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Dissolution kinetics of iron carbonate, illite and labradorite –
CO₂-saline fluid-mineral experiments within the GaMin'11 inter-laboratory
comparison exercise

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Abstract

Experiments to investigate individual CO₂-brine-mineral interactions were designed to provide dissolution kinetics for rock-forming minerals. Separates of an iron carbonate, a clay mineral and a feldspar mineral were stored in flexible Titanium Grade-2 cells together with 2 M NaCl brine and pure CO₂ at 80 °C and 20 (30) MPa for one (iron carbonate), two (clay) and three (feldspar) weeks, respectively. The carbonate separate consists of 96.3±3.2 wt% iron carbonate and 3.7±0.8 wt% quartz with the iron carbonate phase being composed of 72.3±1.4 wt% siderite and 27.7±1.2 wt% ankerite. During the experiments, siderite abundance increased to 83.3±1.5 wt%, while that of ankerite decreased to 16.7±1.4 wt%. The average empirical formula of untreated and treated siderite is Fe_{0.8}Mg_{0.1}Mn_{0.1}CO₃, that of untreated ankerite changed slightly from (Ca_{1.0}Mg_{0.2}Mn_{0.1}Fe_{0.7})(CO₃)₂ to (Ca_{0.9}Mg_{0.3}Mn_{0.1}Fe_{0.7})(CO₃)₂ during CO₂ exposure. Fluid data obtained during these experiments show similar behavior for Ca²⁺ and Mg²⁺, as well as Fe²⁺ and Mn²⁺, respectively. The clay separate initially consists of 84.2±6.9 wt% illite, 11.9±0.4 wt% orthoclase and 3.9±0.2 wt% quartz with untreated illite actually being an illite-smectite mixed-layer mineral composed of 87.2±1.5 wt% illite and 12.8±1.5 wt% Ca-smectite. During the experiments using the clay separate it was found that the composition changed to 88.3±7.8 wt% illite, 9.2±0.5 wt% orthoclase, and 2.5±0.2 wt% quartz, with CO₂-treated illite now consisting of 89.0±1.7 wt% illite and 10.5±1.6 wt% Ca-smectite. Fluid data show, besides others, increase Ca²⁺ concentrations over time. Analyses of the feldspar separate reveal pure labradorite with a stoichiometric composition of Na_{0.5-0.6}Ca_{0.4-0.5}Al_{1.3-1.6}Si_{2.4-2.6}O₈. During labradorite exposure experiments cation brine concentrations (e.g. Ca²⁺, Ba²⁺ and Al³⁺) increased. Based on the acquired geochemical data sets, the experiments using individual mineral separates indicate (i) dissolution of ankerite and stable siderite, (ii) preferred dissolution of the Ca-smectite component out of the illite-smectite mixed-layer mineral, and (iii) dissolution of labradorite.

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1. Introduction

In 2011, Federal Institute for Geosciences and Natural Resources (BGR Hannover), Germany, and United States Geological Survey (USGS Manlo Park), USA, initiated GaMin'11 inter-laboratory comparison exercise for geochemical CO₂-saline fluid-mineral experiments at elevated temperature and pressure conditions [1]. The use of different experimental techniques at different laboratories implicates various advantages and disadvantages regarding sample handling, leakage and/or corrosion. Also measured concentrations of dissolved species and derived kinetic rates may vary due to different experimental techniques. Major objectives of GaMin'11 were (i) strengthening collaboration among experimental laboratories worldwide, (ii) identification of possible problems related to currently used equipment, and (iii) estimation of the variance in kinetic data obtained from gas-fluid-mineral interaction experiments using different experimental approaches for identical starting materials and conditions. In this paper results from corresponding experiments performed at GFZ German Research Centre for Geosciences (GFZ Potsdam) are presented. These provide complementary information to [1] (Ostertag-Henning et al., this issue) regarding the experimental apparatus used and the results obtained at GFZ Potsdam.

