

Experimental Investigation of Mineral Reaction Rates in Venus Relevant Gases

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Introduction

The weathering reactions of rocks and minerals on Venus have been predicted through thermodynamic modeling and experiments for decades, but in recent years, the style and rate of weathering reactions has gained new importance. With the advent of near 1 μm emissivity spectroscopy from orbit, weathering rates are critical to know in order to use this data to constrain ages of lava flows (e.g., [1-2]) and the mineralogical evidence of past environments that may be preserved into the present day due to slow reactions, despite mineral instability in modern atmospheric conditions (e.g., [3]). In order to address weathering rates of a variety of minerals, we established an experimental setup to include the temperature of the Venus surface (460 $^{\circ}\text{C}$), as well as combinations of the most abundant gases of the atmosphere (CO_2 , SO_2 , N_2). This simplified set of conditions allow the investigation of the effect of specific variables in a way that complex experiments cannot address. The combination of both simplified and complex experiments is necessary to understand weathering reactions and rates on Venus. The functionality of our setup is demonstrated here by a set of preliminary experiments using mineral indicators of hydrous or aqueous environments.

Methods

Samples used in these experiments include calcite, biotite, and montmorillonite. Calcite has been demonstrated to react relatively rapidly with sulfur-bearing gas in previous experiments [4-5] and will be a useful point of comparison for our methods. Biotite was shown to react under simulated Venus conditions in past experiments [6], and should provide a reference point for more slowly reacting minerals than calcite. Montmorillonite was chosen in order to test our protocols with a mineral requiring extra protection against post-experiment reaction with the terrestrial environment.

Experiments were conducted using Thermo Fisher Scientific Lindberg/Blue M Mini-Mite horizontal tube furnaces at Wesleyan University. The furnaces have been set up in a flow through configuration so that solid samples are exposed to a fixed gas composition. Gases used are provided in premixed cylinders from AirGas, and compositions are listed in the matrix below (Table 1). The furnaces have also been configured to accommodate three 1/4" or two 1/2" diameter quartz glass process tubes, with gas flow split between them. In some cases, multiple grain sizes of the same mineral were included in single tubes, separated by quartz wool. Experiments were conducted at 460 $^{\circ}\text{C}$ and gas flow rates were monitored with a ThermoScientific GFM Pro flow meter. Tubes were only filled halfway to allow gas to easily flow over the samples, and sample was kept within 10 $^{\circ}\text{C}$ of the hotspot temperature. After running for the desired duration, experiments are terminated by closing the gas flow into and out of the process tubes and shutting off the furnace to cool the sample. The entire furnace assembly is then placed into a glove bag, which is filled with nitrogen gas.

Table 1: Experimental conditions.

Experiment Name	Duration (days)	Gas Composition (Trace Gas)	Temperature	Process Tube	Minerals Included
V1	17	SO_2/N_2 (1800 ppm)	460 $^{\circ}\text{C}$	3/4" alumina	Calcite
V3	18	N_2	460 $^{\circ}\text{C}$	1/4" quartz glass	Montmorillonite, Biotite
V4	87	SO_2/N_2 (1.4%)	460 $^{\circ}\text{C}$	1/4" glass	Montmorillonite, Biotite
V5	19	SO_2/N_2 (1.4%)	460 $^{\circ}\text{C}$	1/2" quartz glass	Calcite
V6	19	$\text{CO}_2/\text{SO}_2/\text{N}_2$ (1.4% SO_2 , 2.1% N_2)	460 $^{\circ}\text{C}$	1/2" quartz glass	Montmorillonite, Biotite
V8	28	SO_2/N_2 (1.4%)	460 $^{\circ}\text{C}$	1/2" quartz glass	Biotite, Calcite

