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Water Rock Interaction [WRI 14]**Mineral solubilities in CO₂-saturated NaCl brine systems**Sebastian Fischer^{a,b,*} and Axel Liebscher^a^aHelmholtz Centre Potsdam, GFZ German Research Centre for Geosciences, Telegrafenberg, D-14473 Potsdam, Germany^bBerlin Institute of Technology, Chair of Mineralogy-Petrology, Ackerstrasse 76, D-13355 Berlin, Germany**Abstract**

Experiments on CO₂-brine-mineral interactions were designed to provide kinetic data for individual rock-forming minerals. Samples of an illite-smectite mixed layer mineral and a labradorite separate were stored in flexible Ti-cells together with 2 M NaCl brine and pure CO₂ at 80 °C and 20 MPa for two and three weeks, respectively. The empirical formulae $K_{0.5-0.7}(Mg_{0.1-0.2}Al_{1.8-1.9})(Al_{0.4-0.6}Si_{3.4-3.6})O_{10}(OH)_2$ and $Na_{0.5-0.6}Ca_{0.4-0.5}Al_{1.3-1.6}Si_{2.4-2.6}O_8$ were calculated for illite and labradorite. X-ray diffraction data with Rietveld refinements reveal a pure labradorite separate. The illite separate is composed of 73.5±1.3 wt% illite, 10.8±1.3 wt% Ca-smectite, 11.9±0.4 wt% orthoclase, and 3.9±0.2 wt% quartz. Based on the acquired geochemical data, the experiments on monomineralic separates indicate (i) preferred dissolution of the Ca-smectite component out of the illite-smectite mixed layer mineral, and (ii) dissolution of labradorite.

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Keywords: CO₂-brine-mineral interaction; monomineralic illite and labradorite separates; batch experiments**1. Introduction**

Geological storage of CO₂ in the subsurface is a key option for reducing anthropogenic gas emissions to the atmosphere and thus to mitigate global warming (e.g. [1]). The presence of CO₂ in a (siliciclastic) storage system will cause complex geochemical reactions between injected CO₂, formation brine and reservoir rock (e.g. [2]). Dissolution of primary minerals (i.e. aluminosilicates) and/or precipitation of secondary minerals (i.e. carbonates) are likely to occur (e.g. [3]). To better understand and characterize single fluid-mineral reactions, and to be able to calculate dissolution rates for individual minerals, relatively simple experiments were designed in the scope of GaMin'11 project. The GaMin'11 project is a round robin inter-laboratory comparison of geochemical experiments in gas-fluid-mineral systems and was initiated by BGR Hannover and USGS, Menlo Park, CA. Project members followed identical starting

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conditions using identical mineral separates and brine compositions. The aim was (i) to provide an estimate of potential variance in kinetic data derived from the respective experiments and (ii) to validate kinetic data for the observed mineral dissolution reactions at P-T conditions relevant for CO₂ storage scenarios. Siderite, illite and labradorite separates were chosen. Siderite is an important mineral in carbonate-bearing, iron-rich reservoirs (e.g. [4]); illite and labradorite are typical in siliciclastic storage environments. In this paper we present results of experiments on illite and labradorite performed at GFZ Potsdam in the context of GaMin'11; siderite experiments are described in Fischer et al. (submitted).

2. Materials & Methods

2.1. Sample Description

Mineral separates of an illite-smectite mixed-layer mineral (Ill-0) and a labradorite (Lab-0) were provided by BGR Hannover; for details see [5] and [6]. Grain sizes are <250 μm for illite, and 100-200 μm for labradorite. Based on EDS measurements, the empirical formula for illite was calculated to be $K_{0.5-0.7}(Mg_{0.1-0.2}Al_{1.8-1.9})(Al_{0.4-0.6}Si_{3.4-3.6})O_{10}(OH)_2$, that of labradorite is $Na_{0.5-0.6}Ca_{0.4-0.5}Al_{1.3-1.6}Si_{2.4-2.6}O_8$. X-ray diffraction calculations reveal disordered illite, Ca-smectite, orthoclase and quartz. The presence of Ca-smectite is consistent with XRF data [6]. Rietveld refinements yield the following composition of the illite separate: 73.5±1.3 wt% illite, 10.8±1.3 wt% Ca-smectite, 11.9±0.4 wt% orthoclase, and 3.9±0.2 wt% quartz. An andesine with An₅₀ was the plagioclase revealing the best fit for the labradorite separate.

