0.11) \times 10^{-7}$	$(8.00 \pm 0.11) \times 10^{-7}$	$(1.33 \pm 0.33) \times 10^{-3}$	$(1.55 \pm 0.55) \times 10^{-2}$	1.39 ± 0.02	0.26 ± 0.13
F1-8	8.28	$(8.40 \pm 0.11) \times 10^{-3}$	$(6.31 \pm 0.08) \times 10^{-4}$	$(7.52 \pm 0.10) \times 10^{-6}$	$(7.41 \pm 0.10) \times 10^{-6}$	$(1.30 \pm 0.33) \times 10^{-3}$	$(5.8 \pm 5.4) \times 10^{-3}$	1.33 ± 0.02	0.21 ± 0.13
F1-9	8.33	$(8.78 \pm 0.12) \times 10^{-3}$	$(6.45 \pm 0.09) \times 10^{-4}$	$(2.53 \pm 0.03) \times 10^{-4}$	$(2.46 \pm 0.03) \times 10^{-4}$	$(2.02 \pm 0.51) \times 10^{-3}$	$(1.11 \pm 0.54) \times 10^{-2}$	1.44 ± 0.02	0.43 ± 0.13
F1-10	8.45	$(8.97 \pm 0.12) \times 10^{-3}$	$(7.22 \pm 0.10) \times 10^{-4}$	$(1.17 \pm 0.02) \times 10^{-4}$	$(1.15 \pm 0.02) \times 10^{-4}$	$(1.54 \pm 0.39) \times 10^{-3}$	$(8.2 \pm 5.5) \times 10^{-3}$	1.45 ± 0.02	0.49 ± 0.13
F1-11	8.39	$(9.00 \pm 0.12) \times 10^{-3}$	$(6.94 \pm 0.09) \times 10^{-4}$	$(1.23 \pm 0.02) \times 10^{-4}$	$(1.15 \pm 0.02) \times 10^{-4}$	$(1.47 \pm 0.37) \times 10^{-3}$	$(2.89 \pm 0.55) \times 10^{-2}$	1.42 ± 0.02	0.40 ± 0.13
F1-12	8.33	$(8.87 \pm 0.12) \times 10^{-3}$	$(7.25 \pm 0.10) \times 10^{-4}$	$(1.19 \pm 0.02) \times 10^{-4}$	$(1.15 \pm 0.02) \times 10^{-4}$	$(1.54 \pm 0.39) \times 10^{-3}$	$(1.64 \pm 0.56) \times 10^{-2}$	1.47 ± 0.02	0.38 ± 0.13

* $\Omega = \log(a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}) - \log(\text{equilibrium constant of calcite; taken to be } -8.48, \text{ Plummer and Busenberg, 1982})$.

Table 5. Initial and final aqueous compositions and calculated Ra partition coefficients and precipitation rate with FDM

Case	pH	Initial Ca (mol kg ⁻¹) in solution	Final Ca (mol kg ⁻¹) in solution	Initial Ra (mol kg ⁻¹) in solution	Final Ra (mol kg ⁻¹) in solution	Final C (mol kg ⁻¹) in solution	Heterogeneous partition coefficient (λ)	Precipitation rate of calcite (nmol mg ⁻¹ min ⁻¹)	Ω^*
F2-1				$(1.62 \pm 0.03) \times 10^{-10}$	$(1.23 \pm 0.03) \times 10^{-10}$		$(1.00 \pm 0.12) \times 10^{-1}$		
F2-2				$(1.64 \pm 0.03) \times 10^{-10}$	$(1.46 \pm 0.03) \times 10^{-10}$		$(4.1 \pm 1.1) \times 10^{-2}$		
F2-3	8.31 $\pm$ 0.11*	$(8.86 \pm 0.68) \times 10^{-3}$ *	$(6.19 \pm 0.67) \times 10^{-4}$ *	$(1.65 \pm 0.03) \times 10^{-10}$	$(1.43 \pm 0.03) \times 10^{-10}$	$(1.18 \pm 0.27) \times 10^{-3}$ *	$(5.6 \pm 1.2) \times 10^{-2}$	2.0 $\pm$ 1.5*	0.19 $\pm$ 0.11**
F2-4				$(1.50 \pm 0.03) \times 10^{-9}$	$(1.20 \pm 0.03) \times 10^{-9}$		$(8.3 \pm 1.2) \times 10^{-2}$		
F2-5				$(1.51 \pm 0.03) \times 10^{-9}$	$(1.36 \pm 0.03) \times 10^{-9}$		$(4.1 \pm 1.2) \times 10^{-2}$		
F2-6				$(1.52 \pm 0.03) \times 10^{-9}$	$(1.38 \pm 0.03) \times 10^{-9}$		$(3.5 \pm 1.2) \times 10^{-2}$		

