Electronic Supplementary Information for

Supercritical CO_2–Brine Induced Dissolution, Swelling, and Secondary Mineral Formation on Phlogopite Surfaces at 75–95ºC and 75 atm

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Summary

9 Pages of relevant GWB (Geochemist's Workbench) calculations, AFM images, TEM information, H_2O in the $scCO_2$ phase calculations, and reactor contamination control description.

A. Calculations of the pH Values and Saturation Indices of Potential Minerals with Geochemist's Workbench (GWB)

Saturation indices of potential minerals and pH values were calculated with Geochemist's Workbench (GWB, Release 8.0, Rockware, Inc.) for four systems, as described below. In each system, the saturation indices of potentially relevant minerals to the system—phlogopite, diaspore, illite, kaolinite, and amorphous silica—are given.

To calculate the initial pH right after CO_2 injection using Geochemist's Workbench, 1 M NaCl was added as the basis specie inputs. The temperature was set appropriately for the system of interest (either 75 °C or 95 °C). The activity of each dissolved species was calculated as the product of the concentration and the activity coefficient. The B-dot equation, which has been shown to be reasonably accurate in predicting the activities of Na^+ and Cl^- ions to concentrations as large as several molal, along with other species to ionic strengths up to about 0.3 to 1 molal,[1] was used to calculate activity coefficients. Finally, the fugacity of the CO_2, estimated as the overall pressure of the system, was used as another basis for GWB calculations. These settings simulated the 1 M NaCl–CO_2 solution right after CO_2 injection.

For the systems involving phlogopite dissolution, the dissolved ion concentrations (K, Mg, Al, and Si) in the bulk solution at the elapsed reaction time measured by ICP-MS were added into the basis for calculation in GWB. These data were then used to calculate the pH of the system based on charge balance, and the saturation indices for potential minerals were also calculated.

1) System 1: $scCO_2$-Brine System at 75 ^{o}C

This system was calculated to determine what the pH and saturation indices would be if no phlogopite elements were in the solution (no K, Si, Al, or Mg). Thus, 1 M NaCl was added as the basis species, the temperature was set at 75 °C, and the fugacity of CO_2 was set at 75 atm. The pH was calculated to be 3.07 ± 0.05, and saturation indices were not calculated, as no minerals of interest could precipitate under these conditions.

2) System 2: $scCO_2$-Brine System at 95 ^{o}C

This system is the same as above, except the temperature was adjusted to 95 °C. The calculated pH was 3.20 ± 0.05, and, as in System 1, no minerals of interest could precipitate under these conditions.

3) System 3: $scCO_2$-Brine-Phlogopite System at 75 ^{o}C at 241 hrs

System 3 utilized the ICP–MS dissolution data for the 75 °C, 241 hour phlogopite flake experiment. Concentrations for Si, Al, Mg, and K were used as a basis, along with CO_2, temperature and 75 atm, to calculate the value of the pH and the values of the saturation indices. The pH was calculated to be 3.10 ± 0.05. The saturation indices were calculated as follows: Phlogopite: -41.15; Diaspore: -2.92; Illite: -15.86; Kaolinite: -7.42; and Amorphous Silica: -2.58.

4) System 4: $scCO_2$-Brine-Phlogopite System at 95 ^oC at 43 hrs

The final system calculated the pH and saturation indices using ICP-MS data from the 95 °C, 43 hour (the longest experiment run at this temperature) phlogopite flake experiment. Concentrations for Si, Al, Mg, and K were again used as a basis for calculations along with CO_2, temperature, and 1 M NaCl. The pH was calculated to be 3.20 ± 0.05. The saturation indices are as follows: Phlogopite: -39.31; Diaspore: -1.92; Illite: -15.10; Kaolinite: -6.61; and Amorphous Silica: -3.00.

Reference:

(1) Bethke, C. M., *Geochemical and biogeochemical reaction modeling*. Cambridge: 2008.