2. Materials & Methods

2.1. Sample Description

Natural, rock-forming mineral powders of an iron carbonate (i.e. siderite-ankerite mixture), a clay (i.e. illite-smectite mixed-layer mineral) and a feldspar (i.e. labradorite) separate were selected, purified and characterized by BGR Hannover. Samples were sent to individual laboratories together with $\geq 99.5\%$ pure Sigma-Aldrich NaCl salt powder and detailed experimental instructions (see Section 2.2 below). The iron carbonate separate was prepared by BRG Hannover according to procedures described in [2]. Through crushing and sieving the separate has a grain size fraction of 100 to 200 μm . Details for the clay and feldspar separates are summarized in [3] and [4], respectively. Grain sizes are $< 250 \mu\text{m}$ for illite, and between 100 and 200 μm for labradorite.

2.2. Experimental Approach

Experimental instructions comprise the following: fluid to mineral weight ratios of 20 to 1, synthetic brine salinity of 150 g/L, P-T conditions of 20 MPa and 80 °C, and run durations of (at least) seven, 14 and 21 days for the iron carbonate, clay and feldspar separate, respectively. Additionally, the synthetic brine had to be CO₂-saturated throughout the entire experiments. One repeat experiment for the illite and labradorite separates, and two repeat experiments for the iron carbonate separate have been performed, respectively.

A hydrothermal rocking autoclave system equipped with flexible Titanium Grade-2 cells allowing for isobaric sampling was used to conduct the GaMin'11 experiments at GFZ Potsdam. Confining pressure was generated and controlled with an air driven fluid pump (Confining Pressure Controller). During heat up, sampling and/or cooling the pressure was held constant using a backpressure regulator [6].

Fluid samples were continuously taken during the runs, while solid samples were recovered after quenching at the end of the experiments [5], [6]. Cations were analyzed by ICP-MS and ICP-AES, respectively, anions by ion chromatography. Moreover, XRD as well as SEM data including BSE imaging and EDX measurements were additionally collected for analysis of solid materials [5], [6].

For more details on the experimental approach please also see [5], [6].

2.3. Analytical Techniques

Fluid samples have been analyzed by ion chromatography (anions) and ICP-MS (cations), respectively. Both XRD and SEM-EDX were used to analyze solid materials. For more details on the analyses of fluids and solid materials the reader is referred to [5], [6].

3. Results and Discussion

3.1. Iron carbonate separate

The iron carbonate separate is composed of 96.3 ± 3.2 wt% iron carbonate and 3.7 ± 0.8 wt% quartz. Rietveld refined XRD data show that the iron carbonate phase initially consists of 72.3 ± 1.4 wt% siderite and 27.7 ± 1.2 wt% ankerite. While siderite abundance increased to 83.3 ± 1.5 wt%, ankerite abundance decreased to 16.7 ± 1.4 wt% during the runs. Constant quartz abundance within analytical error rules out passive enrichment of siderite and indicates concomitant precipitation of siderite and dissolution of ankerite [6]. In SEM-EDX analyses untreated as well as CO_2 -treated siderite both have an average empirical formula of $\text{Fe}_{0.8}\text{Mg}_{0.1}\text{Mn}_{0.1}\text{CO}_3$, that of untreated ankerite changed slightly from $(\text{Ca}_{1.0}\text{Mg}_{0.2}\text{Mn}_{0.1}\text{Fe}_{0.7})(\text{CO}_3)_2$ to $(\text{Ca}_{0.9}\text{Mg}_{0.3}\text{Mn}_{0.1}\text{Fe}_{0.7})(\text{CO}_3)_2$ during CO_2 exposure. Fluid data show similar chemical behavior of Ca^{2+} and Mg^{2+} , and Fe^{2+} and Mn^{2+} , respectively [6]. After rapid increases to maximum levels, Fe^{2+} (and Mn^{2+}) concentration(s) continuously decrease afterwards, whereas Ca^{2+} (and Mg^{2+}) concentration(s) decline slightly and then start increasing again to reach highest level(s) at the end of the experiments. Based on Ca^{2+} and Fe^{2+} concentrations as exemplarily shown in Figure 1, three different time windows with different rates are apparent. While the rates of the initial time window ($1.5\text{E-}06 \text{ mol}^*\text{m}^{-2}*\text{s}^{-1}$ [Ca^{2+}] and $2.4\text{E-}07 \text{ mol}^*\text{m}^{-2}*\text{s}^{-1}$ [Fe^{2+}]) and the second time window ($-1.1\text{E-}07 \text{ mol}^*\text{m}^{-2}*\text{s}^{-1}$ [Ca^{2+}] and $-1.6\text{E-}08 \text{ mol}^*\text{m}^{-2}*\text{s}^{-1}$ [Fe^{2+}]) are relatively similar for both species, the individual rates of the third time window ($3.4\text{E-}08 \text{ mol}^*\text{m}^{-2}*\text{s}^{-1}$ [Ca^{2+}] and $-5.2\text{E-}09 \text{ mol}^*\text{m}^{-2}*\text{s}^{-1}$ [Fe^{2+}]) strongly differ. As opposed to increasing Ca^{2+} brine ion concentration that indicate continuous dissolution of ankerite, decreasing Fe^{2+} ion concentration imply (continuous) siderite precipitation. These observations are in line with SEM investigations (Fig. 2A). Grain surfaces of CO_2 -treated ankerite show strong corrosion (Fig 2B), whereas those of CO_2 -treated siderite are largely unaffected (Fig. 2C).

