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Experimental study on rock-CO_2 interaction processes at HP/HT conditions

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ABSTRACT

The interaction of CO_2-rich fluids with reservoir rocks from two different geothermal settings was studied in a series of batch reaction experiments to improve predictions on mineral alteration reactions under HP/HT reservoir conditions.

Experiments were carried out with a basaltic sample from the Nesjavellir geothermal field in Iceland and a metamorphic schist from the Kızıldere geothermal field in Turkey. The samples were analyzed before and after the batch reactor experiments using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Observed mineralogical changes were correlated with changes in fluid chemistry.

The Icelandic basaltic rock produced an extensive secondary mineral assemblage consisting of clay, chlorite, anhydrite and zeolites. In contrast, the experiment with the metamorphic schist from Turkey produced only small quantities of smectite.

It was concluded that the mineralogy of the Turkish sample is not suited to provide the necessary divalent cations for CO_2 mineralization. Data from the basalt from Iceland indicate a strong control of the initial fluid composition on the resulting secondary mineral assemblage, which, together with the thermodynamically unfavorable high temperature, constrains the CO_2 sequestration.

1. INTRODUCTION

With growing awareness for the rising greenhouse gas concentrations in the atmosphere and their impact on climate change, a great deal of attention was directed to research focused on emission mitigation and carbon capture methods in the last decades (Metz et al. 2005). One of these methods is CO_2 carbonatization, a naturally occurring process and already a major factor in the long-term global carbon cycle (Oelkers et al. 2008). CO_2 is thereby sequestered into carbonate minerals by combining with divalent metal cations in aqueous solutions (Gislason et al. 2010; Metz et al. 2005; Oelkers et al. 2008; Oelkers und Schott 2005).

The research presented here is part of the “Geothermal Emission Control” (GECO) project, which is aiming at lowering the emissions at geothermal power plants by capturing exhaust gases for either reuse or storage. CO_2 sequestration is investigated as one of the storage methods, which is tested at sites in Iceland, Italy, Germany and Turkey. The concept involves the dissolution of waste gases into the water stream that is re-injected into the subsurface. Ideally, the dissolved gases are fixed by mineralization and naturally stored in the long term. Before field testing, laboratory experiments were conducted to investigate CO_2-water-rock chemical interactions. Gaining information on geochemical reactions that can be expected in the subsurface is a key aspect in determining the effectiveness of CO_2 mineralization for the respective lithologies. For this purpose, a series of batch reactor experiments was designed, that simulate the respective reservoir pressure and temperature conditions and enable monitoring of the fluid’s chemical evolution. The results of these experiments are presented here for a basaltic rock sample from the Nesjavellir geothermal reservoir in Iceland and a metamorphic rock sample from the Kızıldere geothermal field in Turkey.

2. MATERIALS AND METHODS

Two rock samples, one drill core from Iceland and one specimen from Turkey, have been used to perform CO_2-water-rock dissolution/precipitation reaction experiments in a heated and pressurized batch reactor. The Icelandic sample originates from a basaltic hyaloclastite drill core from well NJ-18 of the

Nesjavellir geothermal field. It consists of partially palagonized glass shards with interstitial zeolites and minor calcite. Phenocrysts in shards of sideromelane are dominated by plagioclase but pyroxene and olivine are also present. The rock specimen from Turkey is a metamorphic schist with a mineralogy dominated by quartz, accompanied by dolomite/ankerite, mica and Fe-oxide/sulfide. The sample was collected near the village of Yenicekent and represents one of the lithologies of the reservoir section of the injection well at the Kızıldere geothermal field.

Used fluids originate from the test sites in Iceland and Turkey. These comprise effluent water from well NJ-18 of the Nesjavellir geothermal field in Iceland, effluent water from the Kızıldere power plant in Turkey and condensate water that is stored in a pond for reinjection at the Kızıldere power plant.

2.1 Experimental setup

Batch reactor experiments were conducted in a stirred pressure vessel of 1.1 L volume from Parr Instrument (4626 series). All the wetted reactor parts and connections, including the syringe pumps, are made of corrosion resistant Hastelloy C-276. The reactor system is designed for a maximum pressure of 35 MPa and a maximum temperature of 350 °C. Pressure and temperature are monitored via an installed manometer and a thermocouple. Heating is induced through a heating jacket. The reactor has three ports used for fluid injection, fluid sampling and gas supply. The gas supply is connected to a 20 MPa nitrogen gas bottle with pressure regulator that is used to adjust the pressure inside the vessel and purge the sampling line. For fluid sampling, a dipping tube runs from the bottom of the reactor through a pressure valve to an outlet. Slightly opening the valve allows the extraction of small fluid volumes. A similar line is installed for the injection of fluids to the bottom of the reactor. This line is connected to two “Teledyne Isco 500D syringe pumps” that are used for injection purposes.