* Average of F1-1, F1-2, F1-4, F1-5, F1-7 and F1-8. Data from F1-3, F1-6, F1-9, F1-10, F1-11 and F1-12 were not considered for calculation since solutions contained notable concentrations of Ba.

** $\Omega = \log(a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}) - \log(\text{equilibrium constant of calcite is } -8.48, \text{ Plummer and Busenberg, 1982})$.

by thermodynamic calculations for those cases with high pH increase rates; assuming this is due to highest oversaturation, resulting in a maximum amount of precipitation. The calculated precipitation rate of calcite and saturation index values ranged from 10 to 66 nmol mg⁻¹min⁻¹ and from 0.09 to 0.13, respectively. Such precipitation rates for calcite are not considered to be rapid by reference to the value of 40 nmol mg⁻¹min⁻¹ for Ba²⁺, which is defined as slow precipitation by Tesoriero and Pankow (1996). Saturation indices calculated above are also small. Except for these high values, the increase of pH was less than 0.1 per day throughout the experiments.

Generally, gas transfer is assumed to be slower than reactions that produce or consume CO₂ in the aqueous phase. On the other hand, ionic equilibria in the dissolved carbonate system are established very rapidly (Stumm and Morgan, 1996). Highly oversaturated solutions should result in a rapid increase in pH values; the average pH increase of below 0.1 per day may thus be considered to be dominated by slow degassing, assuring that only slight oversaturation is maintained throughout the experiment.

Heterogeneous partition coefficients of Ra and Ba

Processing data from experiments using FDM The measured experimental values of λ , R and Ω are shown for Ba and Ra coprecipitation experiments in Tables 4 and 5, respectively. Values of pH and initial and final concentrations of Ba, Ca and total C were measured in experiments with Ba. For the experiments with Ra, because the concentrations of Ca and total C in solution could not be measured, the average values derived from the experiments with Ba were again adopted.

Saturation indices (Ω) were calculated from the activities of Ca²⁺ and CO₃²⁻, using the equation:

$$\Omega = \log(a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}) - \log(10^{-8.48*}) \quad (4)$$

* equilibrium constant of calcite at 25°C, Plummer and Busenberg (1982).

Ionic strength was calculated from the measured total concentrations of Ca, Ba, Ra and C and pH in solution using the PHREEQC code (Parkhurst, 1995). Activity coefficients were calculated using the Davies equation. The precise calculation of activity depends on using an appropriate model. The values of ionic strength in the present study (from 0.001 to 0.003) are low enough allow estimation of activity coefficients using the Davies equation; all parameters defining ionic strength (total concentration of Ca, C, Ra, Ba and pH) were measured and included in the calculation. For these calculations, the thermodynamic data listed in Table A1 are used for Ba and Ra complexes, whereas data for other species are from Arthur *et al.* (1999). The resulting values of Ω cal-

culated from the above data are shown in Tables 4 and 5.

Values of Ω vary from 0.13 to 0.49. These values indicate that the solution was not far from equilibrium. Terakado and Taniguchi (2006) carried out coprecipitation experiments using the evaporation method. In their study, oversaturation seems to be lower than that in other earlier investigations, since the time to initiate calcite precipitation was longer. Terakado and Taniguchi (2006) estimated a saturation index of 1.15. This value indicates an ion activity product 11 to 12 times higher than the solubility product. The values of Ω in the present study clearly indicate that oversaturation is significantly less than in previous studies and hence precipitation was slower.