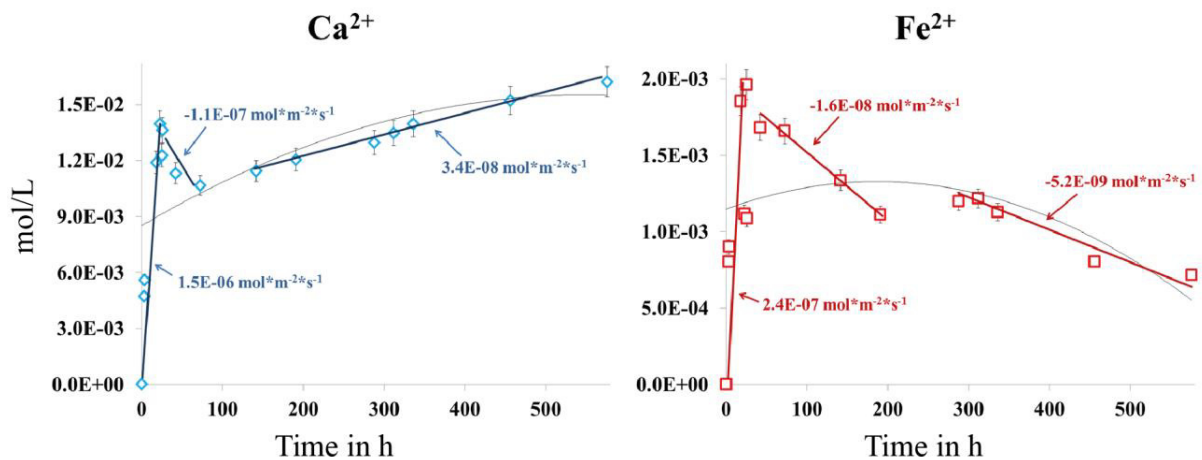


Fig. 1. Fluid data as determined by ICP-MS for experiments using the iron carbonate separate. Despite the fact that results shown belong to three individual experiments, the data is considered as one complete data set [6]. While increasing Ca^{2+} concentration indicates continuous dissolution of ankerite, decreasing Fe^{2+} concentration points towards precipitating siderite.

