On the interaction of minerals and brine with pure / impure CO_2

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Objectives

The aim of this study is the investigation of the long term behavior of mineral phases and fluids in systems convenient for CO_2 injection and storage like saline aquifers or hydrate bearing sediments.

Introduction and Settings

Batch experiments were conducted to investigate the interactions of supercritical CO_2 (>7.4 MPa/ >31°C), brine and rock-forming mineral concentrates (albite, microcline, kaolinite, bentonite, biotite, muscovite, calcite, dolomite, and anhydrite) using a newly developed experimental set-up. The solid to fluid ratio was about 1:50. Experiments with mixtures of supercritical CO_2 (99.5 vol.%) and SO_2 or NO_2 impurities (0.5 vol.%) take into account the incomplete purification of industrial captured CO_2 using the oxyfuel technology. In addition, the vessels were not evacuated before the experiments and therefore contained oxygen (ca. 10 cm^3 per experiment), which is also expected in industrially captured CO_2. Before, during and after the experiments approximately 3 ml of fluids were sampled every time and analyzed for pH instantaneously and for dissolved constituents using ICP-MS and IC. After up to 1000h lasting experiments the dissolution and solution characteristics of the solids were examined by XRD, XRF, SEM and EDS, respectively.

Results

Our results suggest the formation of sulfuric acid and nitric acid, reflected in pH values between 1 to 4 for experiments with silicates and anhydrite and between 5 to 6 for experiments with carbonates. These acids should be responsible for the general larger amount of cations dissolved from the mineral phases compared to experiments using pure CO_2. For pure CO_2 a pH of around 4 was obtained using silicates and anhydrite, and 7 to 8 for carbonates.

Silicates do not exhibit visible alterations during all experiments but released an increasing amount of cations in the reaction fluid during experiments with impure CO_2. Si was obtained in ascending concentrations during experiments with silicates whereas Al and Fe exhibited increasing concentrations only during the beginning of the experiments but were variable towards the end. The amounts of Mg and K in the fluids increased or kept constant during all experiments. Ca behaved variable. Nonetheless, precipitated secondary carbonates could not be identified.

Dissolution of carbonates was observed after both pure and impure CO_2 experiments. The total amount of dissolved constituents in the reaction fluid is at least twice as high for carbonates and anhydrite than for silicates. Anhydrite was corroded by approximately 50 wt.% and gypsum precipitated during experiments with supercritical CO_2+NO_2.

Degassing a rhyolite: are the old Ar-Ar ages real, inherited or excess?

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The aim of this project is to test the resolution of Ar-Ar dating and understand some of the minor anomalies that can affect the fidelity of resulting eruption ages. Few reliable age data exist for post-caldera rhyolitic lavas and domes of the Snake River Plain, USA. The Sheridan Reservoir dome (SRD) has previously been dated by U-Pb geochronology and the published age (~2.07 Ma [1]) overlaps with the generally accepted age of the Huckleberry Ridge Tuff (HRT) (~2.05 Ma [2]). New $^{40}Ar/^{39}Ar$ age data has uncovered possible contamination and higher than expected Ar-Ar apparent ages in feldspar crystals. The SRD post-dates the HRT (C. Wilson, 2011 pers. comm.), but new Ar-Ar ages are older than both the existing U-Pb age for the dome and the generally accepted Ar-Ar age of the HRT.

Extraneous argon, artificially elevating ages may either reflect **1.** excess argon ($^{40}Ar_E$) incorporated into a mineral during crystallization (via diffusion into the mineral lattice or hosted within inclusions) or **2.** inherited radiogenic argon (sourced from a component older than the age of eruption) [3].

To further our understanding of extraneous argon contamination of the SRD phenocrysts, we carried out $^{40}Ar/^{39}Ar$ single-grain fusion dating of feldspar and rhyolitic groundmass. Here we present new age data, where initial results show feldspar ages to be variable and too old, whereas $^{40}Ar/^{39}Ar$ ages obtained from the groundmass are less affected. Diffusion modelling (using DIFFARG [4]) has been carried out to show that these older ages are a consequence of radiogenic argon residing in incompletely outgassed feldspar xenocrysts caught up in the SRD eruption..

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[3] Kelley, S. (2002) *Chemical Geology* **188,** 1-22.
[4] Wheeler, J. (1996) *Computers & Geoscience* **22,** 919 – 929.