

Impacts of organic ligands on forsterite reactivity in supercritical CO₂ fluids

Q.R.S. Miller ^{a*}, J.P. Kaszuba ^{ab}, H.T. Schaef ^c, M.E. Bowden ^d, and B.P. McGrail ^e

^a Department of Geology and Geophysics, 1000 E. University Avenue, University of Wyoming, Laramie, WY 82071, USA

^b School of Energy Resources, 1000 E. University Avenue, University of Wyoming, Laramie, WY 82071, USA

^c Fundamental and Computational Sciences Directorate, Pacific Northwest National Laboratory, P. O. Box 999, MS K8-98, Richland, WA 99352, USA

^d Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P. O. Box 999, MS K8-98, Richland, WA 99352, USA

^e Energy and Environment Directorate, Pacific Northwest National Laboratory, P. O. Box 999, MS K8-98, Richland, WA 99352, USA

* Corresponding author: Quin R.S. Miller

qmillers@uwyo.edu

Tel: 209-920-7846

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Supporting Information

This supporting information contains summaries of the high pressure X-ray diffraction (HXRDX) and electron microscopy methods. Also included are three supplementary figures, Figures S1, S2 and S3.

Summary of HXRDX Methods

Experiments were conducted in a high pressure static reactor with a beryllium cap inside a D8 Discover XRD at Pacific Northwest National Laboratory (PNNL) in Richland, WA. Variations of this setup have previously been described in detail ¹⁻³. Briefly, ~4 mg of forsterite was tightly packed into a PEEK[®] sample holder, which was then attached to the stainless steel base of the reactor. The HXRDX reactor was then positioned using a custom built XYZ stage (Bruker-AXS) and aligned using a laser video alignment system. Following proper alignment, exact amounts of water or 0.1 *m* solutions were added with a

calibrated pipette (Fisherbrand) to a reservoir in the reactor base. This reservoir was below and behind the forsterite sample and ensured the mineral and solution were not in contact. This setup is shown in Figure S2 and additional HXRD schematics can be found in Schaef et al.^{2,4}. The amount of solution used in the experiments (10 μ l) was calculated to be sufficient to saturate the supercritical CO₂ (scCO₂) at 50 °C and 90 bar, with an excess saturation of 892 %⁵. This reservoir of solution was always in contact with the scCO₂ and was never exhausted, even when water condensed from the scCO₂ phase onto mineral surfaces or when hydrated secondary phases precipitated. Assuming 4.2 mg of forsterite with a 26.7 m²/g surface area, a 2 nm water film thickness, and complete conversion of forsterite to nesquehonite and SiO₂, excess water (591 %) will still be available to buffer the water content of the scCO₂. Only when unrealistic assumptions of silica hydration (>10 H₂O per SiO₂) or water film thickness (>50 nm) are added to the aforementioned assumptions does the water saturation of the scCO₂ decrease to below 100%.

HXRD experiments were conducted at 50 °C and 90 bar for ~44 hours. These experimental conditions were selected to simulate reservoir depths relevant to geological carbon sequestration and utilization. Similarly to the methods of Wang et al.⁶, the reactor was pressurized prior to heating, to prevent water vapor from distributing the solutions and moistening surfaces before pressurization. The reactor was first pressurized with CO₂ to 57 bar at room temperature (~23 °C) with a programmable syringe pump (ISCO Model 260D) and heated to 50 °C. Lastly, the pressure was slightly increased to attain a final pressure of 90 bar. This procedure ensured that the mineral powder and the bulk solution in the reservoir remained physically separated. At the conclusion of experiments, the ~0.75 g of CO₂ was rapidly degassed (<3 s) and the reactor was cooled to room temperature. Patterns were collected during quenching to look for evidence of retrograde reactions. The reactor was then carefully opened and the sample was collected for further analysis.