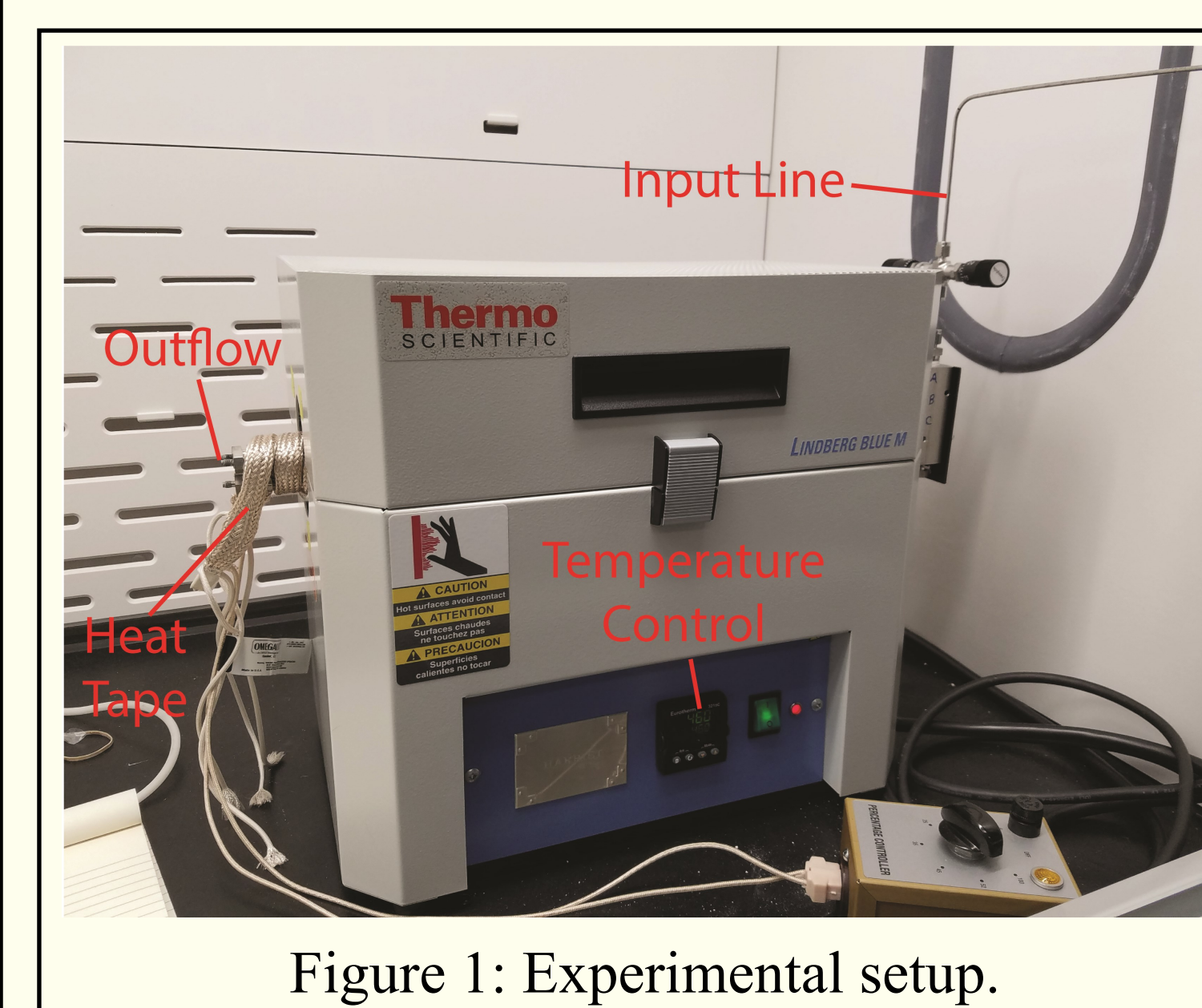


Figure 1: Experimental setup.

The process tubes are then opened, and samples are placed in vials for storage in a desiccator until analysis.

Experimental run products have been analyzed by NIR spectroscopy and Scanning Electron Microscope (SEM). NIR spectroscopy (350-2500 nm) was also conducted in a nitrogen filled glove bag setup, and at this time an aliquot was also extracted for examination on the SEM. SEM examination was conducted using a Hitachi SU5000 Field Emission Gun Scanning Electron Microscope (SEM) equipped with an EDAX Octane Pro EDS detector located at Wesleyan University. Run products examined thus far are discussed below.