2.2 Experimental procedure

For each experiment, the reactor was filled with 750 ml of effluent reservoir fluid and a total rock mass of 75 g from the corresponding location. The rocks were ground to a powder with a grain size <125 µm and placed inside the reactor together with a small rock chip that provides a surface where mineral precipitations can be detected. To prevent the fine sample powder from clogging at the vessel bottom, it was confined in a fine meshed stainless-steel wire basket hanging in the vessel above ground. This allows the use of a magnetic stir bar to keep the fluid agitated. After filling and sealing the vessel, the system is purged with nitrogen to remove air in the headspace. The temperature is then increased to the desired target values of 260 °C and 105 °C for the Icelandic and Turkish experiment respectively. The 105 °C for the Turkish experiment does not correspond to the prevailing temperature deep inside the reservoir, which would be around 200 °C. The 105 °C represent the temperature conditions in close proximity to the injection well at reservoir depth. The pressure is adjusted afterwards to 8 MPa (Iceland) and 17 MPa (Turkey) using the nitrogen supply. Fluids were regularly sampled from the reactor, starting from the day after the initial filling. Each experiment lasted for at least 30 days, during which ten fluid samples of approximately 20 ml were taken.

After an equilibration time of 120 (Iceland) and 145 (Turkey) hours, a fluid enriched with CO_2 was injected into the reactor under in-situ conditions. For the experiment with the Icelandic basalt, distilled water in equilibrium with CO_2 at 0.75 MPa and 25 °C was used. For the Turkish sample, the power plant condensate water was equilibrated with CO_2 at 1.4 MPa and 25 °C. The CO_2 purity was 99 %. Liquid and gas were equilibrated for at least 24 hours. The right amount of fluid was injected to meet the target ratio between reactor fluid and injection fluid of 10:1 for the Icelandic experiment and 11:1 for the Turkish experiment. These ratios correspond to the expected mixing ratios at the injection wells of the respective geothermal power plant. The resulting concentrations of dissolved CO_2 inside the reactor were calculated to 22.5 mmol/l for the Icelandic experiment and 44.1 mmol/l for the Turkish experiment.

2.3 Analytical

Fluid samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) and ion chromatography (IC) to measure the cation and anion concentrations in solution. The ICP-OES measurements were calibrated with standard solutions of 1 ppm, 2 ppm, 4 ppm, 5 ppm, 10 ppm and 20 ppm for the elements Na^+, K^+, Mg^{2+}, Ca^{2+} and Si^{4+}. For the analysis of trace elements, calibration concentrations of 0.01 ppm, 0.05 ppm, 0.1 ppm, 0.5 ppm, 1 ppm and 2 ppm were used. The IC was calibrated for the analysis of Cl^-, NO_3^- and SO_4^{2-} in a range of 1 to 50 ppm. For the analysis of F^-, Br^- and NO^{3-} a calibration range of 0.1 to 10 ppm was used. Whenever necessary, samples were diluted to stay within the calibration ranges. Standard solutions were measured regularly along with the samples to ensure analysis accuracy and to determine the analytical error.

Rock samples were analyzed before and after the batch reactor experiments by X-ray diffraction (XRD) and scanning electron microscopy (SEM) in combination with energy dispersive X-ray analysis (EDX). XRD analyses were performed at the X-ray diffraction and fluorescence service of the petrology and mineralogy platform of the GET laboratory at the Centre National de la Recherche Scientifique (CNRS) in Toulouse, France, using a Bruker D2 Phaser diffractometer. SEM and EDX analyses were performed at the department of geology, mineralogy, and geophysics of the Ruhr University Bochum on a ZEISS-Gemini2-Merlin high resolution thermally aided field emission SEM. Before SEM analysis, the samples were provided with a gold coating to create a conductive sample surface. Images were obtained at an acceleration voltage of 5 kV while the working distance and electron current were adjusted according to the sample´s characteristics. In general, a working distance of about 10 mm and an electron current of 100-200 pA was applied. For EDX analysis, the Oxford Instruments AZtecEnergy X-ray microanalysis software was used.

