Electronic Supplementary Information for

Effects of Sulfate on Biotite Interfacial Reactions under High Temperature and High CO_2 Pressure

Lijie Zhang, Yaguang Zhu, Xuanhao Wu, and Young-Shin Jun

Department of Energy, Environmental and Chemical Engineering,

Washington University in St. Louis, St. Louis, MO 63130

Address: One Brookings Drive, Campus Box 1180
E-mail: ysjun@seas.wustl.edu
Phone: (314)935-4539
Fax: (314)935-7211
http://encl.engineering.wustl.edu/
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*Corresponding Author

Summary

6 pages, including 2 figures and 1 table.

S1. High temperature and high pressure experimental setup

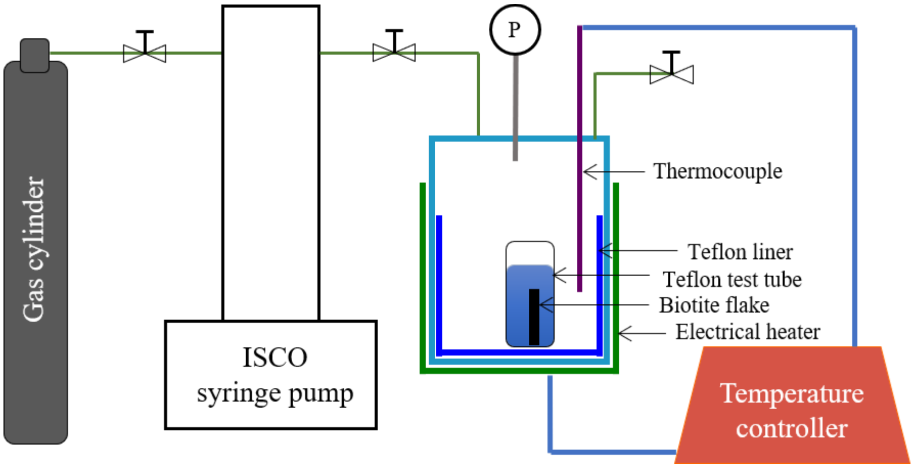

Figure S1 Experimental setup for the high temperature and high pressure batch experiments.[1] Reprinted with permission from Zhang, L.; Jun, Y.-S., Distinctive Reactivities at Biotite Edge and Basal Planes in the Presence of Organic Ligands: Implications for Organic-Rich Geologic CO_2 Sequestration. *Environ. Sci. Technol*. 2015, *49* (16), 10217-10225. Copyright (2015) American Chemical Society.

Table S1 Chemical information about the ligands reported in this study

Ligands	Chemicals	Vendor
Sulfate	Sodium sulfate (>99.0%)	Sigma-Aldrich
Phosphate	Sodium phosphate dibasic (>99.0%)	Sigma-Aldrich
Acetate	Sodium acetate (>99.0%)	EMD Millipore
Oxalate	Sodium oxalate (>99.0%)	Alfa Aesar
DTPMP	50% DTPMP, 15% HCl, 35% H_2O (wt.)	Sigma-Aldrich

S2. Thermodynamic calculations by GWB

The initial pH was calculated by GWB (Geochemists' Workbench, Release 8.0, RockWare, Inc).[1] The thermo.com.V8.R6+.dat database was chosen for the calculation. In the database, the

B-dot equation was used to calculate the activity coefficients of the aqueous species at high ionic strength. The fugacity of 102 atm CO_2 was recalculated to be 76.5 atm, using Duan and Sun's equation.[2] Under our experimental conditions (95 °C, 102 atm CO_2), the initial pH of control solution was calculated to be around 3.2. For sulfate reaction solutions, using GWB simulations, we balanced the pH value of the sulfate solutions to be 3.2 at 95 °C and 102 atm CO_2, with the addition of HCl or NaOH. Then under the same aqueous chemistry conditions, in the simulations, we changed the temperature to room temperature and pressure to ambient pressure to obtain the corresponding pH values. During experiments, we adjusted the pH of the sulfate reaction solutions to the calculated pH values at room temperature and ambient pressure, which resulted in the same pH (pH = 3.2) as the control system at 95 °C and 102 atm CO_2. The pH values after 96 h of reaction were calculated by taking the ICP-OES and IC results as the input for GWB calculations. In this calculation, we assumed that the concentration of Cl^- did not change much, but the loss of the Na^+ equaled the release of K^+ because of cation-exchange reactions between Na^+ and biotite interlayer K^+. Then we obtained the cation activities and pH values.[3] The final pH values for the control, 1 mM, 10 mM, and 50 mM sulfate systems were 3.39, 3.42, 3.46, and 3.36, respectively. Please note that during the thermodynamic calculations, the calculated pH was very sensitive to the input of sulfate concentrations. Considering the error bars of sulfate concentration measurements, we assumed that there were no significant differences in the pH values calculated for the four systems.

S3. AFM measurements

Root-mean-square surface roughness (R_q) is defined as $R_q = \sqrt{\frac{1}{L}\int_0^L \left|Z^2(x)\right| dx}$,[4] where $Z(x)$ is a function that describes the surface profile analyzed in terms of the height (Z) and position (x) of the sample over the evaluation length (L). We used this definition as an indicator of surface roughness. For each sample, at least four locations on the sample surface were measured to determine the roughness. The depth of the cracks in sample surfaces were also measured from the AFM images by taking the average of 20 spots from four representative AFM images. The results are shown in Figure 4.