Preliminary Results

Biotite

After 19 days exposed to a three gas mixture, occasional small particles stuck to the surface of the biotite reacted with sulfur in the gas (Fig. 2B). These parti-

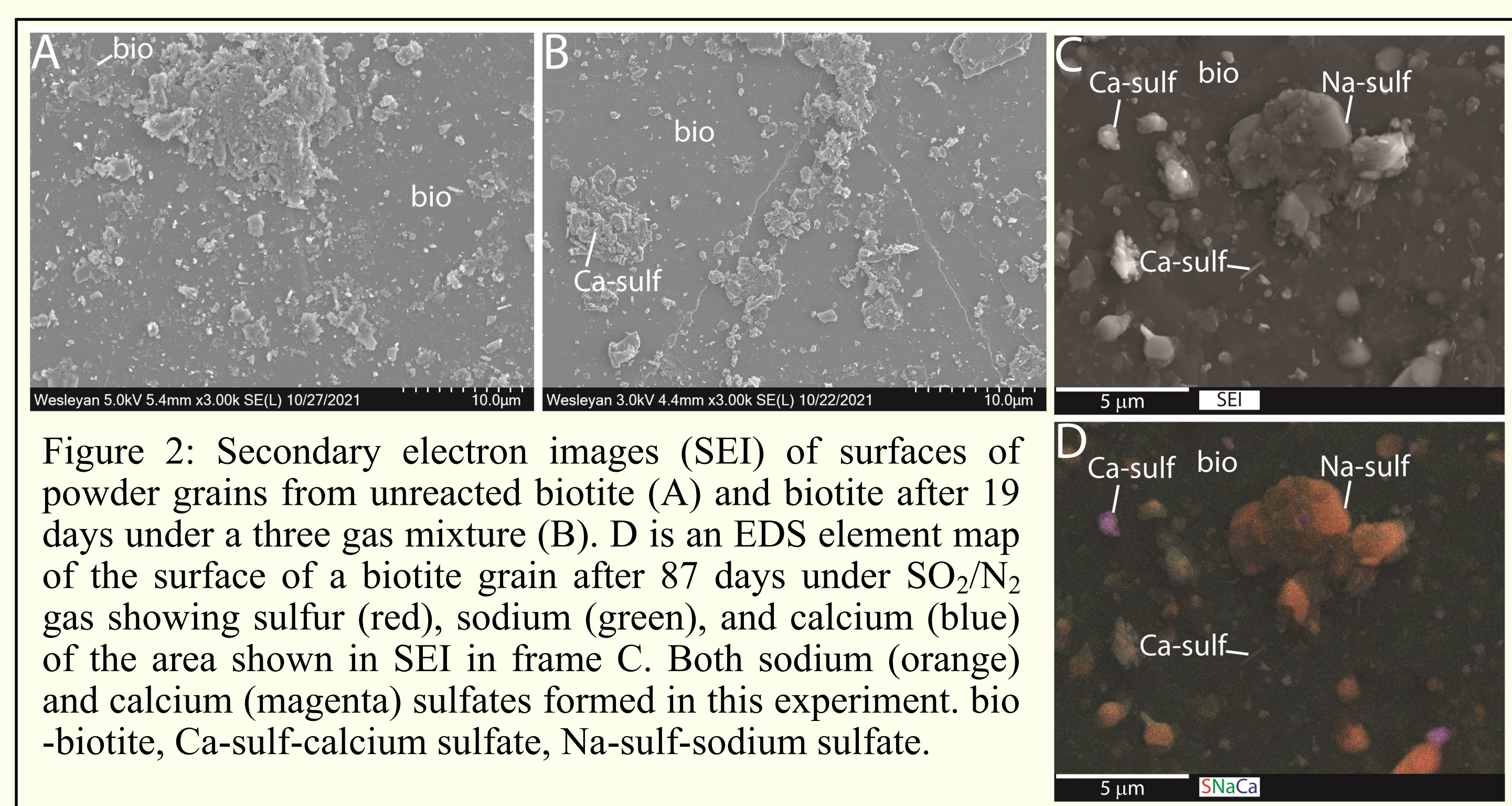


Figure 2: Secondary electron images (SEI) of surfaces of powder grains from unreacted biotite (A) and biotite after 19 days under a three gas mixture (B). D is an EDS element map of the surface of a biotite grain after 87 days under SO_2/N_2 gas showing sulfur (red), sodium (green), and calcium (blue) of the area shown in SEI in frame C. Both sodium (orange) and calcium (magenta) sulfates formed in this experiment. bio-biotite, Ca-sulf-calcium sulfate, Na-sulf-sodium sulfate.