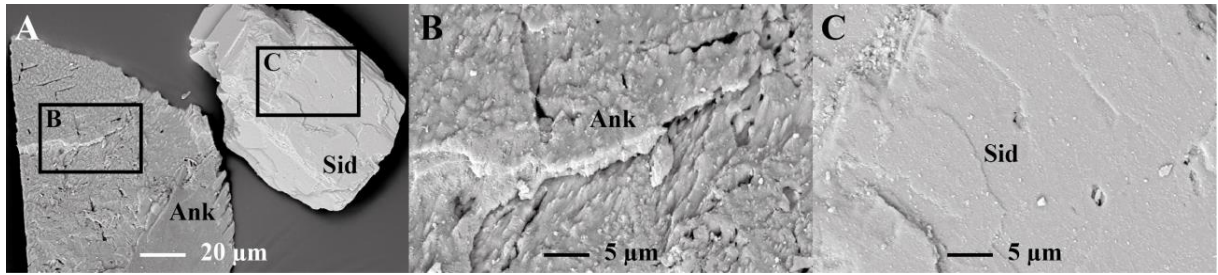


Fig. 2. SEM micrographs taken from experimentally treated iron carbonate separate. While siderite surfaces appear unaffected, those of ankerite are strongly altered.

3.2. Clay separate

The clay separate initially consists of 84.2 ± 6.9 wt% illite, 11.9 ± 0.4 wt% orthoclase and 3.9 ± 0.2 wt% quartz. Rietveld refined XRD data show that the untreated illite is actually an illite-smectite mixed-layer mineral composed of 87.2 ± 1.5 wt% illite and 12.8 ± 1.5 wt% Ca-smectite. Based on SEM-EDX measurements the empirical formula of untreated illite is $K_{0.5-0.7}(Al_{1.8-1.9}Mg_{0.1-0.2})[Si_{3.4-3.6}Al_{0.4-0.6}O_{10}(OH)_2]$. After two weeks of CO_2 exposure the illite separate has a composition of 88.3 ± 7.8 wt% illite, 9.2 ± 0.5 wt% orthoclase, and 2.5 ± 0.2 wt% quartz. CO_2 -treated illite consists of 89.0 ± 1.7 wt% illite, 10.5 ± 1.6 wt% Ca-smectite. No secondary mineral precipitates were detected. Also no significant changes in surface morphologies for any mineral present in the illite separate were detected after CO_2 exposure.

Results of the fluid data from the experiments using the clay separate show similar behavior for K^+ , Ca^{2+} , Mg^{2+} and Al^{3+} concentrations (Fig. 3). It is noteworthy that K^+ , Ca^{2+} , Mg^{2+} concentrations are lower in the repeat experiment, and Al^{3+} concentrations are higher in the first experiment performed using the illite separate. While the rapid increase in the Al^{3+} concentration of the repeat experiment indicates dissolution of fines. K^+ , Ca^{2+} as well as Mg^{2+} concentrations are relatively constant within analytical error from the second sampling to the end of the experiments. Note that elevated Ca^{2+} brine concentrations together with decreased Ca-smectite abundance indicate preferred dissolution of the Ca-smectite component out of the illite-smectite mixed-layer mineral.

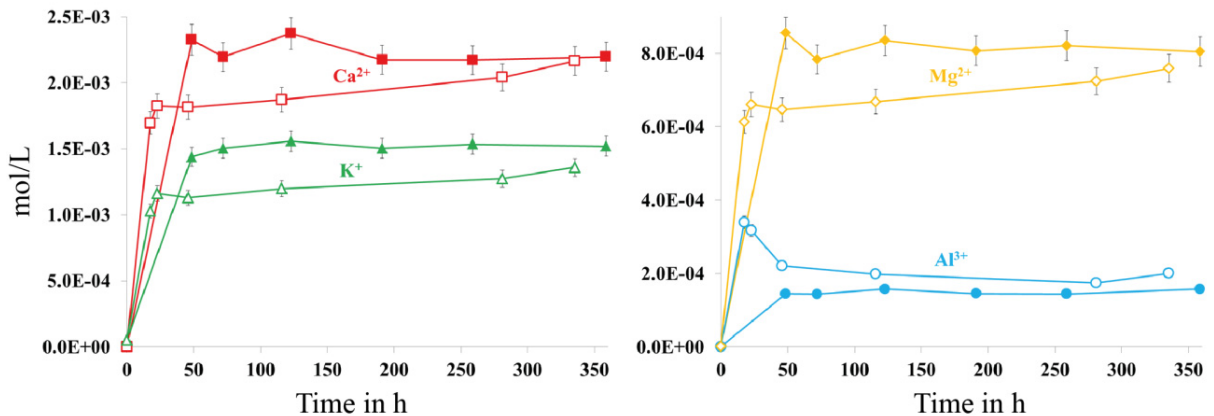


Fig. 3. Fluid data as determined by ICP-MS for experiments using the illite separate. Open symbols delineate the initial, filled symbols delineate the repeat experiment.

