Forsterite [Mg_2SiO_4)] Carbonation in Wet Supercritical CO_2: An *in situ* High Pressure X-Ray Diffraction Study

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Supporting Information

Environmental Science and Technology
17-May-2012

number of pages : 9

number of figures : 4

Summary of in situ High Pressure X-ray Diffraction (HXRD) Experimental Procedure

The pure white powdered silicate was tightly packed into the rectangular sample cavity and compressed with a glass slide to produce a smooth surface. Positioning of the reactor inside the custom built environmental XYZ stage (Bruker-AXS) was accomplished through the use of a laser video alignment system. Following proper alignment, desired amounts of water were added to the base of the reactor before placing the beryllium cap onto the stainless steel base for heating.

Pressurization of the reactor with CO_2 was done using a programmable syringe pump (ISCO), capable of reaching 483 bar. The pump was run until the desired pressure was reached inside the HXRD reactor and a valve separating the two was closed. Pressure inside the reactor was monitored by an Omega transducer connected to one of two ports in the base. Reactor temperature was monitored through a thermocouple positioned in the top of the beryllium cap. Research grade CO_2 was purchased from a local gas distributor (OXARC) and either deionized water (DI) or oxygen-18 labeled water (Fisher) with 97% purity was used in the experiments.

Patterns were collected on a D8 Discover XRD unit equipped with a rotating Cu anode (1.54 Å), göbel mirror, 0.5 mm collimator, and 0.5 mm pin hole (Madison, WI). A GADDS® area detector system positioned at 28.0 °2θ with a measured distance from the sample of 15 cm was used to capture diffraction images. Collection of individual XRD tracings required 200 seconds with power settings of 45 kV and 200 mA. Initially, images were processed with Bruker-AXS GADDS® software before importing into JADE® XRD software to obtain peak positions (°2θ) and intensities. Identification of the mineral phases in the background-subtracted patterns was based on a comparison of the XRD patterns with the mineral powder diffraction files (PDF™)

published by the Joint Committee on Powder Diffraction Standards (JCPDS) International Center for Diffraction Data (ICDD) (Newtown Square, Pennsylvania). Quantitative XRD analysis was carried out using full pattern fitting with the TOPAS software (version 4.2, Bruker AXS Germany). Powder patterns calculated from published crystal structures for forsterite [1] and nesquehonite [2] were matched to the experimental patterns using pseudo-Voigt line profiles. The *in-situ* grown nesquehonite exhibited pronounced preferred orientation, which was modeled with a spherical harmonics approach [3]. The unit cell and line profile parameters for each phase, and preferred orientation for nesquehonite, were established using patterns with a high relative concentration of the relevant phase. Quantification could then be carried out by refining only the scale factors and background. Magnesite was incorporated into patterns when necessary to account for residual intensity in the diffraction peak near 32° 2θ [4]. Surface characterization was obtained from scanning electron microscopy (SEM) and focused ion beam (FIB) SEM after vapor deposition of a thin layer of either carbon or gold onto the sample.

Summary of in situ High Pressure Infrared Spectroscopy (IR) Experimental Procedure

Experiments were conducted at 50° C and 100 bar. Supercritical CO_2 was circulated by an HPLC pump in a closed loop from vessels housed in a laboratory oven to a transmission IR flow cell within a Perkin Elmer Spectrum One IR spectrometer with a 1mm path length. Dilute suspensions of forsterite were pipetted directly onto the ZnSe window resulting in a thin mineral coating. Spectra were obtained by averaging 128 scans that were recorded over the range 4000-700 cm^{-1} with a resolution of 4 cm^{-1}. First, a background spectrum was collected of the flow cell charged with dry $scCO_2$. Then, a vessel containing wet $scCO_2$ was put into the flow loop, and sample spectra were collected at 3-minute intervals for 24 hr. The concentration of water dissolved in the $scCO_2$ was determined to be 30% of the saturation level by using the absorbance

of the HOH bending mode of solvated water (1607 cm^{-1}) as derived from a calibration curve. At the end of the experiment, a vessel containing a desiccant ($CaSO_4$) was put into the flow loop, and a sample spectrum was collected after the water was removed from the system. Spectral contributions of water dissolved in the supercritical phase were removed by subtracting an independently collected spectrum of H_2O dissolved in $scCO_2$ at the same temperature and pressure. Spectra were baseline corrected to facilitate visualization of trends. This correction was carried out above 2400 cm^{-1} by subtracting the line fit through the absorbance values between 790-820 cm^{-1} and 1800-1900 cm^{-1}, and below 2400 cm^{-1} by subtracting the line fit through the absorbance data points between 2550-2600 cm^{-1} and 3850-3900 cm^{-1}.