Comparison between heterogeneous and homogeneous partition coefficients of Ra and Ba Heterogeneous partition coefficients (λ) were calculated using Eq. (3). The values of λ for Ra and Ba were calculated to be in the range from 3.5×10^{-2} to 1.0×10^{-1} and from 5.8×10^{-3} to 3.5×10^{-2} respectively. For Ba, the homogeneous partition coefficient (D) discussed in *Homogeneous partition coefficients of Ra and Ba from the continuous addition method* shows good agreement with these values of λ . Although the mean values of D for Ra determined are 2.5 times as high as values of λ for Ra, considering the scatter in measured values of both D and λ , they can be considered to show reasonably good agreement.

Since values of λ were derived under low saturation conditions and slow R , values of D for Ra and Ba derived by CAM in this study can be argued to represent partition coefficients under equilibrium conditions.

Comparison with the dissolution and precipitation kinetics of calcite

The kinetics of the precipitation reaction have to be evaluated in order to confirm that the value of λ derived in the present study represents partitioning of Ba and Ra under equilibrium conditions. It has been reported that calcite surface dissolution and precipitation kinetics depending on solution composition (Plummer *et al.*, 1978; Chou *et al.*, 1989). Therefore, comparisons between R observed in experiments using FDM and kinetics of dissolution and precipitation on calcite surfaces are made in this section.

Chou *et al.* (1989) presents the rate equations as

$$R_f = k_1 a_{\text{H}^+} + k_2 a_{\text{H}_2\text{CO}_3(\text{aq})} + k_3 \quad (5)$$

and

$$R_b = k_{-1} a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-} + k_{-2} a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-}^2 + k_{-3} a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} \quad (6)$$

Here R_f and R_b are dissolution and precipitation rates, in mol cm⁻²s⁻¹, respectively. Values of $k_{1,2,3}$ and $k_{-1,-2,-3}$ are

rate constants of forward and backward reactions. These constants are given in Table A4. The $a_{\text{H}^+, \text{Ca}^{2+}, \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CO}_3^{2-}}$ parameters are activities of H^+ , Ca^{2+} , H_2CO_3 , HCO_3^- and CO_3^{2-} , respectively. These activities were determined by thermodynamic calculations with the measurements shown in Table 4. Average values used to estimate R_f and R_b and are also given in Table A4.

As a result of the calculations, $R_f = (6.56 \pm 0.02) \times 10^{-11}$ and $R_b = (1.19 \pm 0.89) \times 10^{-10} \text{ mol cm}^{-2}\text{s}^{-1}$ were obtained. These R_f and R_b values can be related to R given in Table 4 by consideration of the surface area of calcite. This specific surface area was determined by the BET method to be $0.45 \text{ m}^2\text{g}^{-1}$. Thus, an average precipitation rate of $(7.2 \pm 5.6) \times 10^{-12} \text{ mol cm}^{-2}\text{s}^{-1}$ is derived from R . This value is significantly smaller than R_f and R_b given above. This indicates that the net coprecipitation reaction in the experiment does not perturb the balance between equilibrium dissolution and precipitation on calcite surfaces. In other words, the values of λ derived in the present study represent partitioning of Ra and Ba between the solid phases and solutions at equilibrium.

CONCLUSIONS

Coprecipitation experiments were carried out to derive homogeneous partition coefficients (D). Measured D at low precipitation rates (R) ($R < 9 \text{ nmol mg}^{-1}\text{min}^{-1}$) were:

$$D_{\text{Ra}} = (1.5 \pm 0.6) \times 10^{-1} \quad \text{and} \quad D_{\text{Ba}} = (1.6 \pm 1.1) \times 10^{-2}.$$

The measured values of D for Ba are in good agreement with literature data. This is the first determination of D for Ra.

