

EXPERIMENTAL ALTERATION OF BASALTIC SILT AT 200-300°C UNDER REACTIVE (CO₂) AND INERT (N₂) ATMOSPHERES. J. A. Hurowitz¹ and N. J. Tosca², ¹Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100, joel.hurowitz@stonybrook.edu, ²Department of Earth Sciences, University of St. Andrews, St. Andrews, KY16 9AL, Scotland, UK, njt6@st-andrews.ac.uk.

Introduction: Despite their utility as tracers of global scale climate on Earth, our understanding of martian clays, and of the martian clay cycle, is in its relative infancy. To provide a foundation for interpreting results from the MSL mission, and to support future Mars investigations, an improved understanding of the martian clay cycle is needed. Here, we present the results of experiments aimed at addressing the question: What is the nature of clay-bearing mineral assemblages that arise from the alteration of basalt on Mars? We focus on the alteration of silt to very-fine sand sized particles of a well-characterized terrestrial analogue from the Columbia River Basalt (CRB) under conditions intended to mimic those that might be experienced during burial diagenesis, low grade metamorphism, and/or hydrothermal alteration: temperatures of 200-300°C under conditions of anoxia in the presence of reactive (CO₂) and inert (N₂) atmospheres.

Basalt Description: The basalt sample used in this study was collected outside of the town of Craigmont, ID from the N1 magnetostratigraphic unit of the Grande Ronde flow of the CRB. At the sample collection site, a roadcut exposes a 10-m thick section of massive, aphanitic basalt that grades upward into progressively more weathered basalt, saprolite, and a paleosol. Our experiments were performed on a sample of basalt collected from the base of the roadcut, designated “LC-01”. Sample LC-01 is one of a suite of samples from the exposed section described in [1].

The chemical composition of sample LC-01 was analyzed using a combination of ICP emission spectroscopy following fusion and acid digestion and Instrumental Neutron Activation Analysis and reveals major, minor, and trace element characteristics typical of the N1 unit of the Grande Ronde basalt [2], with no obvious evidence for chemical weathering.

A thin section of LC-01 was analyzed by optical microscopy and SEM-EDX. LC-01 is characterized by an intergranular to intersertal texture; microscopy based-estimates of the modal mineralogy indicate ~60-65% fine-grained groundmass, made up of 100-300µm plagioclase laths (~50%), 25-100µm anhedral pyroxenes (~25%), and a dark brown isotropic phase (~25%), possibly glass, that is frequently reddish-brown in coloration, potentially indicating oxidation/alteration to Fe-oxide. Roughly 5-10% of the sample is composed of ~25-500µm subhedral to euhedral opaque Fe-Ti oxide minerals. Microphenocrysts make up the remaining 25-30% of the population,

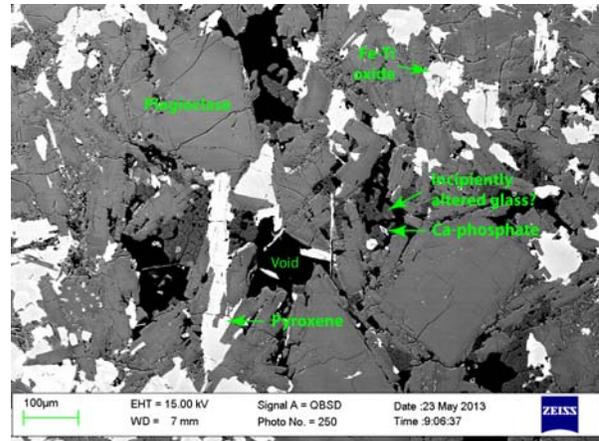


Fig. 1: SEM backscatter electron image revealing typical groundmass phases and textures in LC-01.

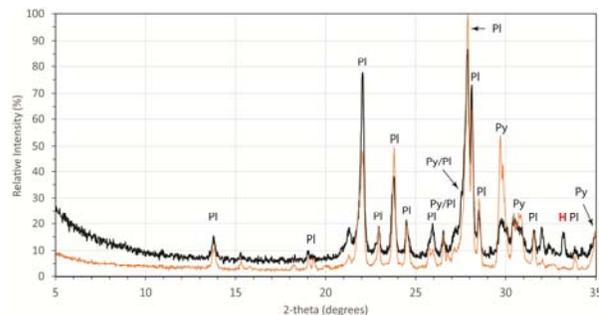


Fig. 2: XRD patterns of LC-01 randomly oriented powder (orange) and oriented <2µm fraction (black), which reveals no evidence of fine-grained alteration phases except for hematite (H). Pl = plag, Py = pyx.

and are composed of roughly equal proportions of zoned plagioclase, usually 500µm by 200µm, but ranging up to 1mm in length, and euhedral to anhedral clinopyroxene, up to 750µm in length, with possible olivine exhibiting brown fracture fill and rims. SEM-EDX analysis indicates that pyroxene compositions vary within and among grains, reveals the presence of minor Ca-phosphate, Na-K-feldspar, and a patchy phase that varies between pure SiO₂ to a Si, Al, K, Na, Fe-bearing composition, possibly igneous glass undergoing incipient alteration (**Fig. 1**).