B. Supporting AFM Images

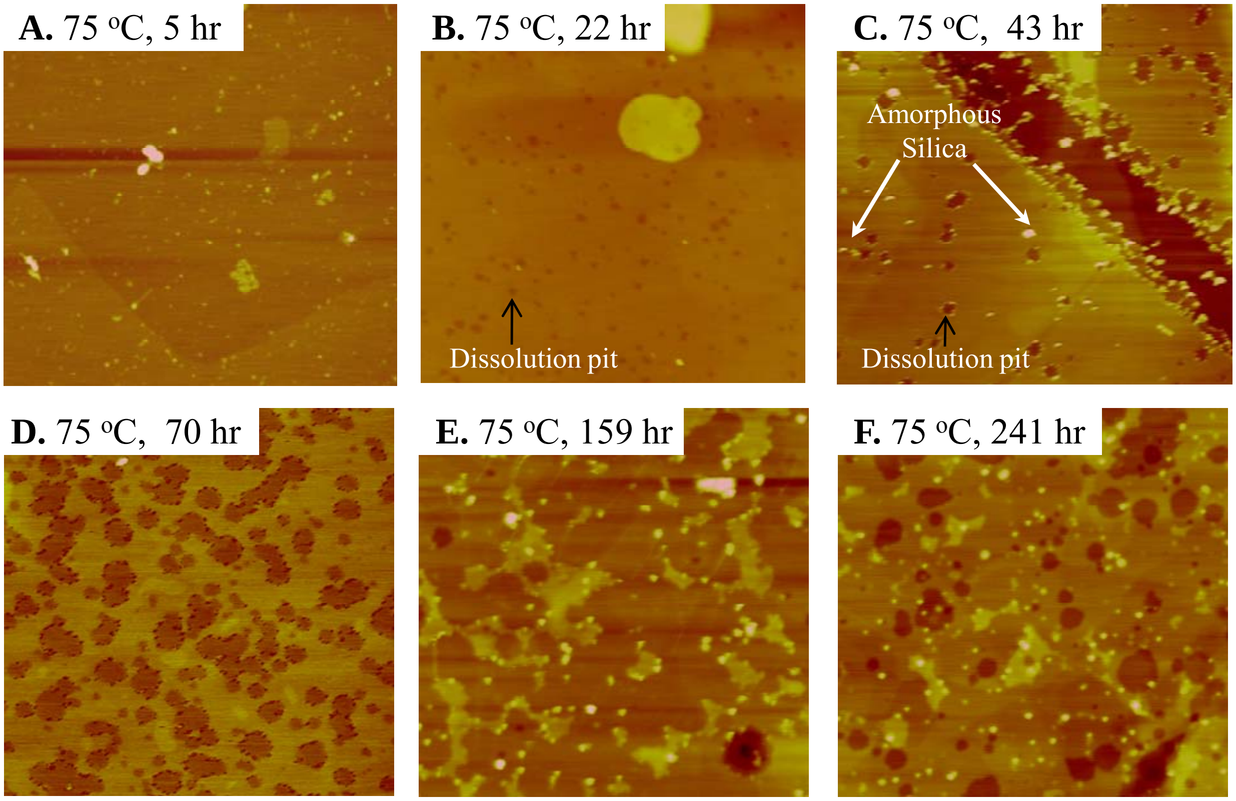


Figure S1. AFM height images detailing the formation of both dissolution pits and amorphous silica nanoparticles in the system at 75 °C and 75 atm. All scans are 3 μm by 3 μm. Times of 5, 22, 43, 70, 159, and 241 hours are represented.