Coprecipitation in experiments using FDM with slow degassing was also carried out. In these experiments low oversaturation was maintained throughout; minimizing the effect of this parameter on the heterogeneous partition coefficients (λ) derived. Since λ and D can be argued to measure similar partitioning on small crystals when close to equilibrium, values of D and λ were compared. For Ba, values of D show good agreement with λ ; for Ra and D and λ can be considered to be in good agreement within the range of uncertainty involved. Therefore, D values measured in this study are considered to represent equilibrium partition coefficients for Ra and Ba.

Values of D for Ra are one order of magnitude larger than those for Ba. It implies that incorporation of Ra and Ba in calcite is not dependent on the compatibility of ionic radii.

Precipitation (and dissolution) kinetics in FDM experiments were estimated in order to confirm that the values of λ represent partition of Ra and Ba between solid

phases and solutions at equilibrium. Inherent precipitation (and dissolution) rates under the experimental conditions are larger than the R values measured in this study. Therefore, it can be concluded that values of λ represent partitioning of Ra and Ba at equilibrium.

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REFERENCES

- Arthur, R. C., Sasamoto, H., Shibata, M., Yui, M. and Neyama, A. (1999) Development of Thermodynamic Databases for Geochemical calculation. Japan Nuclear Cycle Development Corp. Technical Report, TN8400 99-079.
- Busenberg, E. and Plummer, L. N. (1986) The solubility of $\text{BaCO}_3(\text{cr})$ (witherite) in CO_2 - H_2O solutions between 0 and 90°C , evaluation of the association constants of $\text{BaHCO}_3^+(\text{aq})$ and $\text{BaCO}_3^0(\text{aq})$ between 5 and 80°C , and a preliminary evaluation of the thermodynamic properties of $\text{Ba}^{2+}(\text{aq})$. *Geochim. Cosmochim. Acta* **50**, 2225–2233.
- Chou, L., Garrels, R. M. and Wollast, R. (1989) Comparative study of the kinetics and mechanisms of dissolution of carbonate minerals. *Chem. Geol.* **78**, 269–282.
- Curti, E. (1997) Coprecipitation of radionuclides: basic concepts, literature review and first applications. PSI-Bericht Nr. 97-10.
- Curti, E. (1999) Coprecipitation of radionuclides with calcite: estimation of partition coefficients based on a review of laboratory investigations and geochemical data. *Appl. Geochem.* **14**, 433–445.
- Langmuir, D. and Riese, A. C. (1985) The thermodynamic properties of radium. *Geochim. Cosmochim. Acta* **49**, 1593–1601.
- Lorens, R. B. (1978) A study of biological and physical controls on the trace metal content of calcite and aragonite. Ph.D. dissertation, Univ. of Rhode Island.
- Lorens, R. B. (1981) Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite precipitation rate. *Geochim. Cosmochim. Acta* **45**, 553–561.
- Meece, D. E. and Benninger, L. K. (1993) The coprecipitation of Pu and other radionuclides with CaCO_3 . *Geochim. Cosmochim. Acta* **57**, 1447–1458.
- Mucci, A. and Morse, J. W. (1983) The incorporation of Mg^{2+} and Sr^{2+} into calcite overgrowths: influences of growth rate and solution composition. *Geochim. Cosmochim. Acta* **47**, 217–233.
- Parkhurst, D. L. (1995) PHREEQC—User's guide to PHREEQC—a computer program for speciation, reaction-

