

CLAY MINERAL FORMATION AND EVOLUTION IN AN EXPERIMENTAL BASALTIC WEATHERING PROFILE. J. A. Hurowitz, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, MS 183-501, Pasadena, CA 91109, joel.a.hurowitz@jpl.nasa.gov.

Introduction: The OMEGA and CRISM spectrometers onboard the Mars Express orbiter and Mars Reconnaissance Orbiter, respectively, have provided dramatic new insights into the mineralogical and chemical modification of Mars' early formed (Noachian) crust. Data from these spectrometers provide evidence for a period in early Martian history in which aqueous conditions at the surface may have differed significantly from what has been observed thus far at Mars landing sites (Viking, Pathfinder, MER), where water-limited, and in many cases acidic, conditions predominate [1-3]. Evidence for phyllosilicate minerals including smectites (montmorillonite, saponite, nontronite) and kaolinite [4,5] suggest more water-rich and neutral-alkaline pH conditions, possibly similar to those observed in terrestrial basaltic weathering profiles (Figure 1), were present early in Martian geologic history.

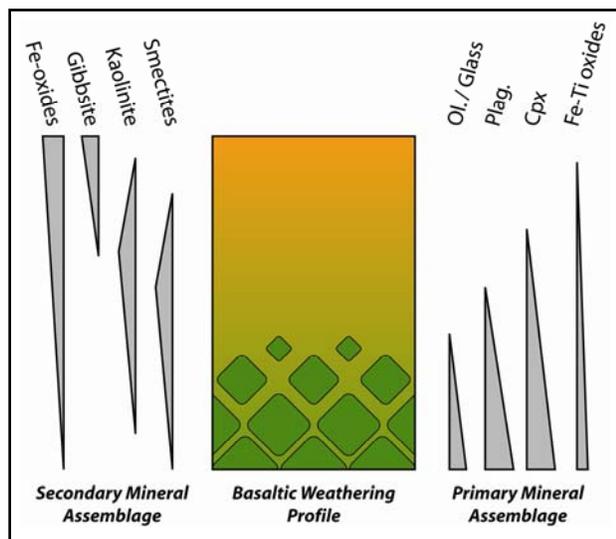


Figure 1: Schematic of a basalt weathering profile showing the relative order of primary mineral breakdown (right) and secondary mineral formation (left) as a function of depth in the profile. After Nesbitt [6].

This work reports on a new experimental approach aimed at understanding basaltic weathering profile chemical evolution processes using a unique packed-bed flow through reactor design that enables *in-situ* analysis of undisturbed solid phase alteration products. These experiments will provide insight into the chemical pathways by which secondary minerals form and evolve under conditions relevant to early Mars.

Methods: Experiments were designed to maximize the rate of clay formation in relatively short-duration experiments (1 mo.) by modifying the smectite synthesis procedures of Harder [7] and Tosca [8].

Experimental: Three reconnaissance flow-through experiments were conducted, differing only in the mineral loaded into each of three sample chambers (Fig. 2). The three minerals used were forsteritic olivine, augite, and Ca-rich plagioclase (bytownite). The minerals were ground separately in an agate ball mill and sieved to retain the 75-150 μ m size fraction. Each sample was sonicated in denatured anhydrous ethyl alcohol to remove ultrafines, dried, and loaded into individual sample chambers. Solids were contained in the sample chambers with 0.2 μ m PEEK frit discs installed at each end of the chambers. The chambers were then installed in a packed bed flow-through reactor analogous to that described in Hurowitz et al. [9]. Temperature throughout the experiments was maintained at 50°C by submerging the sample chambers in a heated water bath.

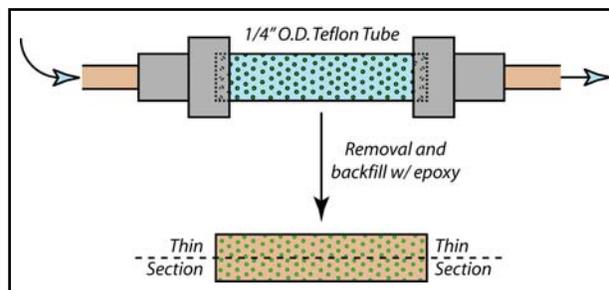


Figure 2: Schematic of sample chamber. During experimentation, the sample chamber is mounted vertically. Use of a 1/4-inch O.D. sample chamber facilitates epoxy impregnation and thin-section preparation, a significant enhancement over previous [9] designs.

Inlet fluids were prepared by dissolving 100g/L $MgSO_4 \cdot 7H_2O$ in Millipore water ($18m\Omega \cdot cm^{-1}$) and acidifying the fluid to $pH=4.6 (\pm 0.3)$ with reagent-grade HCl. The fluids were pumped into the sample chambers at a rate of 10 μ L/min using a multi-channel syringe pump. Effluent samples were collected in polypropylene containers, measured for pH and Eh, and acidified to $pH < 2$ with a mixture of 4% nitric and 2% hydrofluoric acid.

After a period of 11 days of continuous fluid injection, the syringe pump was stopped and the samples were allowed to age in contact with fluid at 50°C for

an additional 15 days. The fluid was then removed from the sample chambers with forced air, and the sample chambers were placed in a 50°C oven to dry.

