

In-Situ Liquid Cell TEM Observations of Silicate Mineral Dissolution

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The chemical weathering of silicate minerals controls in large part the chemical composition of natural waters, such as lakes, rivers, and oceans. Weathering reactions are an important sink for CO₂, and play a critical role in the global carbon cycle, which in turn has implications for climate change. Chemical weathering is also crucial to current environmental issues such as acid mine drainage, and geological CO₂ storage and sequestration schemes. Understanding the mechanisms of mineral dissolution at the nanoscale is therefore a prerogative for predicting and modeling chemical weathering at multiple scales, ranging from the microscale up to the global scale. Even though silicate mineral weathering has been intensely studied both experimentally and in natural settings for many decades now, the exact mechanisms that control dissolution are still being debated. During dissolution in aqueous solutions, multi-cation silicate minerals develop a secondary altered surface phase, which can be either crystalline or amorphous. Understanding how this surface layer develops is a key to understanding the mechanism of dissolution [1-2]. Until recently, post-altered mineral (and glass) surfaces have been examined using conventional TEM and other high-resolution techniques, such as atom probe tomography. However, to better understand the operative mechanism(s), the mineral dissolution process should ideally be examined in situ in their native fluid environment. To address this issue, we are currently employing nanoscale measurements via in situ liquid cell TEM to examine the in situ dissolution of a common chain silicate mineral, wollastonite (CaSiO₃). Preliminary results show that surfaces retreat on the nm-scale and this dissolution can be measured in real time.

Focused ion beam (FIB) milling was used to prepare an electron transparent wollastonite lamella measuring 25µm x 4 µm x 100nm thick for the fluid cell experiments. A Protochips Poseidon holder (for use in a Hitachi HF3300 TEM/STEM) with a liquid layer thickness of 5 µm was used. To reduce Ga implantation and amorphous material on the surface of the FIB lamella, a Fischione Nanomill was operated at 900eV to Ar⁺ mill each side of the sample at 10° for 10min. The FIB sample was then micromanipulated such that the region of interest (ROI) was placed over the 40nm thick SiN membrane of the liquid cell platform and attached to the edge of the Si chip using e-beam deposited C. TEM observations were performed at 300kV and electron dose was minimized by keeping the gun valve closed except when capturing TEM images. The deionized water (DI) flow-rate through the fluid cell was set at rate of 10µL/min.

Figures 1a-d show the FIB fabrication process for the silicate lamella, which was first thinned to electron transparency and then attached to the fluid cell window. Figure 2a shows the bright-field (BF) TEM image of the wollastonite lamella before DI water was introduced into the fluid cell. Note that a crack in the lamella (arrow) occurred during the placement of the top window on the fluid cell. The TEM images shown in Figures 2b-c show evidence for dissolution of the wollastonite localized at the crack after DI water was introduced into the fluid cell. The TEM images and corresponding image intensity profiles across the crack (see inset rectangles in Figure 2) were used to quantify the progression of the

dissolution front. The most reactive area of the sample appeared to be the crack faces, and the corresponding change in BF image contrast indicated that the thickness of the lamella changed in these regions after 76 minutes. Future work will concentrate on supplementing the structural retreat rates with nanoscale chemical data from EFTEM and EELS analyses [3].

[1] R Hellmann *et al*, Phys. Chem. Miner. 30 (2003) p. 192-197.

[2] R Hellmann *et al*, Nature Materials DOI:10.1038/NMAT4172 (2015).