3. RESULTS AND DISCUSSION

The mineralogical changes detected by XRD and SEM after the experiments were correlated with the changes in fluid chemistry during the experiment.

3.1 Icelandic Basalt

After the reactor experiment with the Icelandic basalt, the formerly clean sample surface was extensively covered by a secondary mineral assemblage consisting of zeolites, Fe-Mg-chlorite, clay and anhydrite (Figure 1). Zeolites were mainly identified as Na-rich wairakite. Furthermore, aggregates of zeolites were found at the reactor wall and tubes that resemble in composition clinoptilolite-Na and analcime.

XRD analysis of the altered sample powder confirmed the formation of a wairakite type zeolite containing Na. The results also indicate that chlorite has formed as chamosite. Pyroxenes were analysed as diopside, ferrosilite and aerinite, but have not been observed during SEM analysis. Anhydrite was detected by XRD, but the signal was very low. This is surprising as the SEM images show large anhydrite crystals on the altered sample surface. A comparison of the XRD results from before and after the experiment reveal that the secondary minerals have formed on the expense of Na-chabazite, plagioclase and clay minerals. Calcite has been detected in the assemblage before and after the experiment and there is no indication for a significant change in calcite abundance from XRD or SEM analysis.

3.1.1 Fluid analysis

The initial fluid composition was rich in sulfate and silicon but contained only little aluminum, calcium, magnesium, or iron. These cations were initially supplied by fast dissolution reactions with the basaltic rock powder at the beginning of the experiment. This initiated silicate and anhydrite precipitation, accompanied by a decrease of silicon, aluminum, sodium, potassium and sulfate in solution (Figure 3). Calcium in contrast, which is needed for the formation of anhydrite and wairakite, remained on a constant low level. This indicates that the formation of anhydrite and wairakite is limited by the calcium supply from basalt dissolution. Although precipitation may be the dominating reaction process before CO_2 injection, the demand for calcium makes simultaneous dissolution inevitable. Hence, other cations like magnesium and iron are released as well.

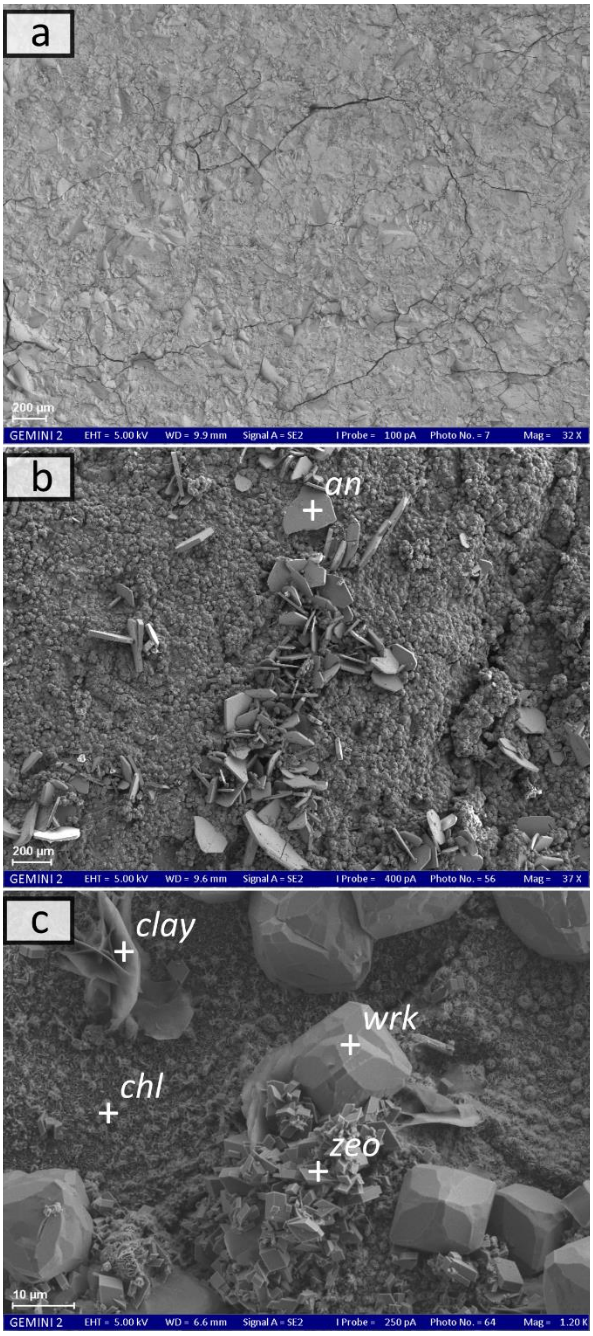

Figure 1: SEM images of the Icelandic basalt before (a) and after (b-c) the experiment. Abbreviations: an = anhydrite; chl = chlorite; wrk = wairakite; zeo = zeolite.