Summary of Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) Analysis Procedure

Mounted samples were placed into the FIB SEM instrument chamber and the air was removed (Helios 600 Nanolab dual beam, FEI Co., Hillsboro, OR). Samples were first scanned with the SEM to examine the surface features and to select sites for FIB milling. SEM imaging was performed with the field emission gun electron column available in the same system, with a SEM beam voltage of 5 kV and ~100 pA current. Prior to milling, a protective carbon cap was deposited on an area of interest. The carbon cap was deposited at 2um wide and 20um using 30 keV and 0.5nA. The stage was moved from 0 degree tilit for SEM, to a 52 degree tilt position for FIB. For FIB milling positively charged gallium (Ga) ions were field emitted from a liquid metal ion source. A first milling pass was made using a 5–7 nA and 30 keV Ga+ energy beam that removed a 25um×2um×2um cross section of the sample. A second (cleaning) pass was made with 0.3–1.0 nA and 30 keV Ga+beam to remove most striations.

Summary of Thermo Gravimetric Analysis Procedure

Thermo gravimetric analysis coupled to mass spectrometry (TGA-MS) was performed on a TG-209F1 (Netzsch Instruments) by heating the samples to 900° C with a heating ramp of 2 °C/min under N_2 flow (20 ml/min). Mass spectrometric analysis was done simultaneously on an Aeolos QMS-403C. Generally between 3 and 4 mg of sample were analyzed while monitoring ion currents corresponding to $H_2{}^{16}O$ (m/z 18), $H_2{}^{18}O$ (m/z 20), $C^{16}O^{16}O$ (m/z 44), and $C^{16}O^{18}O$ (m/z 46). Published TGA-MS data was used to quantify the amount of nesquehonite or magnesite in the reacted samples. A magnesite standard from the Excalibur Mineral Corporation (Peekskill, NY) produced a ~51% weight loss after heating to 850 °C, which is in agreement with Demir et al., [5].