cles are also present in the unreacted biotite (Fig. 2A). The biotite grains themselves do not appear to have reacted. This 250-355 μm fraction of the sample appeared to exhibit magnetic behavior when being manipulated for analysis. The <45 μm fraction exposed to SO_2/N_2 gas for 30 days exhibited similar behavior. This sample also shows a change in its VNIR spectrum consistent with the presence of hematite (Fig. 3). After 87 days exposed to SO_2/N_2 gas, both calcium and sodium sulfates formed, based on EDS analysis. These phases occasionally have some facets, but are largely anhedral. Some occur as small laths, either on grain surfaces or among small particle clusters. They appear to largely be forming from or around particles on the grain surface. VNIR spectroscopy results are shown in Figure 3.

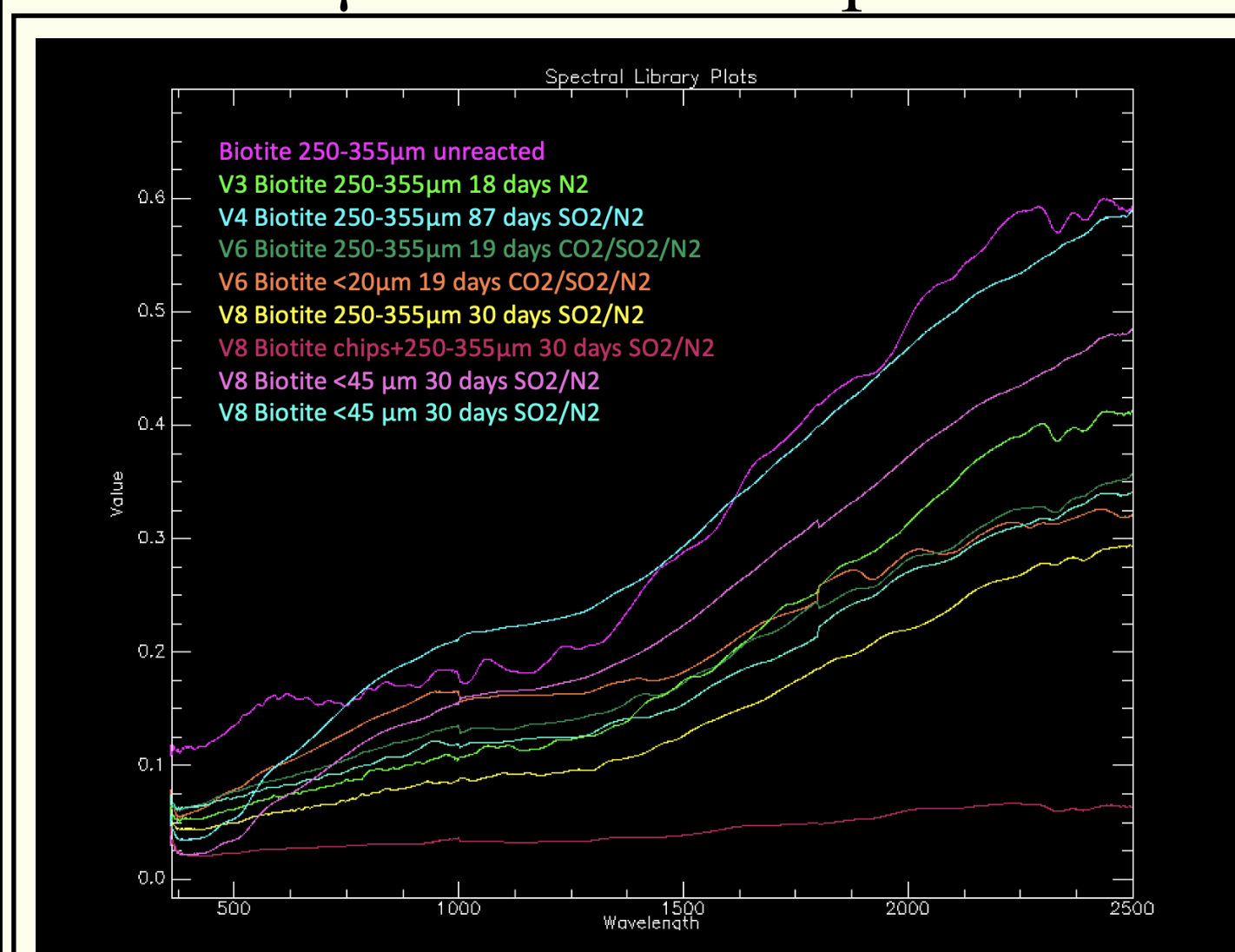


Figure 3: VNIR spectra of biotite measured under N_2 gas.

