

FORMATION OF AQUEOUS MINERALS: IMPLICATIONS FOR THE PAST HABITABILITY OF MARS. S. R. Gainey¹, E. M. Hausrath¹, J. A. Hurowitz² and O. Tschauner¹ ¹Department of Geoscience, University of Nevada, Las Vegas, 4505 S. Maryland Parkway, Las Vegas, NV 89154-4010, USA ²Department of Geosciences, Stony Brook University, 255 Earth and Space Building (ESS), Stony Brook, NY 11794-2100, USA.

Introduction: Liquid-water is the quintessential ingredient for the development and sustenance of life on Earth [1] and would likely be essential in the development of life on Mars. Although liquid-water is no longer present at the Martian surface, the occurrence of aqueous minerals [2] (e.g. requiring liquid water to precipitate) suggests liquid-water has occurred at or close to the Martian surface in the past. Therefore, the search for habitable environments will be closely related to the investigation of aqueous minerals on Mars [3]. Currently, several aqueous minerals have been detected at the Martian surface which include; Fe-(oxyhydr)oxides [4], hydrated silica [5], phyllosilicates [6], carbonates [7], hydrated sulfates [8] and zeolites [9]. Of those minerals, phyllosilicates (and potentially zeolites) suggest past environments in which the activity and pH of water may have been suitable for the development of life [9].

Infrared reflectance data obtained from TES, OMEGA and CRISM have revealed phyllosilicate bearing materials on the Martian surface and represent the strongest evidence for sustained aqueous activity on Mars [6]. A multitude of studies have suggested the presence of phyllosilicates at numerous locations on the Martian surface [6]. However, the mineralogy of these phyllosilicates is heterogeneously distributed both spatially and stratigraphically. Of these locations, Mawrth Vallis represents one of the largest exposures of phyllosilicates on Mars [10] and is characterized by Al-rich clay minerals (kaolinite and montmorillonite) mixed with hydrated silica (opal), which is underlain by an Fe-rich clay (nontronite) [10]. Gale Crater, the landing site of the Mars Science Laboratory, also contains what is believed to be the clay mineral nontronite; this unit then grades into either intercalated beds or a mixed unit of nontronite and sulfate(s) [11]. Clay minerals have been spectrally detected in several locations in/near the Nili Fossae region. The clay minerals occur in distinctive assemblages in which kaolinite and Mg carbonate overlies the Fe and Mg rich smectites [6]. Phyllosilicates, occurring in multiple locations on the Martian surface, are potential mineral indicators of the past aqueous and diagenetic/pedogenic history of Mars.

The observed soils, sediments and/or rocks bearing aqueous minerals not only suggest the past presence of liquid water, but may also elucidate the thermodynamic conditions under which these minerals precipitated. Previous studies in which volcanic glass was altered under alkaline conditions suggests that high

water-rock ratios favor the development of clay minerals, whereas low ratios support the precipitation of zeolites [12, 13]. These studies [12,13] have also suggested that increasing pH favors the precipitation of zeolites over clay minerals. Clay minerals may also be valuable when assessing whether environments were oxidizing or reducing when they formed [14].

Therefore, it is the purpose of this study to experimentally alter a range of igneous rocks under alkaline conditions, varying the water-rock ratio, pH and the redox of the system and examining the suite of aqueous minerals generated under the specified conditions. The results of this study will be useful when assessing the paleo-environment and habitability of Mars.

Experimental Methods: *Starting Materials:* Experiments were conducted using the USGS powdered igneous rock standards, and spanned felsic to mafic compositions (GSP-2, AVG-2, BIR-1 and DNC-1a). Previous studies have characterized the bulk chemistry and mineralogy of these rocks [15].

Experimental Procedure: Following a similar procedure to [12,13], 250 mL acid-washed serum vials contained 0.5-1.0 g of sample and 200 mL of either 5, 0.5 or 0.05 M NaOH solutions which were maintained at 90 °C for 35 days. At the end of the experiment the pH of the solution was recorded. Samples were then vacuum filtered with 0.45 µm disc filters to obtain the solid particulate. The particulate was then air dried at room temperature.

Anoxic experiments were conducted in a similar procedure, but differed in that the starting solution was vigorously bubbled for 2 hours with high purity N₂. To further ensure reducing conditions, sodium dithionite was added to the bubbled solution (1g per 100 mL solution). The powdered material was placed in the serum vial and ~200 ml of solution was immediately added and the vial capped. To ensure no O₂, the head space was then purged with N₂. Samples were then filtered and dried within an O₂ free glove box.

In order to assess the products of alteration by varying water-rock ratios, 1 g of powdered material was added to high density polyethylene bottles which were then filled with either 500, 250, 100, 50, 25 and 10 ml of 1 M NaOH and aged for 3 weeks (21 days) at 90°C. Samples were then filtered and dried under atmospheric conditions.