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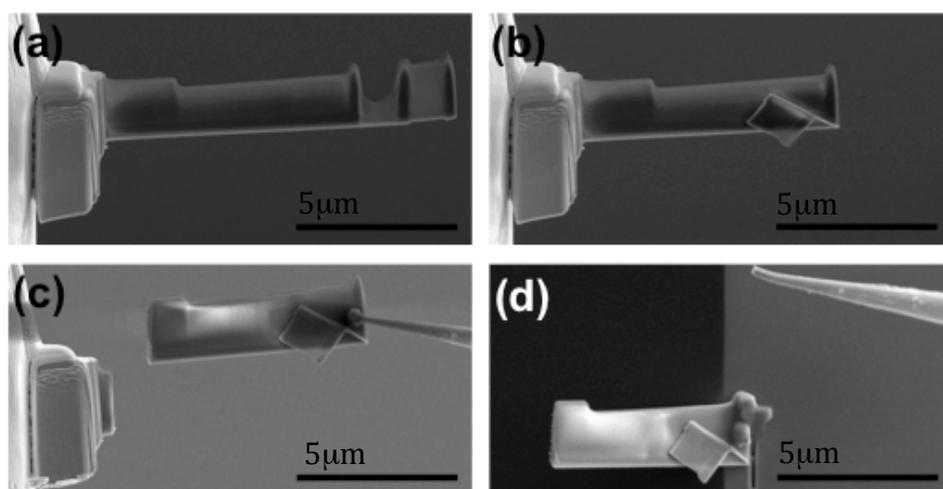


Figure 1. (a) FIB lamella of wollastonite. (b) Thinned window stuck to sample, which was used as fiducial. (c) Lamella after Ar ion milling attached to micromanipulator needle. (d) Wollastonite lamella attached to edge of Si substrate of liquid cell platform with thinned region of interest over SiN window.

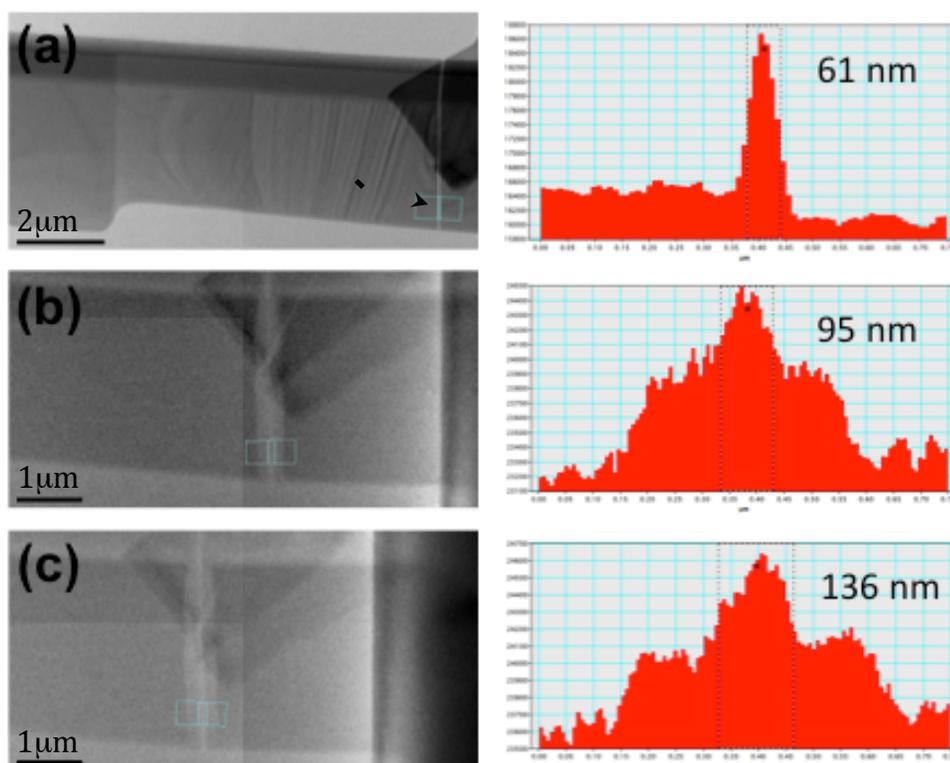


Figure 2. BF TEM images showing (a) silicate lamella with no fluid in cell, with arrow indicating crack. Crack width measures 61 nm. (b) Liquid cell filled with DI water and dissolution observed at crack faces. Crack width measures 95 nm. (c) Imaged 76 minutes after liquid introduced into cell with the crack faces still undergoing dissolution. Crack width measures 136 nm.