The concentrations of magnesium and iron are changing insignificantly. It was therefore concluded that Fe-Mg-chlorite and clay must precipitate as soon as magnesium and iron become available. The decrease in sodium is attributed to the formation of sodium-rich wairakite on the sample surface as well as to analcime and Na-clinoptilolite forming on the reactor wall at the interface between liquid and gas phase. Wairakite has shown to develop substantial solid solutions towards analcime in quartz-free environments at high temperatures (Liou et al. 1991), which is in line with the high sodium content of the wairakite formed during these experiments here. It is, however, unclear whether the wairakite-analcime solid solutions and anhydrite have formed concurrently or in subsequent reactions.

The injection of the CO_2-rich fluid has mainly three effects on the system. First, as distilled water was used for injection, the element concentrations become slightly diluted. Secondly, the fluid volume inside the reactor increases to approximately the volume of the initial filling before extraction of the first samples. This means that precipitates at the reactor wall fall below the water line again. Thirdly, the dissolved CO_2 lowers the pH. However, it remains unclear to which value the pH is lowered exactly as it could be measured only after sample extraction and concomitant decompression and degassing. The significant increase in silicon indicates that dissolution occurred in response to CO_2 injection (Figure 3). The CO_2 concentration in solution could not be monitored with the experimental setup and there were no carbonate minerals detected in the secondary mineral assemblage. Accordingly, there is no evidence for the mineralization of carbon from this experiment. This result contradicts many studies that either successfully sequestered CO_2 into carbonates or predicted sequestration with model simulations (Gysi und Stefánsson 2012a, 2012b; Gysi und Stefánsson 2008; Gysi und Stefánsson 2011; Aradóttir et al. 2012; Gysi 2017). However, most of these experiments and simulations were conducted at temperatures lower than 100 °C. Gysi und Stefánsson (2012b), who conducted experiments at temperatures up to 250 °C, concluded that the sequestration of CO_2 is favored at temperatures below 100 °C where Ca, Mg and Fe are mainly incorporated into carbonates, whereas at higher temperatures clays and zeolites dominate the uptake of divalent cations. This result is in accordance with our findings presented here, with the exception that Gysi and Stefánsson (2012b) reported at least some calcite formation from their high temperature experiment. The lack of calcite formation in this study might be explained by the composition of the initial fluid NJ-18, which was considerably enriched in most elements compared to the natural spring water from Vellankatla that was used by Gysi und Stefánsson (2012b). Especially the high silicon and sulfate concentrations seem to have promoted the preferential incorporation of calcium into zeolite and anhydrite over calcite.

3.2 Turkish metamorphic schist

After the experiment with the metamorphic schist from Turkey, small aggregates of iron-rich smectites have formed in the vicinity of pyrite and iron oxide minerals (Figure 2). Other precipitates were not detected on the sample surface, but silicon oxide was found on the reactor wall and tubes. The formation of smectite during the experiment is in line with field observations from Kızıldere where smectites were found to be associated with hydrothermal alteration of carbonate-rich rocks (Bozkaya et al. 2018).

XRD analysis of the altered sample powder did not reveal major mineralogical changes during the experiment, except for gypsum. Gypsum was detected in the fresh but not in the altered sample. This can either show that gypsum was dissolved during the experiment, or, that gypsum is not distributed homogeneously in the sample and was simply not present in the analyzed powder fraction. This could also explain why gypsum was not observed during thin section microscopy or SEM.