- path, advective-transport, and inverse geochemical calculation. U.S. Geological Survey, Water-Resources Investigations Report 95-4227.
- Pingitore, N. E. and Eastman, M. P. (1984) The experimental partitioning of Ba^{2+} into calcite. *Chem. Geol.* **45**, 113–120.
- Plummer, L. N. and Busenberg, E. (1982) The solubilities of calcite, aragonite and vaterite in CO_2 – H_2O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system CaCO_3 – CO_2 – H_2O . *Geochim. Cosmochim. Acta* **46**, 1011–1040.
- Plummer, L. N., Wigley, T. M. L. and Parkhurst, D. L. (1978) The kinetics of calcite dissolution in CO_2 –water system at 5 to 60°C and 0.0 to 1.0 atm CO_2 . *Amer. J. Sci.* **278**, 179–216.
- Shannon, R. D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* **A32**, 751–767.
- Stumm, W. and Morgan, J. J. (1996) *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. 3rd ed., John Wiley & Sons, Inc., New York, 1022 pp.
- Sverjensky, D. A. and Molling, P. A. (1992) A linear free energy relationship for crystalline solids and aqueous ions. *Nature* **356**, 231–234.
- Terakado, Y. and Taniguchi, M. (2006) A new method for the study of trace element partitioning between calcium carbonate and aqueous solutions: a test case for Sr and Ba incorporation into calcite. *Geochem. J.* **40**, 161–170.
- Tesoriero, A. J. and Pankow, J. F. (1996) Solid solution partitioning of Sr^{2+} , Ba^{2+} , and Cd^{2+} to calcite. *Geochim. Cosmochim. Acta* **60**, 1053–1063.
- Tunusoğlu, Ö., Shahwan, T. and Eroğlu, A. E. (2007) Retention of aqueous Ba^{2+} ions by calcite and aragonite over a wide range of concentrations: Characterization of the uptake capacity, and kinetics of sorption and precipitate formation. *Geochem. J.* **41**, 379–389.

Table A1. Calcite solubility product and equilibrium constants for C, Ba and Ra species

Reaction	logK at 25°C	Reference
$\text{CaCO}_3(\text{calcite}) = \text{Ca}^{2+} + \text{CO}_3^{2-}$	–8.48	Plummer and Busenberg (1982)
$\text{H}^+ + \text{CO}_3^{2-} = \text{HCO}_3^-$	10.329	Arthur <i>et al.</i> (1999)
$2\text{H}^+ + \text{CO}_3^{2-} = \text{H}_2\text{CO}_3(\text{aq})$	16.673	Arthur <i>et al.</i> (1999)
$\text{Ba}^{2+} + \text{H}_2\text{O} - \text{H}^+ = \text{BaOH}^+$	–13.5	Arthur <i>et al.</i> (1999)
$\text{Ba}^{2+} + \text{Cl}^- = \text{BaCl}^+$	–0.498	Arthur <i>et al.</i> (1999)
$\text{Ba}^{2+} + \text{F}^- = \text{BaF}^+$	–0.183	Arthur <i>et al.</i> (1999)
$\text{Ba}^{2+} + \text{CO}_3^{2-} = \text{BaCO}_3(\text{aq})$	2.713	Busenberg and Plummer (1986)
$\text{Ba}^{2+} + \text{H}^+ + \text{CO}_3^{2-} = \text{BaHCO}_3^+$	11.311	Busenberg and Plummer (1986)
$\text{Ra}^{2+} + \text{H}_2\text{O} - \text{H}^+ = \text{RaOH}^+$	–13.5	Langmuir and Riese (1985)
$\text{Ra}^{2+} + \text{Cl}^- = \text{RaCl}^+$	–0.10	Langmuir and Riese (1985)
$\text{Ra}^{2+} + \text{CO}_3^{2-} = \text{RaCO}_3(\text{aq})$	2.5	Langmuir and Riese (1985)
$\text{Ra}^{2+} + \text{SO}_4^{2-} = \text{RaSO}_4(\text{aq})$	2.75	Langmuir and Riese (1985)

Table A2. Estimated values of ionic strength and activities of final solution, for FDM experiment for Ba