Calcite

In both experiments analyzed, the calcite grain surface and small particles reacted to form Ca-sulfate with a blocky texture. The 17 day experiment with higher SO_2 concentration appears to have produced more extensive reaction than the 19 day experiment, and in the 19 day experiment the surface particles tend to have a larger S peak in their EDS spectra compared to the grain surface, suggesting greater degree of reaction in the particles. VNIR spectra show no detectible changes after 17 or 19 days under SO_2/N_2 gas (Fig. 5).

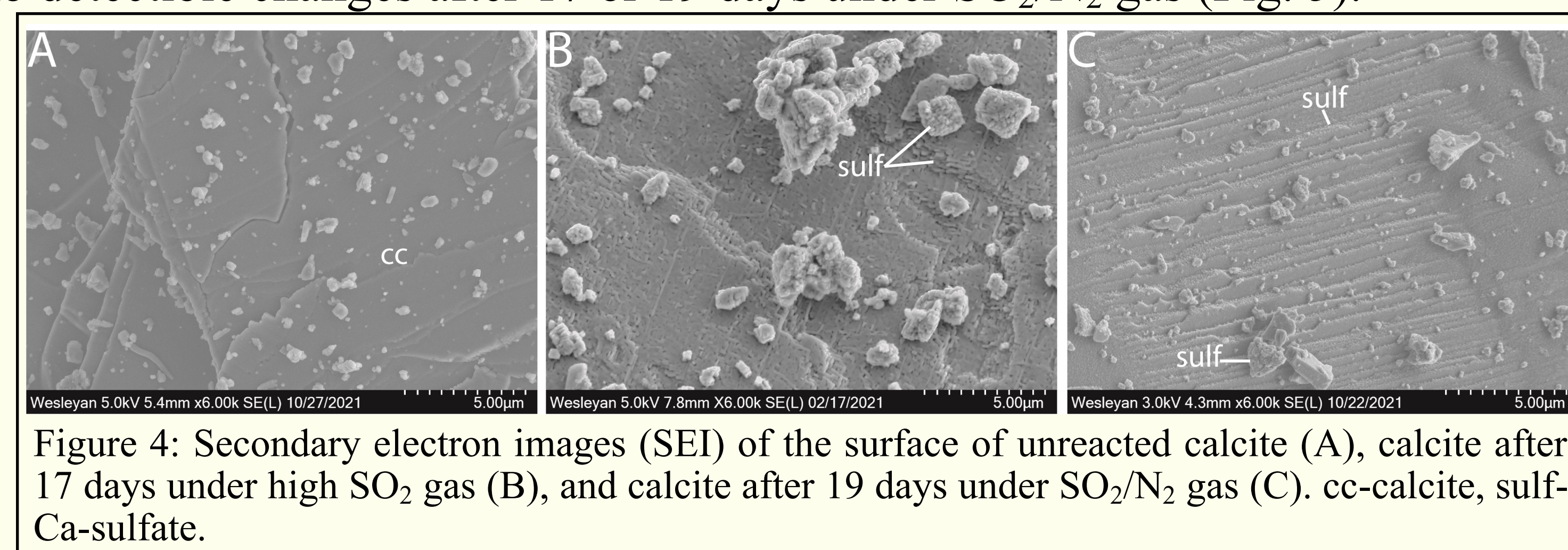


Figure 4: Secondary electron images (SEI) of the surface of unreacted calcite (A), calcite after 17 days under high SO_2 gas (B), and calcite after 19 days under SO_2/N_2 gas (C). cc-calcite, sulf-Ca-sulfate.

