

Supporting Information for

**Effects of Phosphonate Structures on Brine–Biotite Interactions
under Subsurface Relevant Conditions**

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Summary

9 pages, including 2 tables and 8 figures.

S1. High temperature and high pressure experimental setup

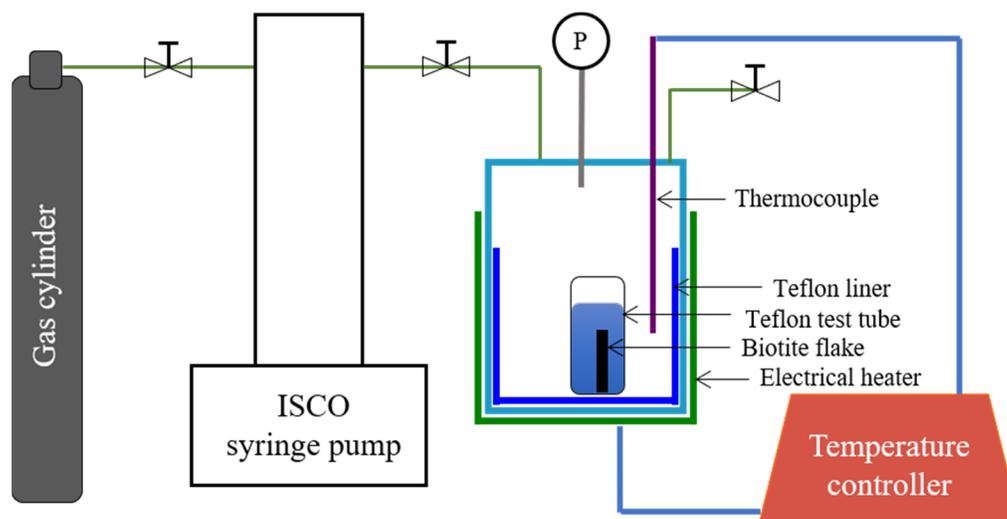


Figure S1 Experimental setup for the high temperature and high pressure batch experiments.¹ Reprinted with permission from Zhang, L.; Jun, Y.-S., Distinctive Reactivities at Biotite Edge and Basal Planes in the Presence of Organic Ligands: Implications for Organic-Rich Geologic CO₂ Sequestration. *Environ. Sci. Technol.* **2015**, *49* (16), 10217-10225. Copyright (2015) American Chemical Society.

S2. Thermodynamic calculations of pH and *in situ* high pressure and high temperature pH measurements

The initial pH of the control solution of 0.5 M NaCl at 95 °C and 102 atm CO₂ was calculated with GWB (Geochemists' Workbench, Release 8.0, RockWare, Inc). 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. Using Duan and Sun's equation considering the effects of temperature and high salinity, the solubility of 102 atm CO₂ at 95 °C and 0.5 M NaCl was recalculated to be 0.65 mol/kg.² Based on the thermodynamic calculation, the initial pH of the control solution was around 3.2. The pH of the 0.5 mM phosphonate solutions was adjusted to be 5.6 under ambient conditions.

A special pH probe (Corr Instruments, San Antonio, TX) was used to measure the initial *in situ* pH at 95 °C and 102 atm of CO₂. The method of pH probe calibration was modified from Shao et al.³ At 95 °C under ambient pressure, the probe was calibrated in 0.5 M NaCl with different pH values, adjusted under ambient conditions. Shao et al. reported that pressure within 1–102 atm

does not affect the calibration. The pH of the calibration solutions at 95 °C was calculated using GWB. After recording the potential of the pH probe at different pH solutions, a calibration curve was obtained to link potentials with pH values at 95 °C. During pH measurements, the probe was placed inside the reactor. For the initial *in situ* (95 °C and 102 atm of CO₂) pH, the pH was measured with 100 mL prepared solutions without adding biotite flakes. The initial *in situ* pH values are shown in Table S2. The measured pH and calculated pH for the control solution were close.

Thermodynamic calculations of pH and mineral saturations in phosphonates systems were not made because detailed thermodynamic data on the phosphonates is not available.

Table S1 Purities of phosphonates purchased from Sigma-Aldrich

Phosphonates Purchased	Composition
IDMP	97% IDMP, solid
NTMP	50% NTMP, 15% HCl, 35% H ₂ O (wt.)
DTPMP	50% DTPMP, 15% HCl, 35% H ₂ O (wt.)

Table S2 Measured initial *in situ* pH of the reaction solutions.