2.2. Experimental Approach

The separates of illite and labradorite were exposed to pure CO₂ and 2 M NaCl brine at 80 °C and 20 MPa. Experiments were performed on a rocking autoclave system equipped with flexible Titanium Grade-2 cells allowing for isobaric sampling. About 5.5 g of powdered separate were filled into the Ti-cell that has a volume of about 150 cm³. The Ti-cell was filled with 2 M NaCl brine, which was prepared from ≥99.5% pure Sigma-Aldrich NaCl salt powder, and pure CO₂. Afterwards, the system was pressurized to 20 MPa and heated to 80 °C thereafter. The brine to mineral weight-ratio was 20 to one. Experimental run durations were two (illite) and three weeks (labradorite), respectively. The experiments were repeated under identical conditions in order to collect two data sets for each separate (i.e. Ill-1, Ill-2; Lab-1, Lab-2), and also to test for reproducibility. To determine time dependent dissolution behavior, successive fluid samples were taken after several different time steps. A total of 2.5 to 3.0 ml fluid was taken during each sampling run; 1.0 ml from the uptake that were poured away, 1.0 ml for cation, and between 0.5 to 1.0 ml for anion analysis. Sampling vials for cation analysis were acidified with 10 μl of 65% pure HNO₃. Solids were washed out of the Ti-cell and filtered after quenching at the end of the run.

3. Results

3.1. Illite Experiments

The reaction of illite with 2 M NaCl brine and CO₂ is characterized by generally increased cation concentrations in the sampled brine. Ca²⁺ and Mg²⁺ show very similar behavior (Fig. 1A). After a sharp and rapid increase to maximum values of $2.6 \cdot 10^{-3}$ and $8.8 \cdot 10^{-4}$ mol/L after 49 h, respectively, both cations slightly decrease and show constant concentration levels (within error) from 72 h to final concentrations of $2.5 \cdot 10^{-3}$ and $8.4 \cdot 10^{-4}$ mol/L after 349 h, respectively. Note that K⁺ could not be determined in ICP-AES measurements (axial plasma) due to Na⁺ peak overlapping. Larger particles are generally composed of very small plates and irregular structures. Smaller crystals and coatings of halite rarely occur in Ill-1.

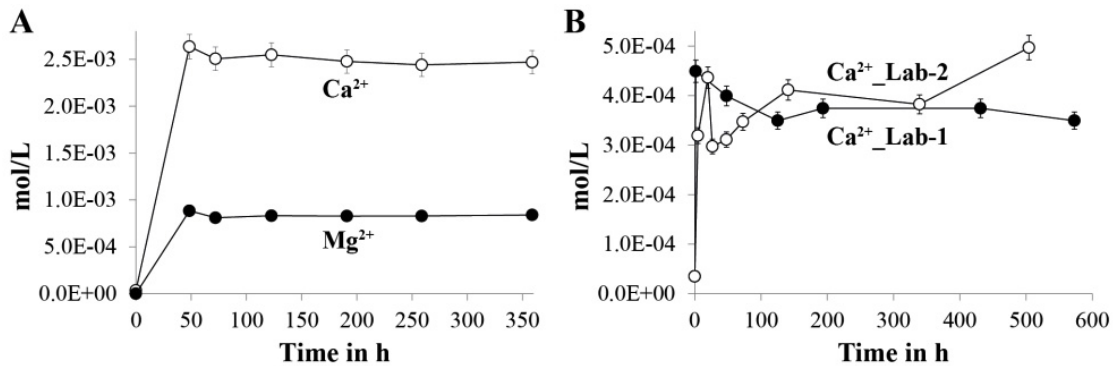


Fig. 1. (A) ICP-AES fluid data of Ill-1; (B) Comparison of fluid data from Lab-1 and Lab-2. 5% error bars are plotted.

About 3.5 wt% of halite is present after the experiment. Normalized mineral abundances on a halite-free basis are 79.0 ± 1.5 wt% illite, 9.3 ± 1.4 wt% Ca-smectite, 9.2 ± 0.5 wt% orthoclase, and 2.5 ± 0.2 wt% quartz. Apart from halite (which precipitated during sample drying after the experiments), no other newly formed mineral phase was detected. Some illite and Ca-smectite peaks show changes in peak shape and intensity. Scanning electron microscopy (SEM) investigations of grain surfaces prior to (Ill-0) and after the experiments (Ill-1 and Ill-2) did not reveal significant changes for phases of the illite separate (Fig. 2A and 2B).