Product Characterization: Powder X-Ray Diffraction (XRD) data were collected for altered samples, using a PANalytical X'Pert Pro X-Ray Diffraction

Spectrometer at 40 kV and 20 mA using CuK α radiation. Patterns were taken under atmospheric conditions. To further evaluate alteration products and distinguish between clay minerals, Scanning Electron Microscopy, Energy Dispersive Spectroscopy and Raman Spectroscopy images and spectra were taken of altered and unaltered samples to evaluate morphology and chemical composition.

Results and Discussion: Experiments with constant water-rock ratios and high pH (5M NaOH) favored the precipitation of clay minerals and the zeolites; hydroxyl sodalite and erionite (Figure 1). This is consistent with the past studies of [12,13], in which clay minerals and zeolites were the primary alteration products. Under less alkaline conditions (0.5 and 0.05 M NaOH), zeolites were the primary alteration product. The zeolites formed (phillipsite, natrolite, garronite and analcime) contain less Na than hydroxy sodalite which is likely a direct result of lower Na concentrations within the system.

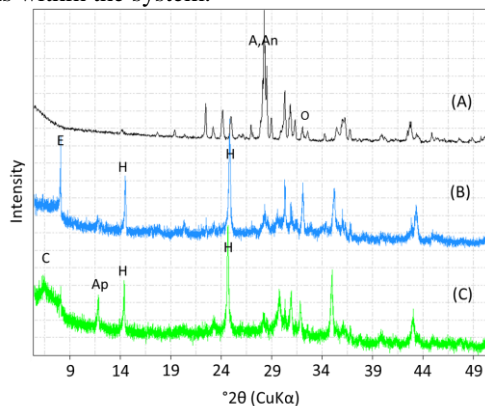


Figure 1: XRD patterns taken of (A) unaltered basalt (BIR-1a), A,An denotes augite and anorthite, O represent olivine (B) Altered basalt under oxic conditions (5M NaOH-oxic) where the primary alteration products are (E) erionite and (H) hydroxyl-sodalite. (C) Altered basalt under reducing conditions (5M NaOH-10% Na-dithionite) the alteration products include (C) clay minerals, (Ap) Apophyllite and hydroxyl-sodalite.

Under reducing conditions, the precipitation of clay minerals and zeolites was favored under the most alkaline conditions (5M NaOH). However, when compared to oxidizing conditions, diffraction suggests the clay minerals exhibit better crystallinity and are potentially more abundant (Figure 1). Hydroxy sodalite was still a primary alteration product. Under less alkaline conditions (0.5 and 0.05 M NaOH) zeolites (phillipsite, natrolite, garronite and analcime) and the phyllosilicate apophyllite were the primary alteration products. However, under reducing conditions the zeolites and the phyllosilicate apophyllite appeared to be better crystallized and potentially more abundant.

Preliminary results of the water-rock ratio experiments agree with the past observations of [12,13] in

which clay mineral precipitation was favored under high water-rock ratios (Figure 2). This is evident within the SEM images which suggest more abundant and larger phyllosilicate aggregates in high water rock ratio experiments. However, the abundance of zeolites is still under investigation as well as the role of glass as starting material in affecting their precipitation.

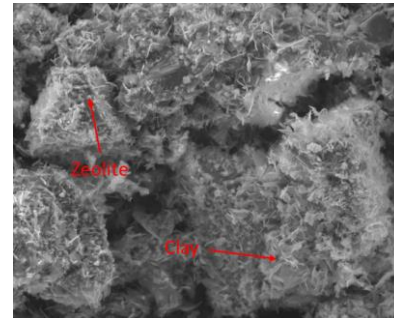


Figure 2: SEM image of altered basalt (BIR-1a), at a water: rock ratio of 500mL to 1g powder. The platy morphology may be indicative of clay minerals, while the spherical materials may represent a zeolitic material.

Conclusions: The association of clay minerals and zeolites in Mawrth Vallis and Nili Fossae suggests intermediate to high water-rock ratios at the time of precipitation. Specific zeolite minerals are difficult to determine through infrared spectroscopy, however, the zeolite analcime has been detected in the Nili Fossae region [6]. This zeolite only formed through the alteration of DNC-1a-dabase (0.5 M NaOH). This suggests the parent material(s) were potentially mafic. The ratio of phyllosilicates to zeolites may also suggest reducing conditions as phyllosilicates were favored in the presence of Na-dithionite.

Currently, further investigation is in progress to determine specific clay minerals, and their implications when assessing the oxidation state. Experimental alteration of igneous rocks provides a useful means of assessing the paleo-environmental conditions of Mars.

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