

**CLAY MINERAL ASSEMBLAGES DERIVED FROM EXPERIMENTAL ACID-SULFATE BASALTIC WEATHERING.** N. J. Tosca<sup>1</sup>, <sup>1</sup>Dept. of Organismic & Evolutionary Biology, Harvard University, Cambridge, MA 02138 USA; [ntosca@fas.harvard.edu](mailto:ntosca@fas.harvard.edu)

**Introduction:** Clay-bearing assemblages identified on the ancient martian surface have the potential to yield detailed paleo-environmental constraints on the Noachian climate. The formation of clay minerals in low-temperature aqueous environments is dependent on a number of parameters including initial pH, chemistry, temperature, host lithology, drainage and hydrology [1,2]. As a result, the formation of clay minerals from chemical weathering has been studied for decades by a number of techniques [2]. However, the formation of clay minerals at low-temperature is notoriously slow and difficult to achieve in the laboratory.

Closed-system basaltic weathering experiments were conducted on pristine analog olivine-basalt and basaltic glass at a variety of water-to-rock ratios and initial pH. The experiments were run at controlled conditions for 295 days and almost all of the experiments have yielded enough clay to be separated and analyzed in detail and linked to the parent aqueous solution. These experiments capture a limited range in environmental variables but offer a unique opportunity to connect the formation of specific clay minerals to aqueous chemistry in a controlled experimental setting.

**Methods:** The starting materials used in the study, a crystalline olivine-basalt and a glassy scoriaceous basalt, were obtained from Ward's Natural Science. The crystalline basalt is dominated by augite and plagioclase and contains olivine with accessory Fe-Ti oxides and residual glass. The scoria is fine-grained and glassy, highly vesicular and dominated by plagioclase and pyroxene. Bulk samples of starting materials were cut on all sides to attempt to remove surface features, and then crushed to 74-420  $\mu\text{m}$  and <74  $\mu\text{m}$  size fractions. Ultrafine particles were removed by periodic rinsing and sonication in acetone.

Experiments were run in 50 mL centrifuge tubes capped under ambient oxidizing atmosphere with Teflon tape and were placed in a 25( $\pm$ 1) $^{\circ}\text{C}$  water bath for up to 295 days. Initial solutions were prepared with reagent grade  $\text{H}_2\text{SO}_4$  at initial pH values of 2, 3 and 4. For each lithology, pH value and size fraction, water-rock ratios (W/R) were set at 1 and 10.

Over the course of the experiments, pH measurements were taken periodically. After terminating the experiments, the residual aqueous solution was separated, filtered and analyzed by DCP-AES for major cation abundances and UV/vis spectrophotometry for  $\text{SO}_4$  abundances. Bulk samples were rinsed with deionized water (DI) and analyzed by SEM-EDS with unaltered samples for comparison. To remove and concentrate fine-grained alteration minerals including clays,

samples were subject to 7 minute sonication/rinse cycles with de-ionized water to remove the finest fraction [3]. The <2 $\mu\text{m}$  fraction was separated by gravity settling, flocculated with 0.1 M  $\text{CaCl}_2$  and briefly rinsed with deionized water [3]. Oriented specimens were prepared for powder XRD analyses ( $\text{Cu K}\alpha$ ), including glycolation and heat treatments.

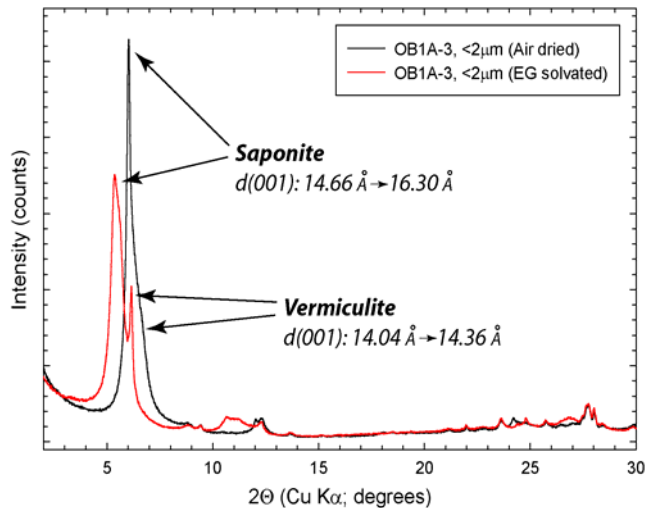
**Aqueous chemistry:** In all experiments, pH levels increased rapidly within the first 7 days and then increased slowly, changing little after approximately 36 days; nearly all of the initial acidity neutralized by this time. The final pH values were markedly higher in low water-rock ratio experiments and finer particle size (higher specific surface area) experiments, and with initially higher pH. The maximum final pH (8.35) was measured in an experiment with olivine basalt (<74  $\mu\text{m}$ ) at a W/R of 1 and an initial pH of 4. Few of the experiments reached a final pH above 8, while the majority fell between 6.0 and 7.5. In higher W/R experiments with coarser-grained olivine basalt (74-420  $\mu\text{m}$ ) at an initial pH of 2, the final pH after 295 days was 4.04 – the lowest final value measured.

Thermodynamic speciation calculations were performed with Geochemist's Workbench, using the LLNL thermodynamic database (4; version v8.r6+) to assess mineral saturation states and calculate component activities. For all solutions analyzed, carbonate minerals were undersaturated. Some hydrated clay minerals were variably oversaturated, including montmorillonite ( $\log(Q/K)$  from 1.4 to 4.7), nontronite (10.9 to 17.5), beidellite (2.9 to 6.6), kaolinite (3.7 to 6.5) and gibbsite (0.4 to 2.7). Saponite and vermiculite were strongly undersaturated, ranging from a  $\log(Q/K)$  of -6.3 to -18.3 and -12.2 to -16.5, respectively.