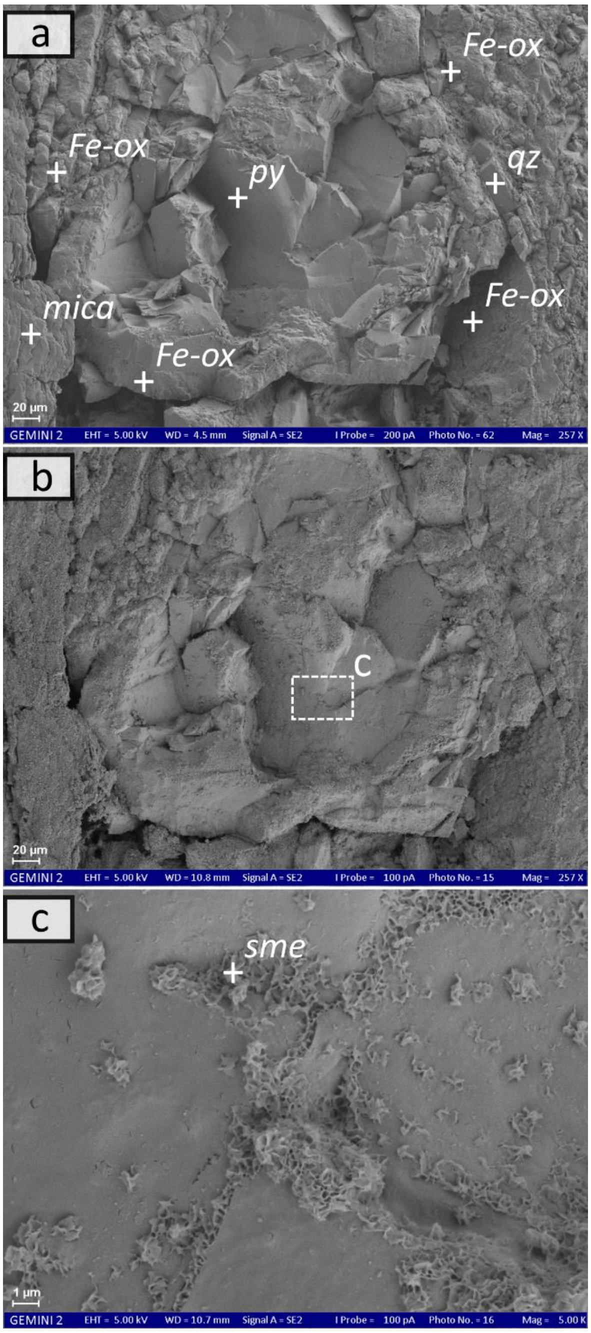

Figure 2: SEM images of the Turkish metamorphic schist before (a) and after (b-c) the experiment. Image c is a magnified section from image b. Abbreviations: Fe-ox = iron oxide; py = pyrite; qz = quartz; sme = smectite.