Experimental condition	Initial <i>in situ</i> pH
Control	3.0
0.5 mM IDMP	3.2
0.5 mM NTMP	3.2
0.5 mM DTPMP	3.2

S3. Contact angle measurement

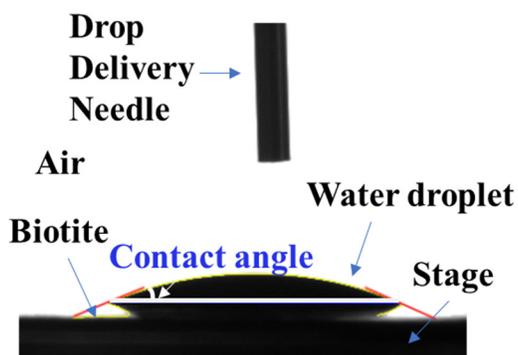


Figure S2 Image taken during contact angle measurements under ambient condition.

The absolute values of contact angles measured under ambient conditions can be different from those obtained at high temperature and high CO₂ pressure. However, based on our previous report, the general trend of contact angles among the biotite samples reacted in different systems should be the same.⁴

S4. UV-Vis analyses

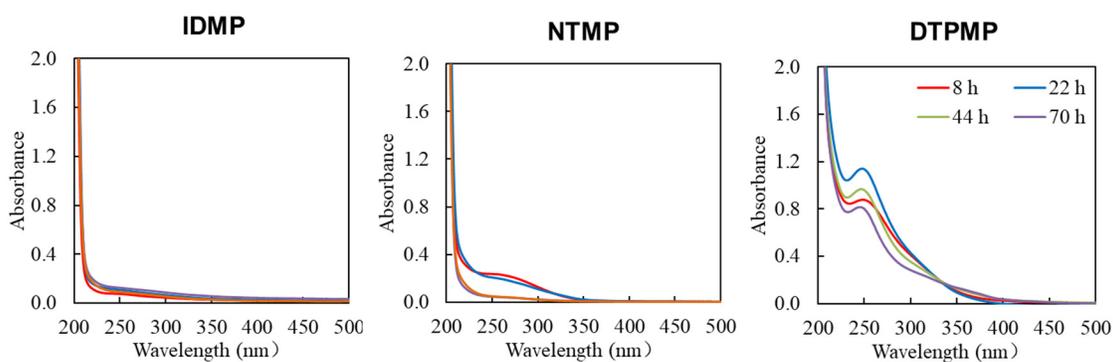


Figure S3 UV-Vis spectra of the reacted phosphonate solutions.

S5. SEM and TEM measurements

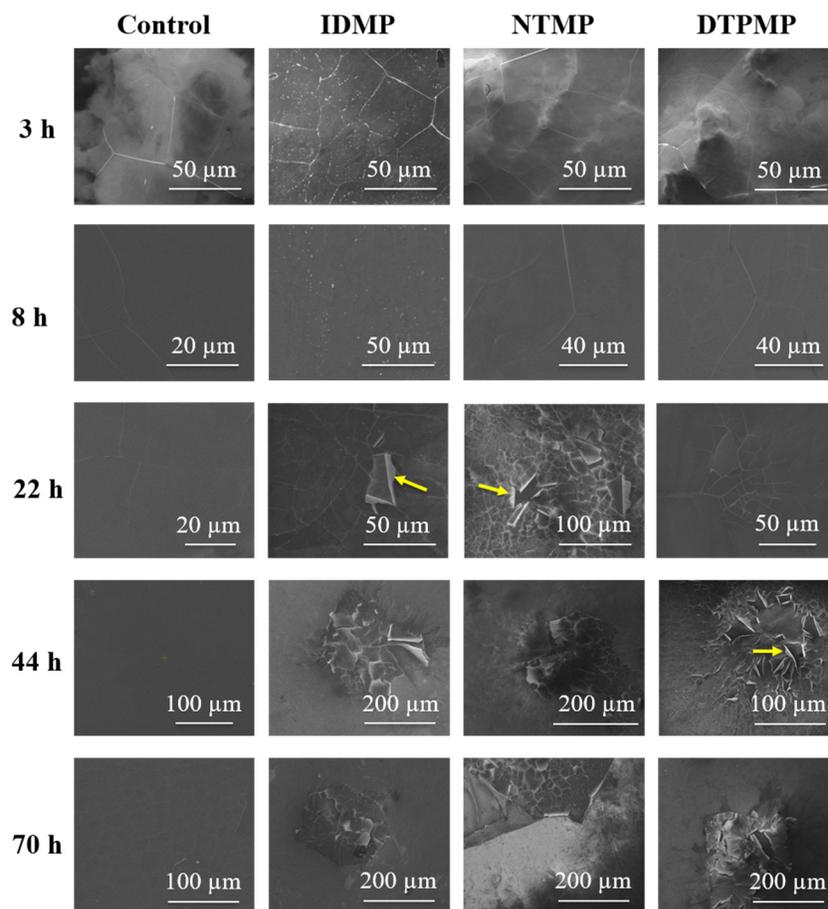


Figure S4 SEM images of reacted biotite basal surfaces. The yellow arrows indicate bent surface cracked layers.