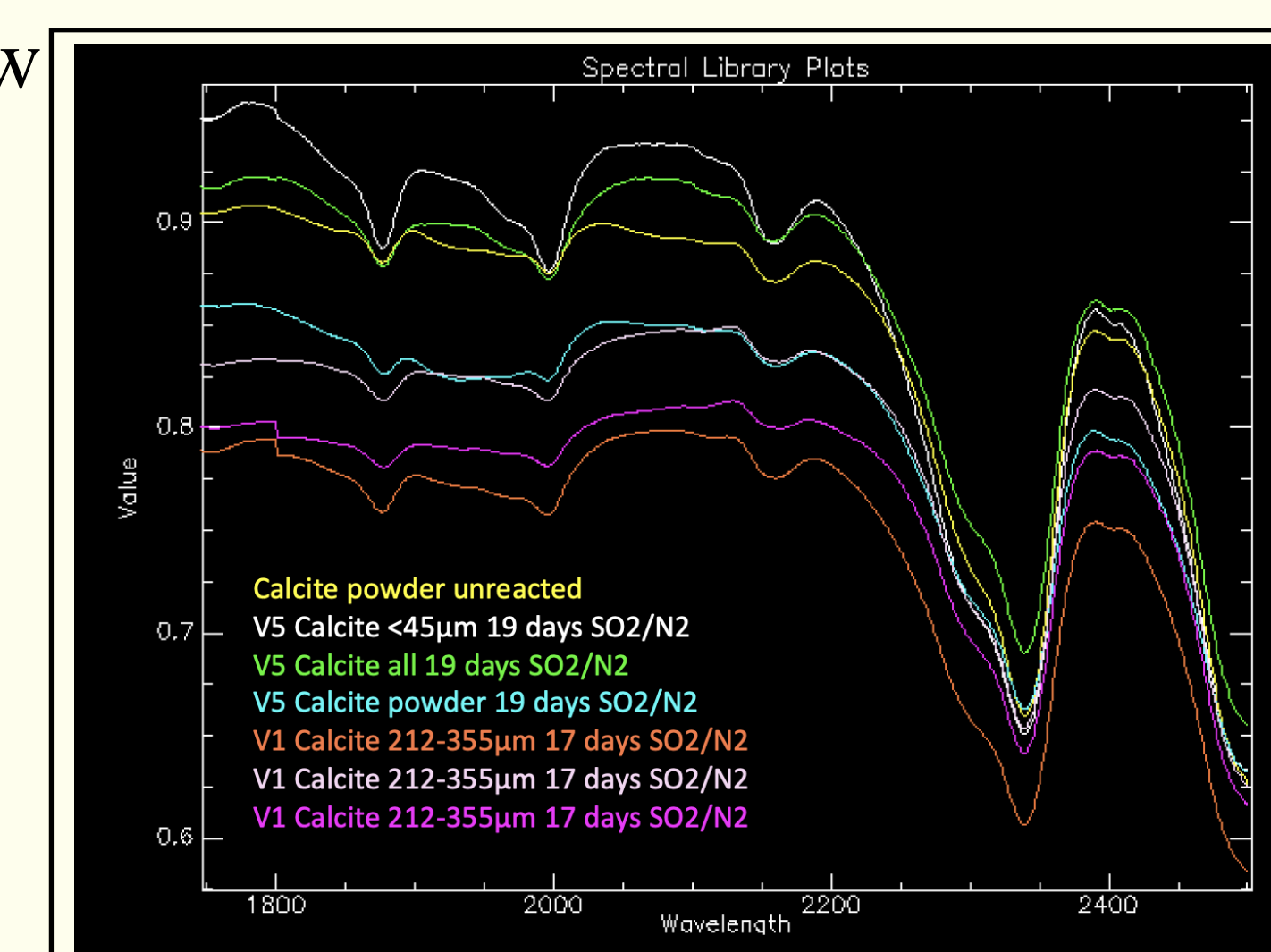


Figure 5: VNIR spectra of calcite measured under N_2 gas.

Montmorillonite

In both experiments, (19 days, three gas mix; 87 days, SO_2/N_2 mix) the small particles on the montmorillonite grains appear to have reacted with sulfur in the gas. It is difficult to determine if specific grains of secondary minerals have grown, as the exterior of the montmorillonite grains are covered in small particles of montmorillonite, but sulfur was present in all locations measured by EDS. The S peak appeared slightly more intense after 87 days vs. 19 days. VNIR results show montmorillonite loses water (1900 nm band) under all three gas mixtures in as little as 18 days, but has not completely dehydrated after 87 days. The 1400 nm OH band changes position and the 2210 nm band shifts to slightly shorter wavelengths in as little as 18 days. A ~2300 nm feature is visible as a shoulder in the 18/19 day experiments, but deepens in the 87 day experiment.