A GADDS[®] area detector system positioned at 28 °2 θ was used to capture diffraction images, which were collected every 200 seconds with power settings of 45 kV and 200 mA. The images were processed with Bruker AXS GADDS[®] software before importing into JADE[®] XRD software to obtain peak positions, intensities, and designations in conjunction with the powder diffraction file databases. Preliminary XRD analysis was conducted by visually inspecting the changes in the processed diffractograms and the Debye-Scherrer reflections of the GADDS[®] images. Quantitative XRD analysis was carried out using full pattern fitting with TOPAS software (version 4.2, Bruker, AXS Germany) to obtain wt. % abundance of each crystalline phase with respect to the total mass of crystalline sample. Powder patterns calculated from published crystal structures for forsterite (Mg₂SiO₄)⁷, magnesite (MgCO₃)⁸ and nesquehonite (MgCO₃·3H₂O)⁹ were matched to the experimental patterns using pseudo-Voigt line profiles. The unit cell and line profile parameters of forsterite and the secondary carbonates were established using the initial alignment and final reacted patterns, respectively, recorded without the Be cap on place. Additionally, the Be cap and PEEK[®] sample holder contributed small peaks to the patterns. These contributions were identified by comparing an initial scan with the cap removed. Secondary nesquehonite exhibited preferred orientation, which was modeled with a spherical harmonics approach¹⁰. The uncertainties associated with the quantification procedure are \pm 5 wt. %, which were determined by internal corundum standards² and ex situ carbonate quantification^{1,3} in our previous studies.

Summary of Electron Microscopy Methods

Reacted grains were further characterized using scanning electron microscopy coupled with energy dispersive spectrometry (SEM/EDS). Reacted grains (~1 mg) were mounted with adhesive carbon tape and coated with a thin layer of carbon. Samples were imaged and analyzed with either a JEOL JSM-5900LV or JSM-5800LV microscope (JEOL USA, Inc., Peabody, MA), both equipped with an OXFORD Instruments INCA Energy 200 X-ray detector (Oxford Instruments, Concord, MA) calibrated with Cu foil.

Figure S1

XRD characterization (Scintag XDS 2000, 40 kV and 30 mA) of the nanocrystalline synthetic forsterite sample on a zero background quartz plate indicated a virtually pure forsterite that matches PDF #034-0189.

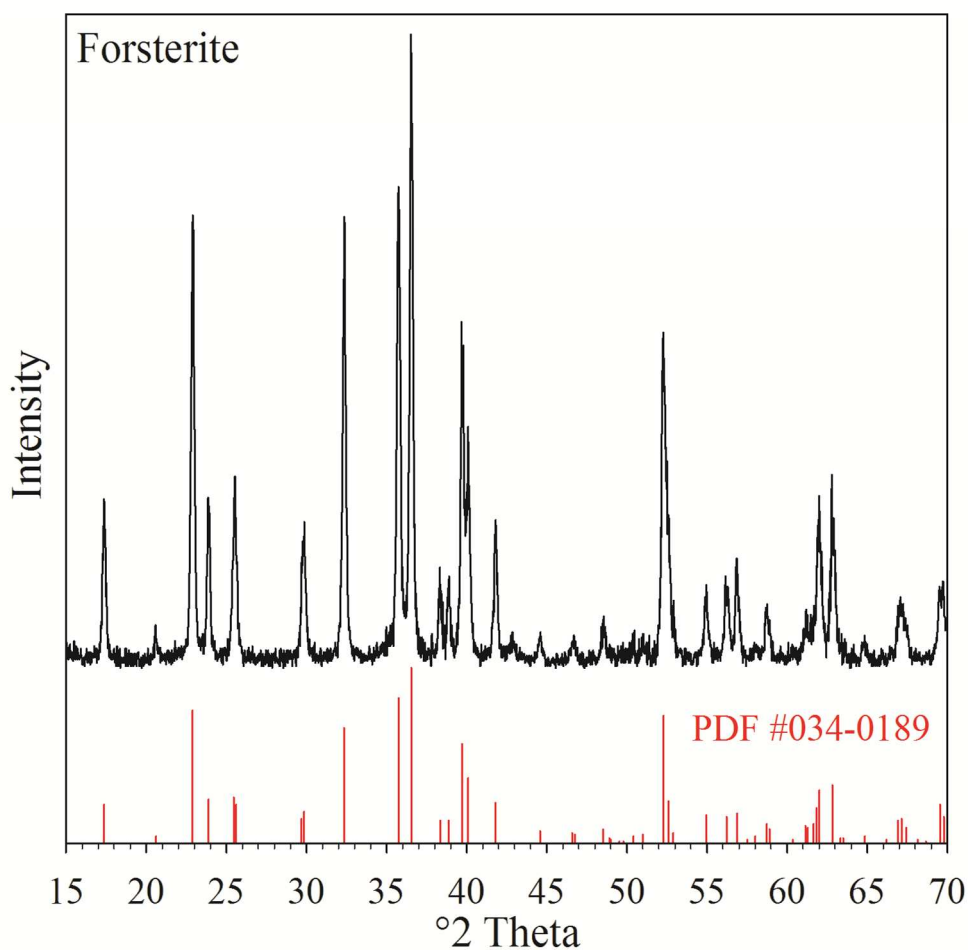


Figure S2

Partial schematic of the HXRD reactor (components such as pressurization lines and Be cap not shown) that illustrates the separation of the sample holder and the solution reservoir, which is situated below and behind the forsterite sample.