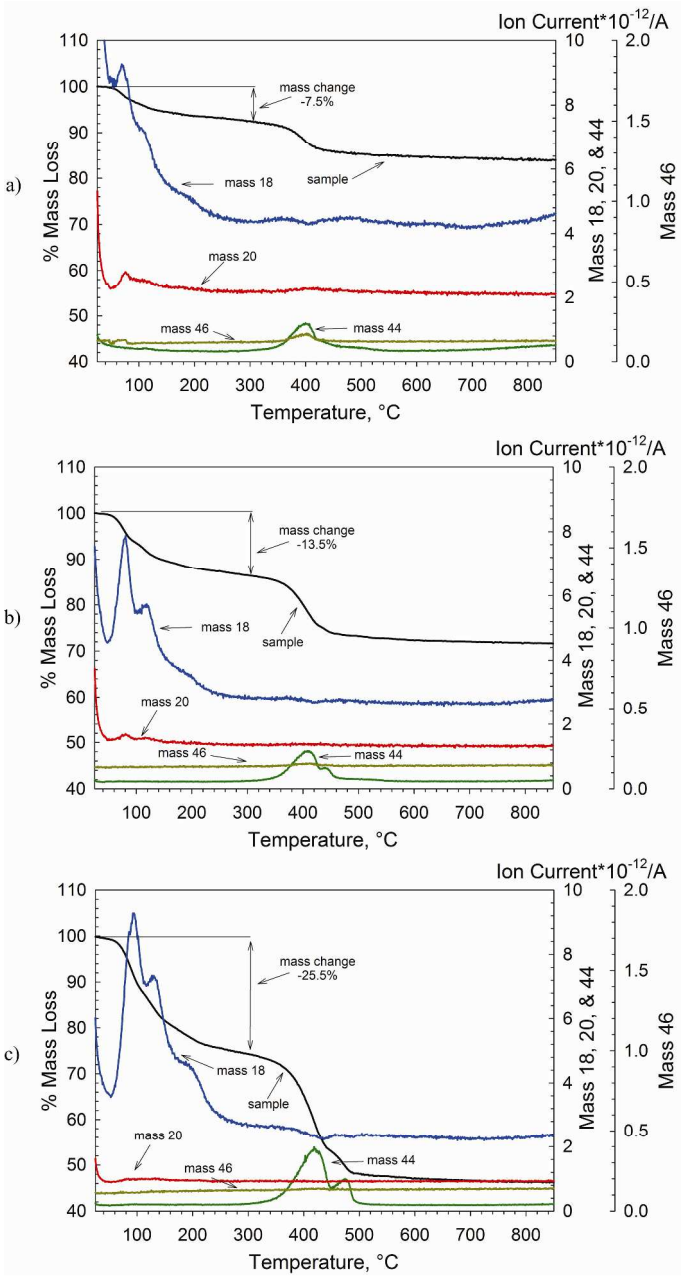

Figure S1. Results obtained from TGA-MS of post reacted sample from a) **EXP # 3**, b) **EXP # 4**, and c) **EXP # 5** illustrating the decomposition of nesquehonite and changes to ion current (m/z) for masses 18 ($H_2{}^{16}O$), 20 ($H_2{}^{18}O$), 44 ($C^{16}O^{16}O$), and 46 ($C^{16}O^{18}O$).

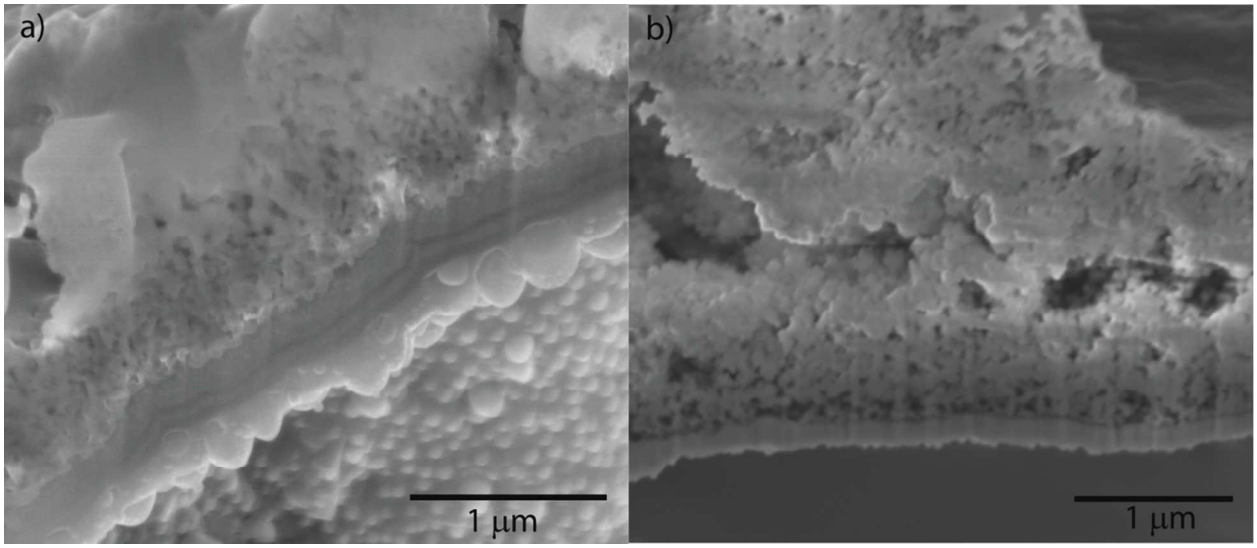

Figure S2. Cross section profiles obtained from FIB-SEM of post reacted samples from a) **EXP # 3** and b) **EXP # 4** that show a structured layer forming on the surface of the forsterite.