Thin-Section Preparation: After drying, the sample tube containing the solid sample was vacuum impregnated with a commercial low-viscosity epoxy, dried, and thin sectioned along the long axis (Fig. 2). One half of the sample chamber was mounted and polished for petrographic analysis, while the other half was prepared for analysis by scanning electron microscope (SEM) and electron microprobe (EMP).

Analytical: Effluent pH, Eh and temperature were measured immediately after each sample was collected; correct operation of the Eh probe was verified by measurement of Zobell's solution. Dissolved Si, Ti, Al, Fe, Mn, Ca, Na, and P were measured on a Thermo iCAP 6300 radial view ICP-Optical Emission Spectrometer using matrix-matched spectral standards.

Results: To date, only solution phase analyses have been conducted; representative results for dissolved Si and pH are shown on Figure 3. Experimental pH levels are elevated relative to the input solution (pH = 4.6) to values between ca. 6.0-9.0. Eh (not shown) remained relatively constant throughout, yielding pe values between ca. 7.0-8.0. Under such pH and redox conditions rapid Fe-oxidation is to be expected, which explains why Fe was not detected in the majority of fluid samples collected.

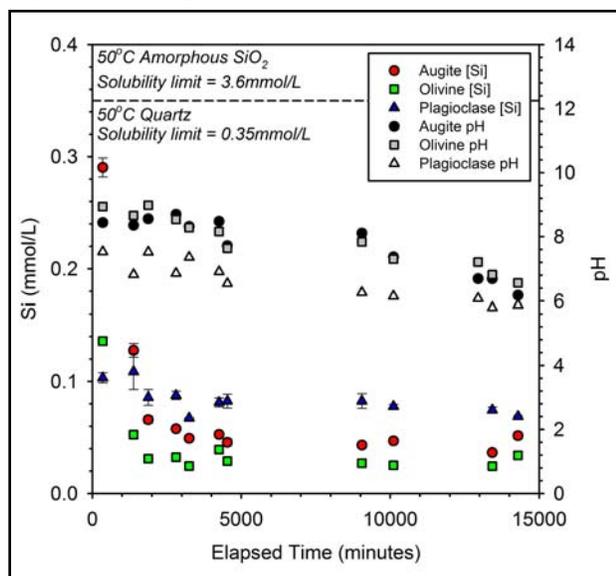


Figure 3: Si concentration (left y-axis) and pH (right y-axis) as a function of time. Note that Si concentrations are well below the 50°C solubility limit for both quartz and amorphous silica.

Harder [7] reports that conditions favorable for low-T montmorillonite synthesis include: (1) low con-

centrations of dissolved Si (well below the solubility limit of amorphous silica), (2) neutral to alkaline pH, and (3) high concentrations of dissolved Mg^{2+} . The Mg^{2+} is necessary to form an initial octahedrally coordinated brucite-like layer upon which to build phyllosilicate structures. These conditions are met by the experimental system indicating that conditions may have been favorable for smectite mineral formation. Simulations of fluid speciation and mineral saturation state using the Spec8 program (part of the Geochemist's Workbench®), however, indicate undersaturation with respect to all phases in the final fluid samples collected (~14,500 minutes, Fig. 3) prior to halting the syringe pump for aging.

Future Analyses: Solid phase analyses for these reconnaissance experiments will consist of petrographic analysis for secondary phase identification and abundance estimates, EMP analysis for chemical composition, and SEM analysis coupled with electron backscatter diffraction for morphology and mineralogy, respectively. If clay mineral formation proves successful under current conditions, the experiments will be replicated and the solid samples will *not* be epoxied. Instead the solids will be collected for analysis by X-ray diffraction and VIS-NIR spectroscopy.

Summary: Thus far solution chemistry results suggest favorable conditions for smectite precipitation during sample aging, a possibility that will be fully evaluated using thin section analysis. If successful, these reconnaissance experiments will provide a template from which to evaluate a wide range of processes related to clay mineral formation and evolution in weathering profiles, including variables such as fluid chemistry, temperature, and primary mineralogy. In addition, analysis of solid reaction products by VIS-NIR spectroscopy will allow for quantitative comparison of experimental run products to remote datasets collected by the OMEGA and CRISM spectrometers.

References: [1] J. A. Hurowitz and S. M. McLennan, (2007) *EPSL*, 260, 432-443. [2] D. W. Ming, et al., (2006) *JGR*, 111, doi:10.1029/2005JE002560. [3] N. J. Tosca, et al., (2005) *EPSL*, 240, 122-148. [4] J.-P. Bibring, et al., (2005) *Science*, 307, 1576-1581. [5] J. F. Mustard, et al., (2008) *Nature*, 454, 305-309. [6] H. W. Nesbitt, (2002) *Geochemistry of Sediments and Sedimentary Rocks: Evolutionary Considerations to Mineral Deposit-Forming Environments*, D. Lentz, 39-51. [7] H. Harder, (1972) *Chem. Geo.*, 10, 31-39. [8] N. J. Tosca, et al., (2008) *GCA*, 72, A952-A952. [9] J. A. Hurowitz, et al., (2005) *JGR*, 110, E07002, doi:10.1029/2004JE002391.