Case	Ionic strength	Activity coefficient of monovalent ion	Activity coefficient of divalent ion	Activity of Ca^{2+} (mol kg ^{–1}) in solution*	Activity of CO_3^{2-} (mol kg ^{–1}) in solution*	Activity of Ba^{2+} (mol kg ^{–1}) in solution*
F1-1	$(1.68 \pm 0.25) \times 10^{-3}$	0.95	0.83	$(4.81 \pm 0.24) \times 10^{-4}$	$(1.00 \pm 0.25) \times 10^{-5}$	$(5.92 \pm 0.30) \times 10^{-7}$
F1-2	$(1.66 \pm 0.25) \times 10^{-3}$	0.95	0.83	$(4.68 \pm 0.23) \times 10^{-4}$	$(1.06 \pm 0.26) \times 10^{-5}$	$(5.69 \pm 0.28) \times 10^{-6}$
F1-3	$(2.55 \pm 0.38) \times 10^{-3}$	0.95	0.80	$(4.99 \pm 0.25) \times 10^{-4}$	$(1.05 \pm 0.26) \times 10^{-5}$	$(1.89 \pm 0.10) \times 10^{-4}$
F1-4	$(1.78 \pm 0.27) \times 10^{-3}$	0.95	0.83	$(4.89 \pm 0.24) \times 10^{-4}$	$(1.02 \pm 0.25) \times 10^{-5}$	$(5.83 \pm 0.29) \times 10^{-7}$
F1-5	$(1.89 \pm 0.28) \times 10^{-3}$	0.95	0.82	$(5.12 \pm 0.26) \times 10^{-4}$	$(9.1 \pm 2.3) \times 10^{-6}$	$(5.96 \pm 0.30) \times 10^{-6}$
F1-6	$(2.56 \pm 0.38) \times 10^{-3}$	0.95	0.80	$(5.06 \pm 0.25) \times 10^{-4}$	$(8.8 \pm 2.2) \times 10^{-6}$	$(1.90 \pm 0.10) \times 10^{-4}$
F1-7	$(1.98 \pm 0.30) \times 10^{-3}$	0.95	0.82	$(5.33 \pm 0.27) \times 10^{-4}$	$(1.13 \pm 0.28) \times 10^{-5}$	$(6.48 \pm 0.32) \times 10^{-7}$
F1-8	$(1.91 \pm 0.29) \times 10^{-3}$	0.95	0.82	$(5.05 \pm 0.25) \times 10^{-4}$	$(1.08 \pm 0.27) \times 10^{-5}$	$(6.02 \pm 0.30) \times 10^{-6}$
F1-9	$(3.01 \pm 0.45) \times 10^{-3}$	0.94	0.79	$(4.84 \pm 0.24) \times 10^{-4}$	$(1.85 \pm 0.46) \times 10^{-5}$	$(1.89 \pm 0.10) \times 10^{-4}$
F1-10	$(2.52 \pm 0.38) \times 10^{-3}$	0.95	0.80	$(5.54 \pm 0.28) \times 10^{-4}$	$(1.85 \pm 0.46) \times 10^{-5}$	$(9.02 \pm 0.45) \times 10^{-5}$
F1-11	$(2.45 \pm 0.37) \times 10^{-3}$	0.95	0.80	$(5.38 \pm 0.27) \times 10^{-4}$	$(1.55 \pm 0.39) \times 10^{-5}$	$(9.05 \pm 0.45) \times 10^{-5}$
F1-12	$(2.53 \pm 0.38) \times 10^{-3}$	0.95	0.80	$(5.60 \pm 0.28) \times 10^{-4}$	$(1.41 \pm 0.35) \times 10^{-5}$	$(9.03 \pm 0.45) \times 10^{-5}$

*Activity calculated considering speciation and activity correction. Thermodynamic data from Arthur *et al.* (1999) and Busenberg and Plummer (1986). Activity coefficient calculated using Davies equation.

APPENDIX

Saturation indices (Ω) were calculated from the activities of Ca^{2+} and CO_3^{2-} ; thermodynamic data used in this calculation shown in Table A1. Estimated values of ionic strength, activities and saturation indices of final

solution, for FDM experiment for Ba and Ra are given in Tables A2 and A3, respectively.

Inherent kinetics of dissolution and precipitation on calcite surfaces were also estimated from the activity of reacting species. Data used for this estimation are given in Table A4.