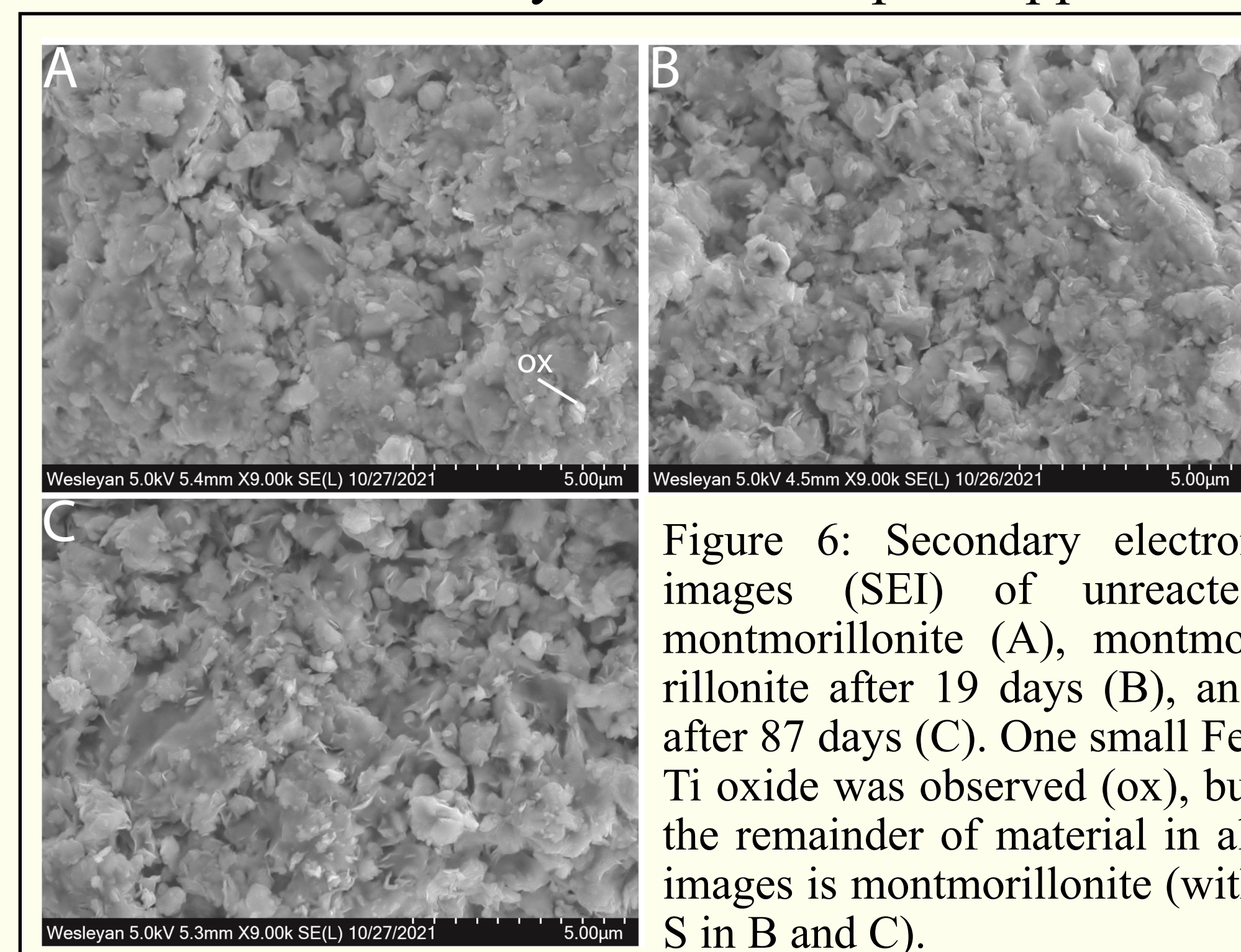


Figure 6: Secondary electron images (SEI) of unreacted montmorillonite (A), montmorillonite after 19 days (B), and after 87 days (C). One small Fe-Ti oxide was observed (ox), but the remainder of material in all images is montmorillonite (with S in B and C).