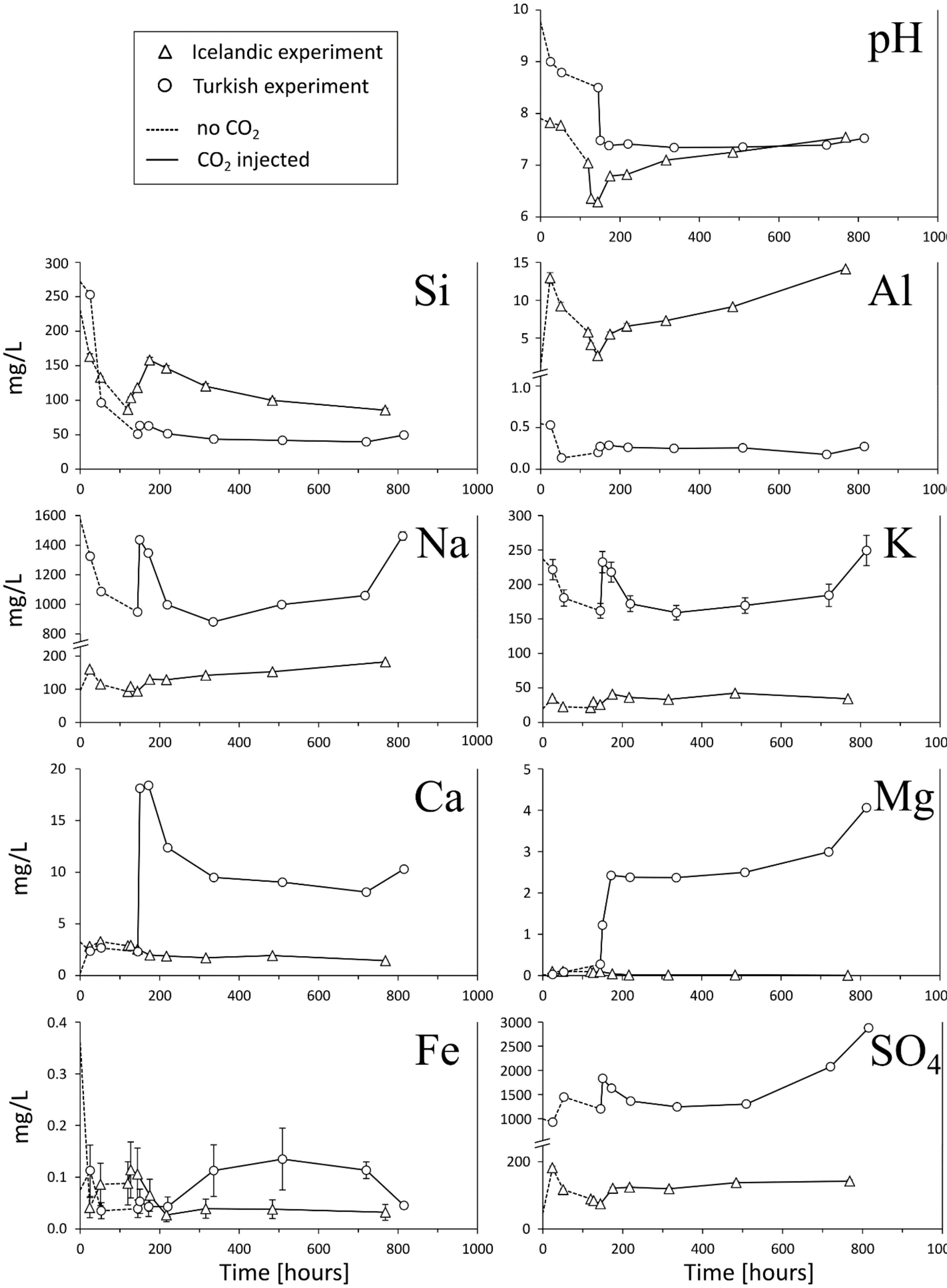

Figure 3: Evolution of the fluid chemistry during the Icelandic and Turkish experiments. The time of injection of the CO_2-rich fluid is indicated in the diagrams by the switch from dotted to solid lines. Error bars are included for all measurements but generally do not exceed the size of symbols.

3.2.1 Fluid analysis

The decreasing pH at the beginning of the experiment is an indication for precipitation processes. Precipitates have been found predominantly in form of silicon oxide at the reactor wall. The pH was further lowered by injection of the CO_2 rich fluid, which caused an increase of calcium, magnesium and sulfate concentrations. The rising calcium and magnesium concentrations are attributed to dolomite dissolution. The increase in sulfate is caused by dissolution reactions with pyrite and gypsum. However, calcium and sulfate seem to partially recrystallize as their concentrations decrease again shortly after injection.

Indications for CO_2 sequestration were not observed from the alteration mineralogy. The metamorphic rock may not be suitable for carbonate mineralization as its mineralogy provides an insufficient supply of divalent cations. Calcium, magnesium and iron are present, but already bound to carbonate phases. Furthermore, Figure 3 shows that pyrite dissolution is not releasing iron into solution. It is assumed that pyrite is altered to form an Fe-oxide residue and only sulfate is dissolved.

4. CONCLUSIONS

For none of the tested lithologies carbonates were observed to form at the applied pressure and temperature conditions. Even though it is possible that they may have formed undetected in very small quantities, the overall conclusion is that CO_2 was not mineralized during the relatively short reaction period of about 30 days.

The experiment with the basaltic rock from Iceland produced a secondary mineral assemblage composed mainly of zeolite, anhydrite, chlorite, and clay. The absence of newly formed carbonates was attributed to the high temperature and the initial fluid composition enriched in silicon and sulfate. The metamorphic quartz-schist from Turkey has a mineralogy that is not suited for a sufficient supply of divalent cations necessary for effective CO_2 sequestration. Small amounts of smectite were the only observed secondary minerals from this experiment.

It would be beneficial to extend this research with more, prolonged experiments. This could show if the encountered reactions are actually complete after the short reaction period considered here. Furthermore, it would be of interest to test additional rock types that ensure an adequate supply of divalent cations.

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