Table A3. Estimated values of ionic strength and activities of final solution, for FDM experiment for Ra

Case	Ionic strength	Activity coefficient of monovalent ion	Activity coefficient of divalent ion	Activity of Ca^{2+} (mol kg- H_2O^{-1}) in solution*	Activity of CO_3^{2-} (mol kg- H_2O^{-1}) in solution*	Activity of Ra^{2+} (mol kg- H_2O^{-1}) in solution*
F2-1						$(1.01 \pm 0.02) \times 10^{-10}$
F2-2						$(1.21 \pm 0.03) \times 10^{-10}$
F2-3	$(1.8 \pm 0.3) \times 10^{-3}^{**}$	0.95**	0.83**	$(4.98 \pm 0.47) \times 10^{-4}^{**}$	$(1.03 \pm 0.15) \times 10^{-5}^{**}$	$(1.18 \pm 0.02) \times 10^{-10}$
F2-4						$(9.9 \pm 0.2) \times 10^{-10}$
F2-5						$(1.12 \pm 0.02) \times 10^{-9}$
F2-6						$(1.14 \pm 0.02) \times 10^{-9}$

*Activity is calculated considering speciation and activity correction. Thermodynamic data of Arthur et al. (1999) and Langmuir and Riese (1985) were used. Activity coefficients calculated by Davies equation.

**Average of F1-1, F1-2, F1-4, F1-5, F1-7 and F1-8. Data from F1-3, F1-6, F1-9, F1-10, F1-11 and F1-12 not considered for average calculations since solutions contained notable concentrations of Ba.

Table A4. Kinetic constants of forward and backward reaction, solubility product of reaction and activity of H^+ , Ca^{2+} , $\text{H}_2\text{CO}_3(\text{aq})$, HCO_3^- and CO_3^{2-}

Reaction* ¹	k_i^{*2}	k_{-i}^{*3}	$K_{i,SP}^{*4}$
$\text{CaCO}_3(\text{calcite}) + \text{H}^+ \xrightleftharpoons[k_{-1}]{k_1} \text{Ca}^{2+} + \text{HCO}_3^-$	8.91×10^{-5}	1.26×10^{-6}	7.06×10^1
$\text{CaCO}_3(\text{calcite}) + \text{H}_2\text{CO}_3(\text{aq}) \xrightleftharpoons[k_{-2}]{k_2} \text{Ca}^{2+} + 2\text{HCO}_3^-$	5.01×10^{-8}	1.57×10^{-3}	3.20×10^{-5}
$\text{CaCO}_3(\text{calcite}) \xrightleftharpoons[k_{-3}]{k_3} \text{Ca}^{2+} + \text{CO}_3^{2-}$	6.46×10^{-11}	$1.86 \times 10^{-2}^{*2}$	3.31×10^{-9}
$a_{\text{H}^+} = (4.8 \pm 1.3) \times 10^{-9}^{*5}$			
$a_{\text{Ca}^{2+}} = (5.11 \pm 0.59) \times 10^{-4}^{*5}$			
$a_{\text{H}_2\text{CO}_3(\text{aq})} = (1.19 \pm 0.58) \times 10^{-5}^{*5}$			
$a_{\text{HCO}_3^-} = (1.20 \pm 0.52) \times 10^{-3}^{*5}$			
$a_{\text{CO}_3^{2-}} = (1.23 \pm 0.69) \times 10^{-5}^{*5}$			

*¹Equations are from Chou et al. (1989).

*²Chou et al. (1989).

*³ k_{-1} and k_{-2} calculated by the equation of $K_{i,SP} = k_i k_{-i}^{-1}$, Chou et al. (1989).

*⁴Solubility product $K_{i,SP}$ calculated from the data in Table A1.

*⁵Activity of each species calculated by geochemical calculation code PHREEQC (Parkhurst, 1995) with total carbon, total calcium and pH data for each experimental case listed in Table 4. From the variation of those calculated data, average and uncertainty (2σ) were conducted.