Rietveld refined XRD data indicate dissolution of Ca-smectite, orthoclase and quartz, and a presumably relative enrichment of illite. The coherent increase and behavior of Ca²⁺ and Mg²⁺ in the experimental brine point to preferred dissolution of Ca-smectite in the illite-smectite mixed layer silicate.

3.2. Labradorite Experiments

The XRD analysis revealed the presence of labradorite as the only mineral phase present. Neither in untreated (Lab-0), nor in CO₂-treated labradorite samples other minerals were detected. The comparison of both diffractograms (Lab-0 and Lab-1) shows only very minor differences in peak size; peak shape and position are congruent. The reaction of labradorite with 2 M NaCl brine and CO₂ yields generally increased cation concentrations in the sampled brine. The evolution of fluid data with time shows slight differences between Lab-1 and Lab-2. In both experiments it is apparent that in Ca²⁺ displays very rapid concentration increases within the first hours (Fig. 1B). In Lab-1, Ca²⁺ reached maximum concentrations of $4.5 \cdot 10^{-4}$ mol/L after two h. This maximum is followed by decreasing concentrations to $3.5 \cdot 10^{-4}$ mol/L Ca²⁺ after 125 h. From then on Ca²⁺ levels are constant (within error) till the end of the experiments after 573 h. In Lab-2, Ca²⁺ concentrations show a less steep increase and reach a first maximum of $4.4 \cdot 10^{-4}$ mol/L after 20 h, which is followed by a steep decrease to $3.0 \cdot 10^{-4}$ mol/L after 27 h. From that point on, Ca²⁺ concentrations tendentially increase again to $5.0 \cdot 10^{-4}$ mol/L at the end of the experiment after 504 h. Optical inspection of grain surfaces on SEM micrographs reveals slight changes during the experiments. While clean surfaces and steps are typical for untreated labradorite (Fig. 2C) CO₂-treated labradorite grains display corrosion textures on edges, and dissolution holes on plane surfaces (Fig. 2D).

While XRD data neither show changes in labradorite composition nor newly formed phases, the significantly increased Ca²⁺ concentrations and the presence of corrosion textures on CO₂-treated labradorite grains clearly point toward labradorite dissolution in the course of the experiments. Experimental fluid data reveals slightly different Ca²⁺ behavior between Lab-1 and Lab-2. While Ca²⁺

evolves to steady concentration levels after approximately 100 h in Lab-1, the tendential increase of Ca^{2+} in Lab-2 from 27 h on is either signifying continuous dissolution, or the trend could be blurred by the last sample after 504 h that yielded the highest Ca^{2+} concentrations of all measured labradorite samples and could thus be an outlier.

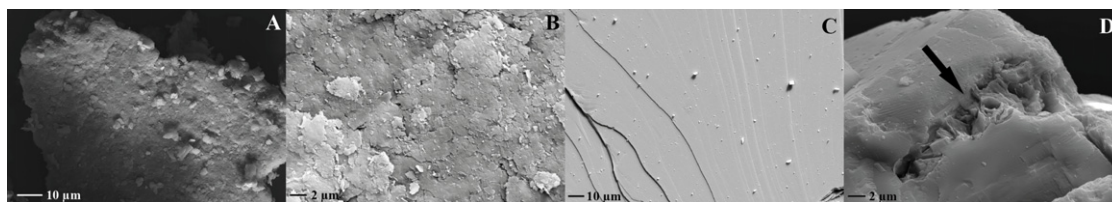


Fig. 2. (A) Typical appearance of illite in untreated sample; (B) Detailed surface structure of a CO_2 -treated illite; (C) Smooth surface of a typical untreated labradorite; (D) Corrosion texture (arrow) on a CO_2 -treated labradorite.

4. Conclusions

The experiments on monomineralic separates are generally characterized by increasing cation concentrations in the sampled brine, which are caused by CO_2 -brine-mineral interactions. Rapid and steep initial increases in ion concentrations are related to fast dissolution kinetics of fines (i.e. micro-scale particles originating from crushing of source material). Results of experiments on the illite separate point toward dissolution of Ca-smectite out of the illite-smectite mixed layer mineral. Data from labradorite experiments show slight corrosion of labradorite. It is noteworthy that in none of the so far performed experiments on mineral separates a newly formed (carbonate) mineral was detected.

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