

Kinetics of Nontronite Dissolution and Implications for Mars. S. R. Gainey¹, E. M. Hausrath¹ and J. A. Hurwitz², ¹ Department of Geoscience, University of Nevada, Las Vegas 4505 S. Maryland Parkway, Las Vegas, NV 89154-4010, ² Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, MS 183-501 Pasadena, CA 91109.

Introduction: Spectral observations from the CRISM and OMEGA spectrometers onboard the Mars Reconnaissance and Mars Express orbiters have detected signatures indicative of clay minerals and the mineraloid allophane [1-7]. Phyllosilicates are primarily located in the Mawrth Vallis region, Nili Fossae, north of the Syrtis Major Volcanic Plateau, and the future landing site of the Mars Science Laboratory, Gale Crater [1,8]. Clay minerals generally form from the hydrolysis of silicate minerals, and at surface conditions would require the past presence of large, long standing bodies of liquid water, a requirement for life as we know it [1,5,9].

Stratigraphic relationships and age estimates from crater counts suggest that clay minerals detected from orbit on Mars are ancient and are therefore likely to have been altered by diagenetic and pedogenic processes subsequent to their formation. Exposed stratigraphic units in the Mawrth Vallis region indicate a transition from a Fe-Mg rich clay with a spectral signature consistent with nontronite to an overlying Al-rich smectite, potentially montmorillonite mixed with kaolinite and silica [3,9,10]. Current hypotheses addressing this transition include: volcanic, sedimentary, pedogenic and hydrothermal processes [9]. Currently, few works have examined nontronite dissolution kinetics and clay to clay alterations under Mars relevant conditions. Studying these processes would provide a better understanding of the processes and mineralogy observed at the Martian surface.

Therefore, it is the purpose of this research to determine the dissolution rates of nontronite and identify secondary precipitates. This study will produce the first nontronite dissolution rates and second BET specific surface area to our knowledge, permitting further elucidation of the physical and chemical processes acting in the Mawrth Vallis region and on the surface of Mars.

Methods: *Experimental:* Three flow through reactors were maintained with input solutions at pH = 0.88, 1.69 and 3.01. Reactors were modeled after [11]. Reactors were constructed from 5.6 cm of Teflon tubing with an inner diameter of 0.5 cm and were acid-washed prior to use. Nontronite samples were powdered and sieved to 325-100 mesh (45-150 μm), and then 0.7 – 0.8 g was loaded into each open column. After the sample was loaded, the solution was pumped up through the columns from the bottom until they were filled, to ensure no bubbles were present, after which

the outlet tubing was attached. Input solutions were prepared from 18.2 M Ω water and trace element grade HCl to the three pH values, and were in equilibrium with atmospheric O₂. Three sterile 60 ml syringes were filled with each solution and loaded in an Orion Sage Syringe pump, model 362. Flow rates were set to 0.16 ml per hour for the first 837 hours, and 0.32 ml/hr for the remaining 437 hours. Solutions flowed through acid-washed 0.062 cm I.D. Teflon tubing, approximately 10 cm of which was submerged in the 26 °C water bath to ensure constant temperature conditions before the solution entered the columns. The solutions flowed from the 0.062 cm Teflon tubing, through a 0.45 μm filter, into the bottom of the columns to maximize saturation and minimize preferential flow paths. From the top of the columns effluent solution flowed through another 0.45 μm filter, through 0.062 cm diameter Teflon tubing, and into 3 sterile syringes, in which the solution samples were collected. Every 24-48 hours, the filled output syringe was replaced with an empty sterile syringe, and output solution chemistry analyzed.

Analytical: Effluent collected as described above was measured to determine flow rates, output pH, and elemental chemistry including Al, Ca, Fe, Mg, Na, S, and Si concentrations. Flow rates were determined by weighing the effluent discharged since the last sampling period, and dividing the weight by that time period (24-48 hours). A 2 ml sample of solution was measured for pH using a Fisher Scientific Accumet Excel XL 15 pH meter (1%) standardized with 4, 7, and 10 pH solutions. Remaining solution samples were diluted and acidified with high-purity HNO₃ for elemental analysis. Concentrations of Al, Ca, Fe, Mg, Na, S, and Si in output effluent were determined with a Thermo iCAP 6300 radial view Inductively Coupled Plasma-Optical Emission Spectrometer with 10 percent nitric acid matrix-matched standards for elemental analysis, in the JPL Astrobiology and Planetary Geochemistry Laboratory.