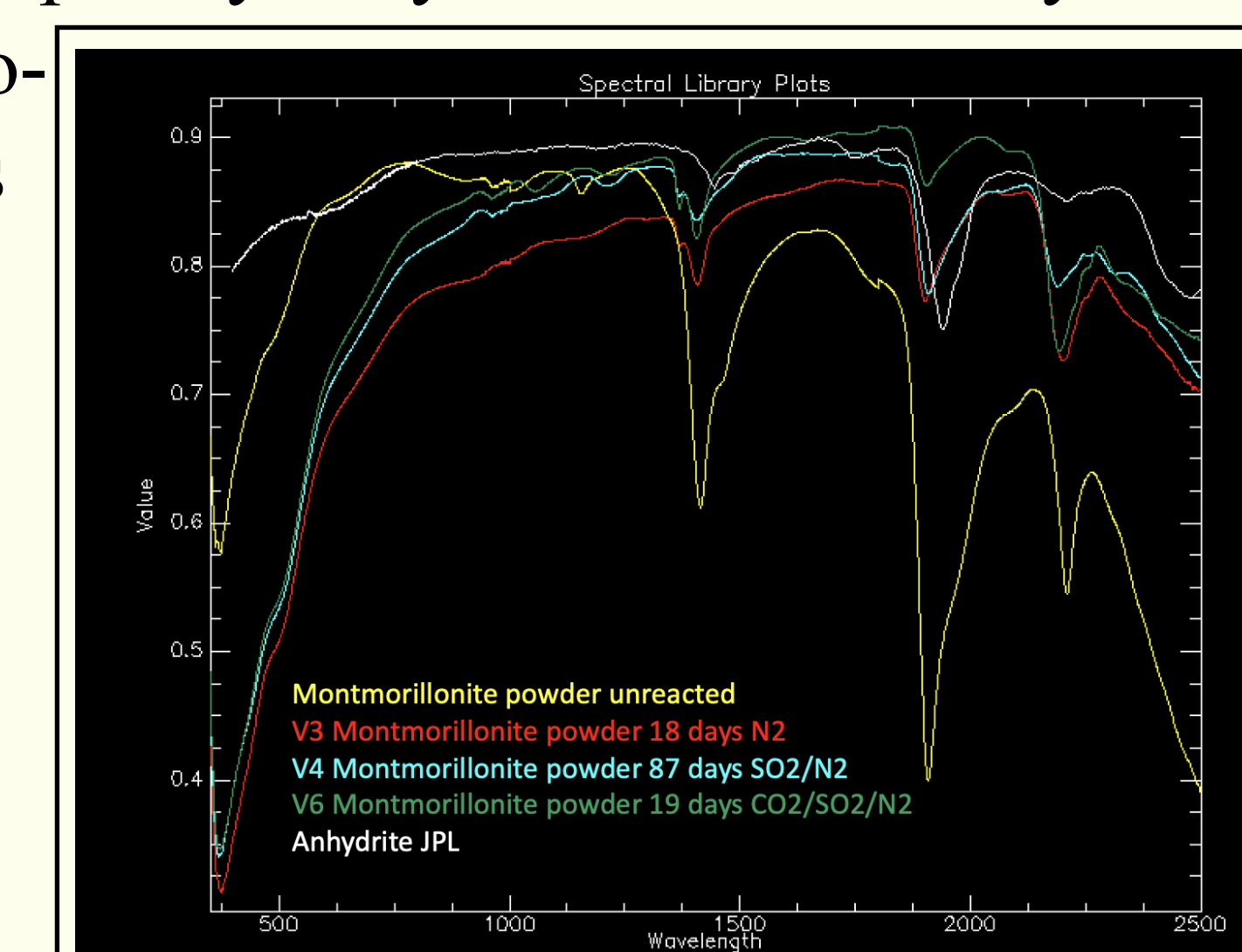


Figure 7: VNIR spectra of montmorillonite measured under N_2 gas.

Future Work

Experimental protocols are still being developed to better be able to constrain mineral reaction rates. This includes improved sample preparation methods to remove fine particles stuck to mineral powder grain surfaces and testing of storage methods to ensure no post-experiment rehydration occurs before NIR measurement.

Once protocols are in place, this work will expand both minerals being studied and analytical techniques employed. An important point of comparison to be made is between results obtained in this setup and results from complex facilities such as the Glenn Extreme Environment Rig (GEER), in order to determine the effect of variables such as pressure and additional trace gases such as water vapor and halogens.

References

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