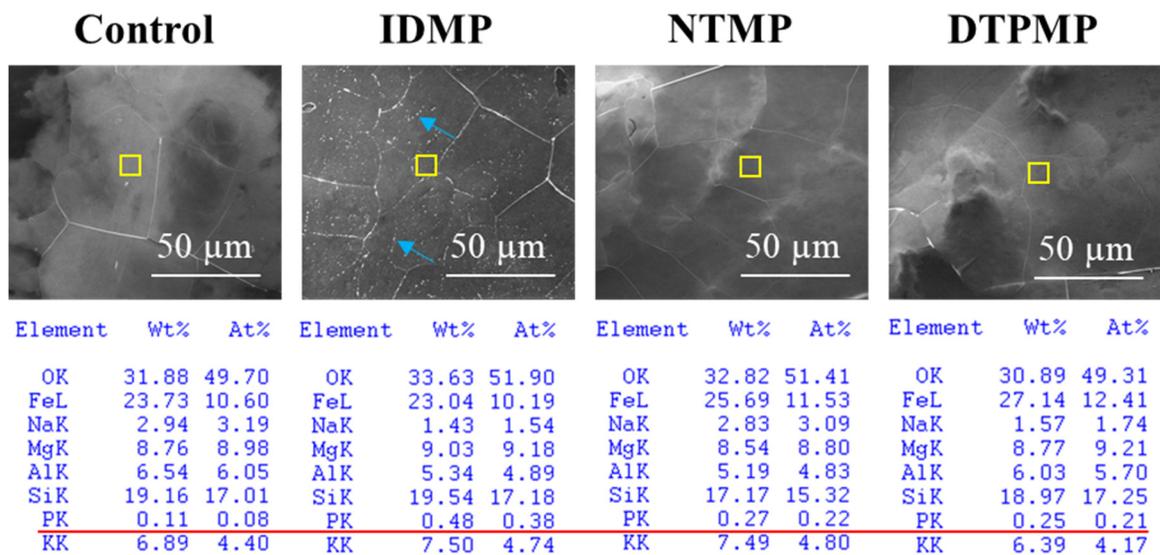


Figure S5 SEM-EDX analyses of biotite basal surfaces after 3 h reaction. The blue arrows point to the spherical particles. The yellow boxes indicate the EDX measurement locations.

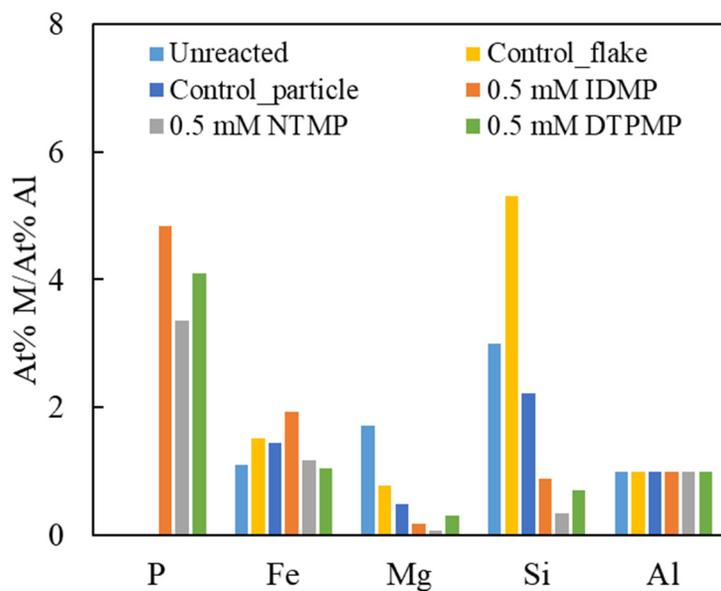


Figure S6 TEM-EDX results for representative small spherical particles formed in reaction solutions after 70 h under 95 °C and 102 atm CO₂. M/Al indicates the atomic ratio of M (Fe, Mg, Si, P, and Al) to Al.