Although hydrated clay minerals are not often observed to reach thermodynamic equilibrium on these time scales, apparent equilibrium with  $\text{SiO}_2$  polymorphs appears to correlate with the initial pH of the experiments. For experiments with an initial pH of 2, amorphous silica was at equilibrium. For initial pH values of 3 and 4, chalcedony and quartz were at equilibrium saturation, respectively. In addition, all experiments (assuming that all measureable Fe is in the ferric state) are at equilibrium saturation with respect to amorphous Fe-hydroxide (nominally  $\text{Fe}(\text{OH})_3$ ).

**Clay mineralogy:** A variety of clay minerals were identified by SEM-EDS and powder XRD of <2 $\mu\text{m}$  size fractions. For example, final products separated from an experiment with olivine basalt at a W/R = 1 and an initial pH of 3 included saponite and trioctahedral ver-

miculite. The  $d(001)$ -spacings of Ca-saturated, air dried samples and ethylene glycol solvated samples fall neatly within the range of reported values using from this treatment (Fig. 1; 2,5). Further, extended duration scans of randomly oriented samples ( $<2\mu\text{m}$  fraction) yielded two distinct 060 reflections at  $1.54\text{ \AA}$  (vermiculite) and  $1.53\text{ \AA}$  (saponite). Additional smectite phases



**Figure 1.** Powder XRD profiles of (oriented aggregates;  $<2\mu\text{m}$  fraction) final products separated from an experiment with olivine-basalt at a  $W/R = 1$  and an initial  $\text{pH} = 3$ .

were separated from several other experiments and they exhibit distinct behavior in XRD treatments.

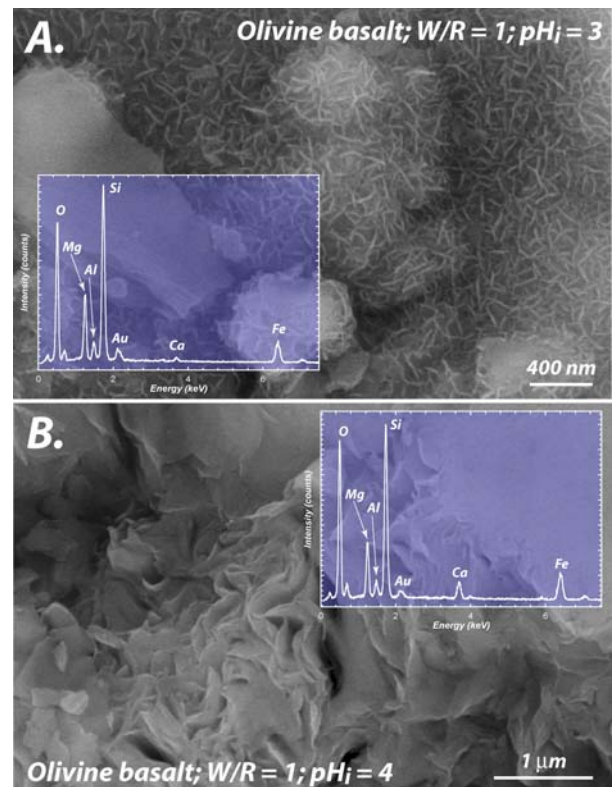
SEM-EDS analyses of all experiments show a broad range of clay textures and morphologies. For example, several experiments exhibit “cornflake” morphology typical of smectite neoformation and void-filling crystallization (Fig. 2A; see 6). Also, crinkly smectite morphology and dehydration features are common throughout altered samples (Fig. 2B). SEM-EDS analyses also indicate clay formation by possible transformation, where crinkled books of hydrated phyllosilicates originated either by filling micro void space and/or as products of structural transformation.

There is no indication of carbonate minerals from SEM or EDS, but hydrated Fe-hydroxide phases have been identified. Both of these observations are consistent with analyses of solution chemistry.

#### Insights into clay formation on Noachian Mars:

The clay mineralogy produced in these experiments illustrates a physical scenario that could be an important process in generating smectite-dominated alteration assemblages on Noachian Mars. The interaction of acidic water with a basaltic substrate under low-water rock ratios is a relatively efficient process in generating smectite-bearing assemblages at low temperature. Parameters such as reactive surface area, water-rock ratio and initial pH all control: (1) the time scales required to

reach the pH window of clay mineral formation, and (2) aqueous cation concentration at the time clay formation is initiated. By varying each of these parameters, a range of final pH values was reached when the experiment was terminated. The resulting variability in clay mineral assemblages allows a different look at the ef-



**Figure 2.** (A.) Scanning electron micrograph of void-filling smectite indicative of neoformation (Inset: EDS analysis). (B.) Scanning electron micrograph of smectite with crinkly morphology (Inset: EDS analysis).

fects of chemistry and weathering parameters on clay mineralogy and chemistry. Most importantly, extracting alteration products and linking mineral chemistry to solution chemistry is a valuable step in relating variables such as particle size, initial pH, water/rock ratio and duration of chemical weathering to clay minerals identified in Noachian lithologies.

**References:** [1] Güven, N. (1988) in: *Hydrous Phyllosilicates*, Rev. Min., 19, MSA. [2] Meunier, A. (2005) *Clays*, Springer, 472 pp. [3] Moore, D. & Reynolds, R. (1997) *X-Ray Diffraction & the Identification & Analysis of Clay Minerals*, Oxford, 378 pp. [4] Delany, J. & Lundeen, S. (1990) *The LLNL thermochemical database*, LLNL Report, 150. [5] Suquet, H. (1975) *Clays Clay Min.*, 23, 1. [6] Velbel, M. & Barker, W. (2008) *Clays Clay Min.*, 56, 112.