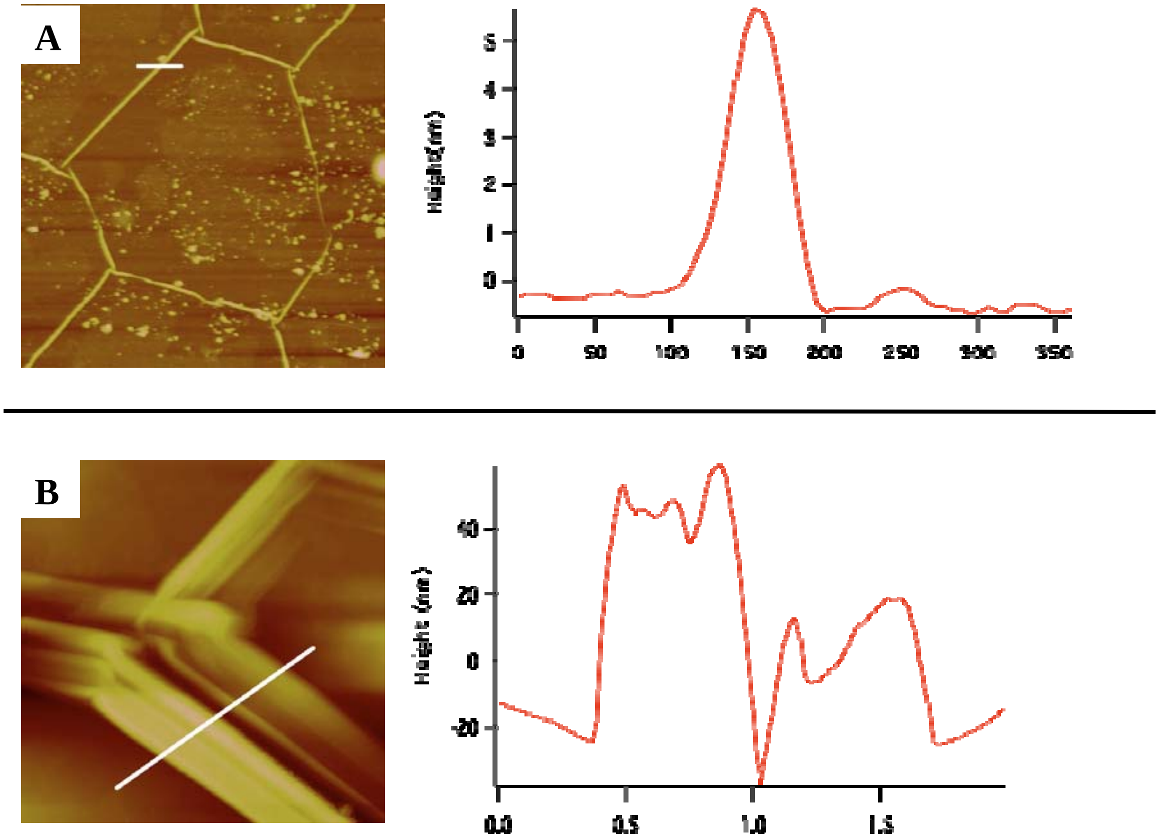


Figure S2. Comparative height mode images and corresponding height profiles for illite at experimental times of 3 hrs (**A**) and 241 hrs (**B**) at 75 °C. The lines in the height images indicate the path for which the height profiles were found.The illite strand pictured at 241 hrs is roughly ten times taller than the strand shown at 3hrs.

C. Supporting Calculations

Calculations to estimate the amount of H_2O in the $scCO_2$ phase

To estimate the amount of H_2O present in the $scCO_2$ phase in our experiments, we made the following assumptions and calculations:

1) The density of the $scCO_2$ is roughly 160 kg/m^3(**1**)
2) The volume available for the $scCO_2$-H_2O phase in the reactor is approximately 230 mL.
3) The mol fraction of H_2O in CO_2 at 60°C is 0.0047, and at 90°C it is 0.0145 (Figure 2 from ref (**2**)).

The number of mols of CO_2 in the vessel was calculated to be ~0.831 mol. This value would yield a maximum of 0.004 mol H_2O vapor in the $scCO_2$ phase at 60°C (or approximately 0.06 g) and 0.012 mol H_2O at 90°C (or approximately 0.2 g). Considering that we also added ~ 20 mL of DI water to the reaction vessel inside the liner, the reaction system should be liquid-dominated.