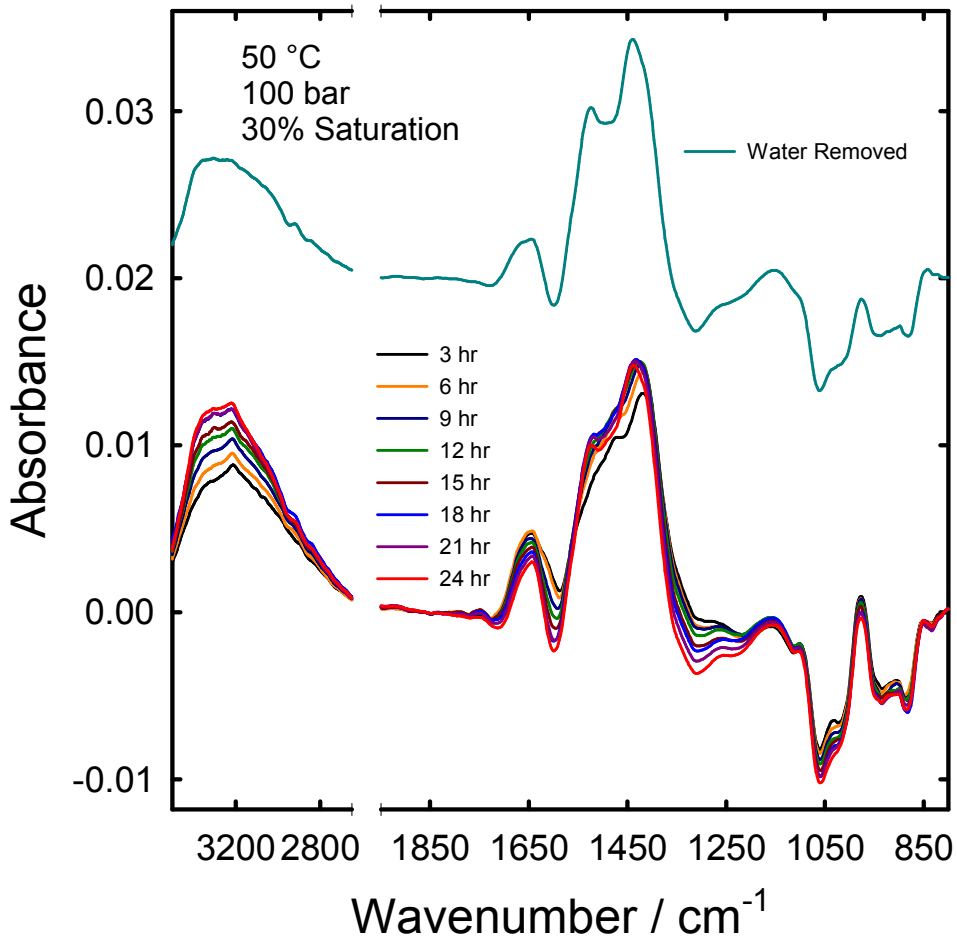

Figure S3. Infrared spectra as a function of time during the reaction of forsterite with $scCO_2$ at 50°C, 100 bar, and 30% water saturation for a period of 24 hours. The background spectrum in each experiment was of the transmission IR flow cell pressurized with dry $scCO_2$ in the beginning of the experiment and with the unreacted forsterite overlayer on one of the ZnSe windows. The spectrum of water dissolved in the $scCO_2$ has been subtracted. Also shown is a spectrum collected at the end of the experiment after removing the water from the $scCO_2$ (offset for clarity).

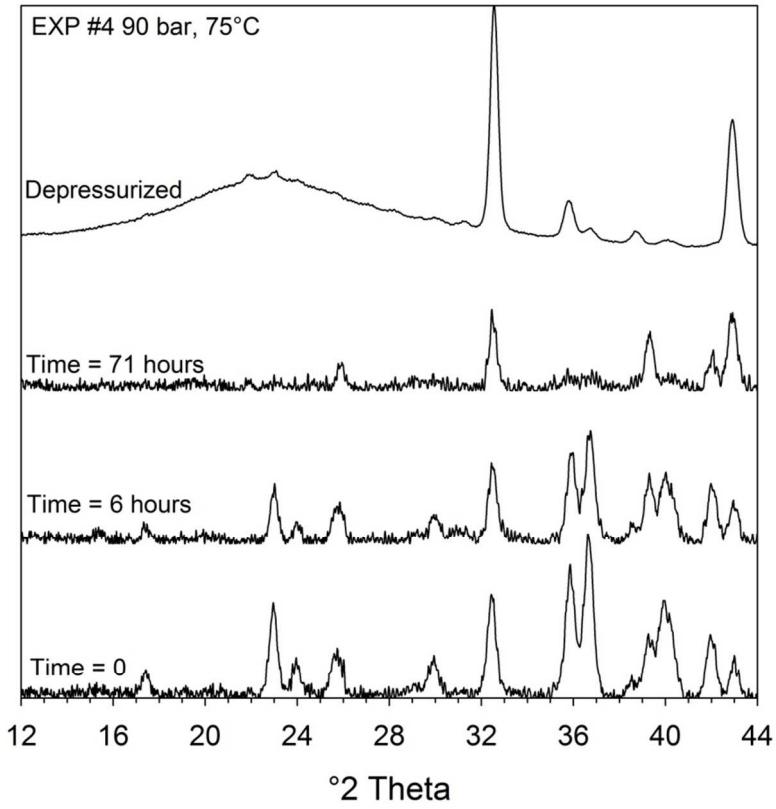

Figure S4. Results obtained from *in situ* HXRD experiments (**EXP # 7**) reacting forsterite with H_2O saturated $scCO_2$ at 75° C and 90 bar at time 0, 6, and 71 hours. The depressurized pattern was collected without background subtraction to better illustrate the presence of amorphous material.

References

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