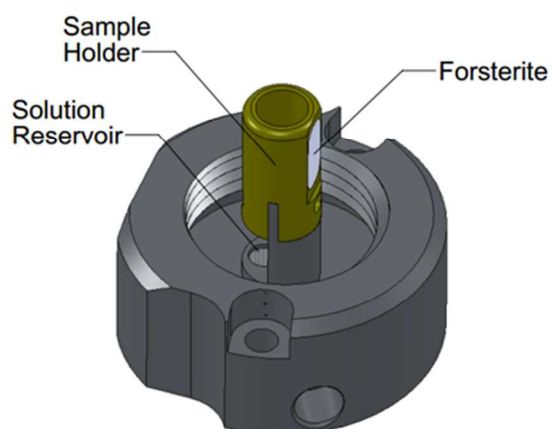
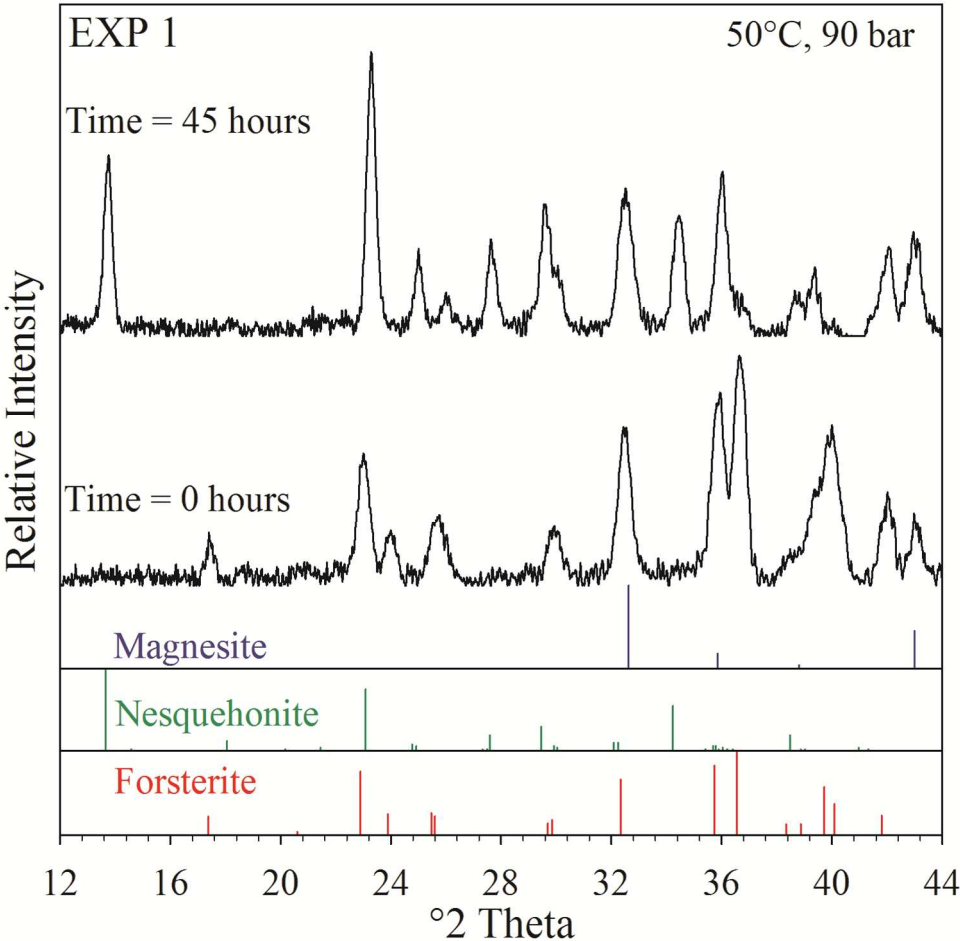


Figure S3

Comparison of the *in situ* unreacted and reacted (45 hrs) patterns for EXP 1 demonstrating the disappearance of the forsterite peaks due to dissolution, and the growth of carbonate peaks due to carbonation. Patterns are offset for clarity.



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