References:

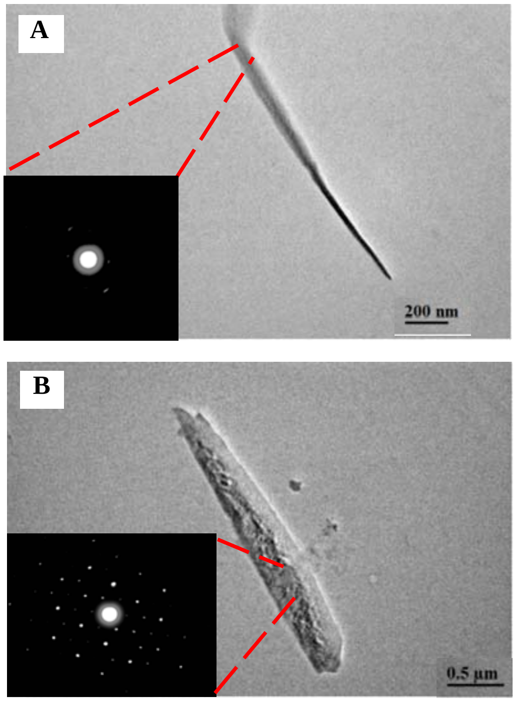
(**1**) R. Stryjek, J. H. Vera, *PRSV: An Improved Peng –Robinson Equation of State for Pure Compounds and Mixtures*. The Canadian Journal of Chemical Engineering, **64**, April 1986

(**2**) Spycher, N. and Pruess, K. *Geochimica et Cosmochimica Acta*. **2005**, 69, 3309.

D. HR-TEM Data for secondary mineral phase identification

HR–TEM was used to analyze branch–like particles on the surface of reacted phlogopite powder, and the electron diffraction pattern of a representative particle is shown in Figure S4. Several d–spacings were measured and compared to those of illite ($(K,H3O)(Al,Mg)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$), and three of the best matches are tabulated in

Figure S4. These d–spacings also correspond to high intensity peaks of illite (10.02231, 3.34077, and 5.01116 Å), lending strong evidence for the existence of illite in the system. However, these d–spacings are also similar to other minerals, namely muscovite and smectite. HR–TEM also suggests the existence of diaspore, an aluminum oxyhydroxide mineral (Figure S4B). In addition, we could not find any significant support for kaolinite's presence, which was found in similar experiments at 95°C and 102 atm. (**1**) This apparent absence could be due to the different temperature and pressure conditions used in the experiments. We cannot rule out the possibility that kaolinite was formed under our experimental conditions. However, if it was formed, the amount must have been too small to be detected with HR-TEM.



Illite

Measured d-spacing (Å)	Reference d-spacing (Å)	Peak intensity
10.0320	10.02231	62.7%
3.3440	3.34077	54.3%
5.0160	5.01116	37.5%

Diaspore

Measured d-spacing (Å)	Reference d-spacing (Å)	Peak intensity
4.0128	3.98748	100%
2.0900	2.07729	48.1%
1.3742	1.3752	21.2%
2.3330	2.35632	9%
2.3886	2.38932	4.4%

Figure S4. HR-TEM results. Particles and their diffraction patterns are on the left, and measured d-spacings are compared to actual d-spacings and corresponding peak intensities of (A) illite and (B) diaspore.

Reference:

(**1**) Shao, H.; Ray, J. R.; Jun, Y.-S. *Environ. Sci. Technol.* **2010**, *44*, 5999.

E. High pressure and high temperature experimental setup

Reactor Contamination Control: Contamination can result from the construction material that the reactor is made of – HC alloy C-276, although, based on our pre-test, this material has the best resistance against corrosion under $scCO_2$ conditions. In our regular process, we paid attention to this aspect. Briefly, we performed high-pressure CO_2 and high-temperature experiments without a PTFE tape cover to check for contamination. Under these conditions, it was found that the metal elements in the alloy dissolved into the CO_2 saturated water, perhaps dropping from the top of the reactor to the test tube, although a liner was added to avoid the contamination from the reactor wall. Adding Teflon tape with small holes prevented water drops from getting into the test tubes directly, but still allowed CO_2 gas to enter the test tube and equilibrate with the saline water in it. We also added a blank water test tube to check for any contamination in each batch.

Reference:

(**1**) Shao, H.; Ray, J. R.; Jun, Y.-S. *Environ. Sci. Technol.* **2010**, *44*, 5999.