Results & Discussion: *Si Concentration in Out-put Solutions:* Si release during dissolution under three pH conditions and two flow rates is depicted in Figure 1. All experiments showed that the most rapid release of Si occurred during the initial 150 hours. Doubling the flow rate (0.16 to 0.32 ml/h) decreased the Si concentrations in out-put solutions. Si concentrations followed the order: pH 0.88 > 1.69 > 3.01.

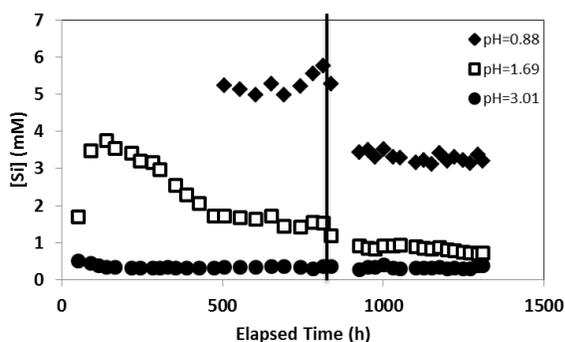


Figure 1: Si concentration as a function of time. The black vertical line represents the change in flow rate from 0.16 to 0.32 ml/h.

Stoichiometry of Weathering: Stoichiometry of dissolution was determined throughout the experiment. Nontronite dissolution at pH 0.88 showed an initial removal of Al > Fe ~ Si. As time progressed the release of Al, Fe and Si reached the same proportions as the parent mineral [12], indicating stoichiometric dissolution. At pH 1.69 significantly more Al than Fe was released. The elemental release followed the order Al > Si > Fe, indicating the remaining material would be enhanced in Fe and depleted in Si and Al relative to the parent material. At pH 3.01 both Al and Fe were below detection, indicating preferential loss of Si, or precipitation of Al and Fe containing minerals.

Calculating Nontronite Dissolution Rates: Nontronite dissolution rates were calculated for each steady state (at 0.16 and 0.32 ml/h marked by less than 5% variation for three 24-48 hour sample periods), from Si concentrations in out-put solutions. The dissolution rates were normalized to the BET surface area (reacted material) for each pH and the stoichiometry of the unreacted standard (NAu-1) as determined by [12], and are presented in Figure 2.

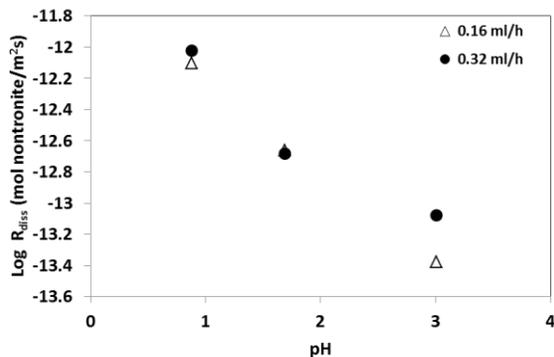


Figure 2: Log dissolution of nontronite from silicon release as a function of pH.

Conclusions: Results suggest the preferential removal of Al relative to Si and Fe during the initial dissolution at pH 0.88 and 1.69, with pH = 0.88 approaching stoichiometric ratios as the experiment progressed. With Al and Fe immobile at pH = 3.01. This suggests that under oxidizing conditions, acidic leaching of nontronite would enrich the daughter mineral in Fe. Therefore, if a similar process was acting on the Martian surface, it would not likely produce the observed Al-rich uppermost layer of the Mawrth Vallis region.

These results also represent the first kinetic data on nontronite dissolution to our knowledge and suggest the long term stability of nontronite at the Martian surface. These dissolution rates are significantly slower than the primary minerals of basalt, including apatite, olivine, pyroxene, plagioclase and basalt glass [13,14]. This suggests that, once nontronite formed, it would likely persist at the Martian surface for prolonged periods relative to basalt.

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