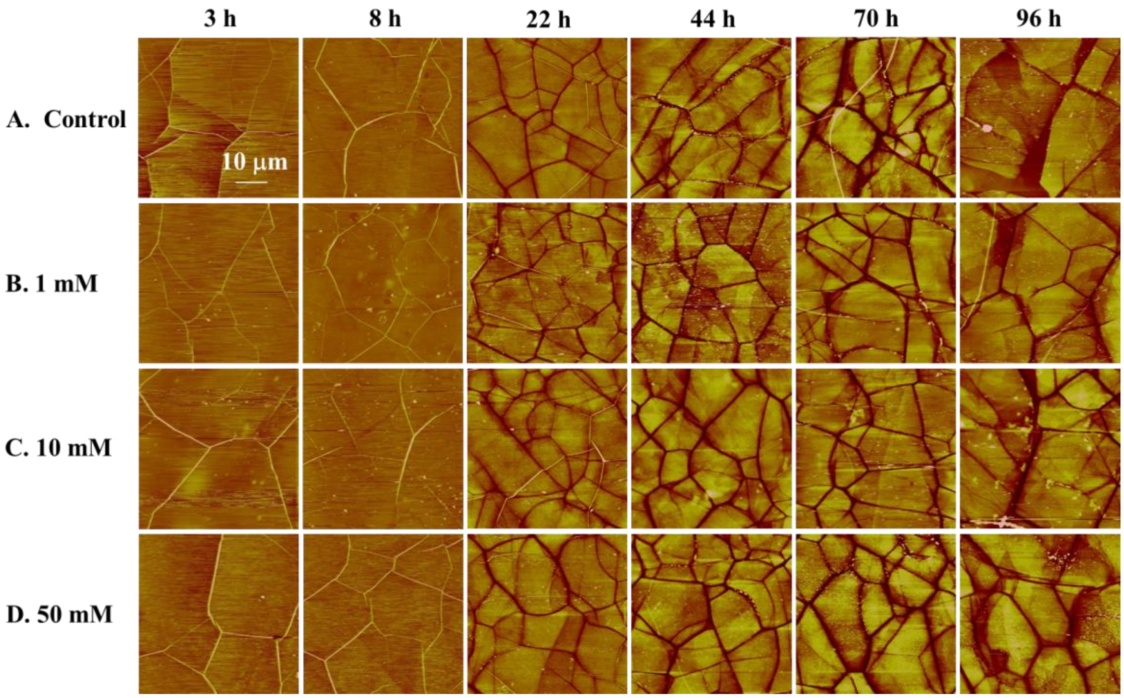

Figure S2 Height mode AFM images of biotite basal surfaces after reaction with different concentrations of sulfate at 95 °C and 102 atm CO_2. The AFM images are 50 µm × 50 µm. The height scale is 60 nm.

S4. XPS measurements

X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II, Ulvac-PHI with monochromatic Al Kα radiation (1486.6 eV)) was used to investigate the surface functional groups of oxygen on biotite. The C 1s (284.8 eV) spectrum was taken as the energy reference. Narrow scans of O 1s spectra were analyzed with Shirley background subtraction. The pass energy for the narrow scans was 23.5 eV. The fittings of O 1s photolines were conducted based on the Gaussian-Lorentzian algorithm, using Multipak V 7.0.1 (Ulvac-PHI, Inc.). Both bridging oxygens (T–O–T, T: tetrahedral site) and terminal oxygens (T–OH) are present on the surface of aluminosilicates.[5-6] Water molecules are also on the mineral surface. In XPS analyses, the oxygen peak in the range of 528–536 eV was deconvoluted. According to the literature,[7-8] the peak with a binding energy of around 530.0 eV was assigned to bridging oxygen (O^{2-}), the peak with a binding energy of 531 eV was assigned to hydroxyl oxygen (–OH), and the peak with a binding energy of 533 eV was assigned to water molecules (H_2O). Next, the percentages of oxygen species at the biotite surface after reaction under 95 °C and 102 atm CO_2 were obtained.

Table S2 Percentage of biotite surface species of oxygen after reaction at different conditions

	O^{2-} (%)	**OH (%)**	**H_2O (%)**
1 M NaCl	5.5	89.2	5.3
1 M NaCl+10 mM oxalate	5.4	91.2	3.4
1 M NaCl+10 mM acetate	6.2	87.5	6.3

S5. Impact of supercritical CO_2 on the effect of sulfate

The controlled high CO_2 pressure makes the reaction solution acidic (~3.2). At this pH, the dominant sulfate species is SO_4^{2-}. If the reaction were done at high pressure without CO_2 gas, for example, with N_2 gas, the pH of the reaction solution will be around neutral, and the dominant sulfate species would still be SO_4^{2-}. Given this sulfate speciation, CO_2 would not impact the effect of sulfate on biotite dissolution. However, at acidic pH, biotite dissolution is faster and more cracks will be formed on biotite basal surfaces, which will result in more sulfate adsorption on biotite basal surfaces. In addition to this pH effect induced by the presence of CO_2, intercalation of CO_2 molecules into biotite interlayers will would enhance biotite surface cracking and promote dissolution, likely leading to more sulfate adsorption on biotite basal surfaces. Hence, wettability alteration of biotite by sulfate was likely enhanced under high CO_2 pressure.

References

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