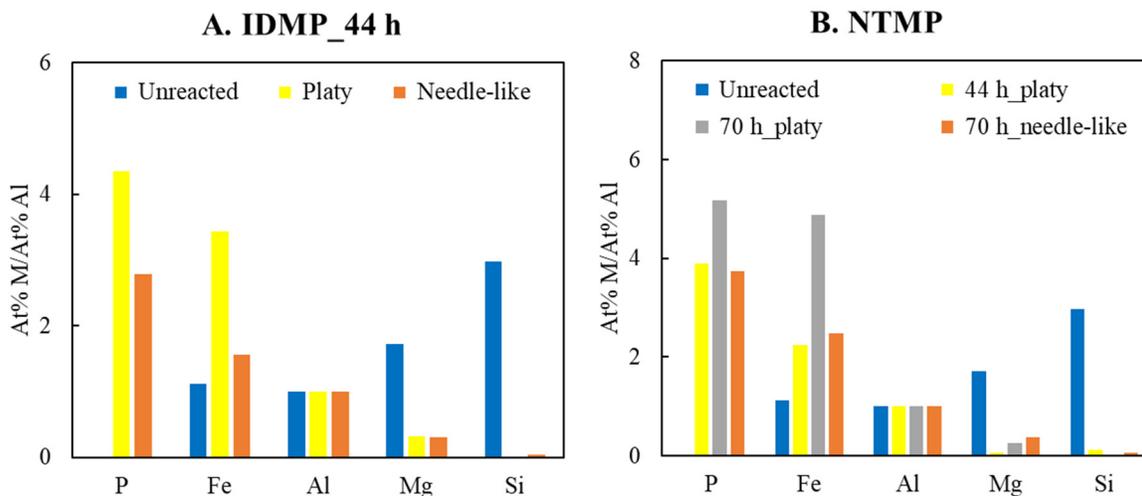


Figure S7 SEM-EDX results for representative particles formed (Figure 6) (A) in the IDMP system after 44 h reaction and (B) in the NTMP system after 70 h reaction at 95 °C and 102 atm CO₂. M/Al indicates the atomic ratio of M (M = Fe, Mg, Si, P, and Al) to Al.

S6. Evolution of total aqueous P concentrations

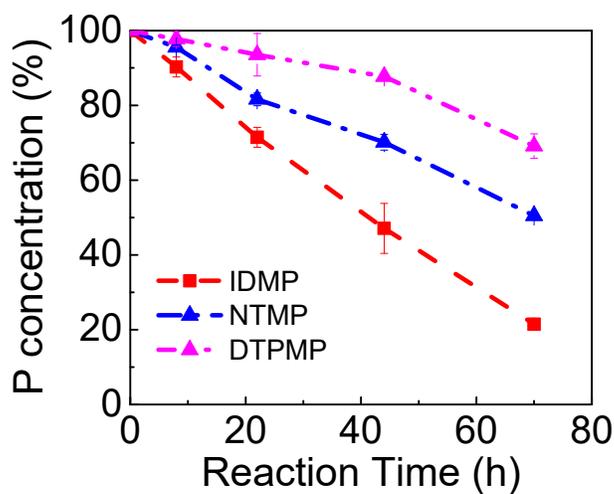


Figure S8 Evolution of total aqueous P concentrations with time after reaction under 95 °C and 102 atm CO₂. Error bars are standard deviations of triplicate samples in duplicate experiments.

S7. Accuracy of the experimental apparatus

The experimental protocols for the high temperature and high pressure experimental apparatus have been well developed in our group. We used at least triplicate samples in duplicate experiments for every experimental conditions, and we found that they were reproducible. Second, to the best of authors' knowledge, there is no literature reporting biotite dissolution under conditions similar to ours (high temperature, high CO₂ pressure, and high salinity), hence we could not include literature data from others for comparison. However, the results for the control and 0.5 mM DTPMP systems were consistent with those reported in our recent paper.⁵ Third, the thermodynamic calculations of pH and the *in situ* high temperature and high pressure pH measurement of the control system (S2) confirmed that the experimental setup works well. Based on the thermodynamic calculation, the initial pH of the control solution was around 3.2 at 95 °C and 102 atm CO₂. The measured initial *in situ* pH of the control solution was around 3.0. These close values of the measured pH and the calculated pH for the control solution suggested the accuracy of the experimental apparatus because pH can be strongly affected by aqueous chemistries in the system. Therefore, we believe the accuracy of the experimental apparatus is well established.

References

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2. Duan, Z.; Sun, R., An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. *Chem. Geol.* **2003**, *193* (3), 257-271.
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