Finally, XRD analysis was performed using Cu Kα radiation on a randomly oriented powder sample of LC-01 and an oriented sample of the <2µm fraction that was prepared by sonication, centrifugation, and filter transfer onto a zero background quartz plate [3]. Analysis of the data reveals patterns dominated by plagioclase, pyroxene, and Fe-Ti oxide, with possible

minor contributions from olivine, cristobalite, and sanidine. The only difference between the two samples was the presence of a peak at $33.5^\circ 2\Theta$ in the $<2\mu\text{m}$ sample, consistent with hematite (Fig. 2).

Experimental Methods: Approximately 1kg of hand-sample sized LC-01 material was broken down into cm-sized fragments and fed into a hardened steel jaw crusher to produce basalt fragments of $<3\text{-}5\text{mm}$ size. These fragments were then sieved to separate the $>1\text{mm}$, $125\mu\text{m}\text{-}1\text{mm}$, $45\text{-}125\mu\text{m}$, and $<45\mu\text{m}$ fractions.

Alteration experiments were conducted in two 450mL Parr Instruments stainless steel non-stirred pressure vessels fitted with borosilicate glass liners. 10 grams of the $45\text{-}125\mu\text{m}$ fraction and 100mL of ultrapure water were loaded into the silica glass liners, the reactor vessels sealed, and the reactors purged for a period of 1 hour with N_2 or CO_2 using gas inlet and outlet ports on the vessel heads. After purging was complete, the gas ports were sealed, and the reactor placed into a digitally controlled heater jacket. The reactors were maintained at 200°C for a period of 44 days. Afterward, the reactors were removed from their heater jackets and allowed to cool to room temperature, which required ~ 3 hours. The vessels were opened, fluid pH and Eh were measured, liquid and solid samples were separated from each other, and the solids were dried at 45°C and stored in a vacuum desiccator.

Preliminary Results: At the completion of the N_2 headspace experiment, we measured a solution pH = 7.7 and Eh = -40mV . The solution was cloudy and white owing to the presence of 1.0 gram of suspended solid material that formed during experimentation. The suspended solids were collected by centrifugation and XRD analysis revealed it to be amorphous; it is presumably amorphous silica derived from basalt or the borosilicate liner. A basalt-free control experiment is in progress to determine the source of this material.

An oriented sample of the $<2\mu\text{m}$ fraction was prepared from the altered solids for XRD analysis and also reveals the presence of amorphous material, as well as a distinct low-angle reflection at ~ 7 degrees 2Θ (Fig. 3), consistent with an 001 reflection from a clay mineral. This reflection is not present in the unaltered LC-01 sample and was not visible in a randomly oriented powder sample of the altered material from this experiment. Glycolation of the $<2\mu\text{m}$ fraction resulted in a peak shift to lower 2Θ , consistent with a neoformed smectite (Fig. 3). In addition, a number of new peaks in the randomly oriented powder sample from this experiment occur between $62\text{-}64$ degrees 2Θ (not shown), consistent with a dioctahedral clay structure.

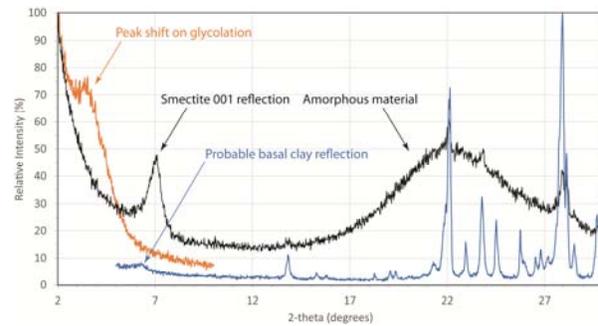


Fig. 3: XRD patterns of the oriented $<2\mu\text{m}$ fraction of LC-01 altered under N_2 (black), and after glycolation (orange), and a randomly oriented powder of LC-01 altered under CO_2 (blue).

At the completion of the CO_2 headspace experiment, solution pH was 5.5 and Eh = -480mV and the solution in this case was clear. XRD analysis of a randomly oriented powder sample from this experiment also reveals the presence of a low angle reflection at ~ 6.25 degrees 2Θ that is not present in the unaltered LC-01 sample. Work is currently in progress to isolate the $<2\mu\text{m}$ fraction from this experiment and determine if this is also a neoformed clay mineral.

Summary and Future Work: Our results indicate that clay minerals and amorphous silicates are readily formed at 200°C as a result of reactions between unaltered basalt and ultrapure water under anoxic conditions in the presence of an inert gas. This mineral assemblage is somewhat surprising given the elevated temperature of our experiments, where more diagenetically mature phases (e.g., quartz, illite, chlorite) might be expected to form. Preliminary results under a reactive CO_2 headspace indicate the development of extremely reducing conditions and the possible formation of a clay mineral at pH = 5.5, again somewhat surprising given the relatively acidic fluid conditions. These experiments provide promising early results for understanding the formation of basalt-hosted clay mineral assemblages under diagenetic, burial metamorphic, and hydrothermal conditions on Mars.

We will report on control experiments, solution chemistry analyses and additional solid phase analyses to provide a more complete understanding of secondary phase forming reactions in our 200°C experiments. In addition, we will report on initial results from identical experiments conducted at 300°C .

References: [1] Thomson, B.J. et al. (in press) *EPSL*; [2] Riedel, S.P. (1982) *Idaho Bureau of Mines and Geology Bull.*, 26, 77-101; [3] Moore, D.M., & Reynolds, R.C., (1997) *XRD and the ID and Analysis of Clay Minerals*, 379pp.