3.3. Feldspar separate

The feldspar separate consists of pure labradorite that has an initial empirical formula of $\text{Na}_{0.5-0.6}\text{Ca}_{0.4-0.5}\text{Al}_{1.3-1.6}\text{Si}_{2.4-2.6}\text{O}_8$ as determined from SEM-EDX measurements. In order to check for data reproducibility, two identical runs have been completed with the labradorite separate. Compared with the untreated starting material, CO_2 -treated labradorite indicates slight alteration textures on grain surfaces, identical mineral composition and no secondary precipitate. During the labradorite experiments, increased Ba^{2+} , Ca^{2+} and Al^{3+} brine concentrations (Fig. 4) in line with corroded grain surfaces [5] clearly suggest labradorite dissolution. For Ba^{2+} , Ca^{2+} and Al^{3+} concentrations minor differences between the initial and repeat experiment are apparent over time. The reason for the slight difference in brine evolution is unclear, but might be related to analytical artifacts.

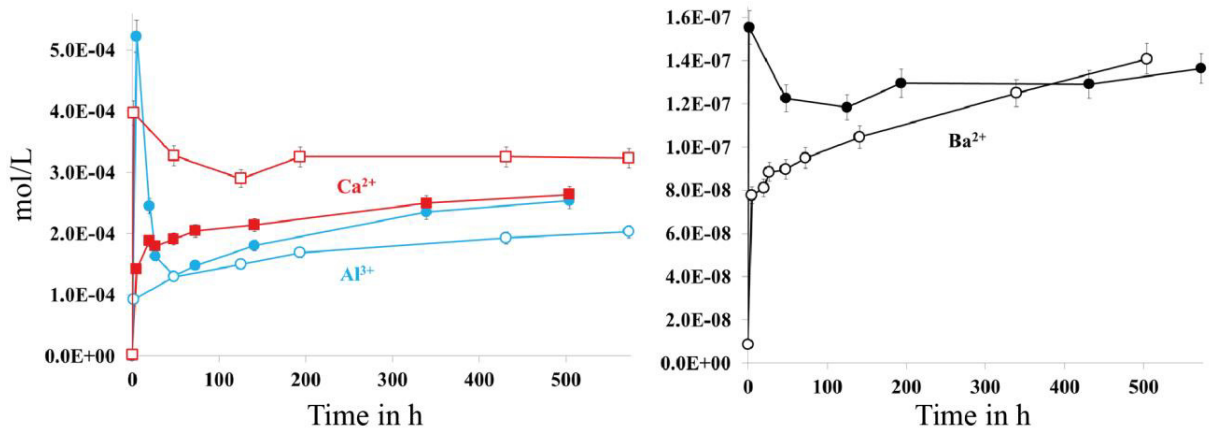


Fig. 4. Fluid data as determined by ICP-MS for experiments using the labradorite separate. Open symbols delineate the initial, filled symbols delineate the repeat experiment.

4. Conclusions

- Repeat experiments for individual mineral separates show similar, but not identical results regarding fluid concentrations.
- Geochemical-mineralogical analysis of the CO_2 -exposure experiments show dissolution of ankerite, Ca-smectite and labradorite, respectively, as well as stable siderite.
- Fluid data of the iron carbonate separate reveal different kinetic rates depending on the considered time window.
- While experiments using clay and feldspar separates reached kinetic equilibrium (i.e. dissolution plateaus), fluid concentrations of experiments using the iron carbonate separate still change even after >550 h.
- No secondary minerals have been detected in any experiment.

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