AQUEOUS ALTERATION OF BASALTIC GLASS UNDER A SIMULATED MARS ATMOSPHERE.

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Introduction: For the past several years we have been performing experiments designed to produce brines under Mars-simulated conditions. Previously, we had generated and analyzed Mars-analog brines by allowing a mixture of minerals derived from SNC mineralogy [1] to soak in pure water under a synthetic current-Mars atmosphere [2] and under a gas similar to the present Mars atmosphere but with added acidic gases [3]. The latest version of these experiments incubates basaltic glass, obtained from recent Kilauea flows (Mother's Day flow in December 2002), in pure water under a present-day Mars analog atmosphere at 25^{o}C. This abstract and our presentation will discuss the composition of these Mars-analog brines and implications for Mars surface chemistry.

The MER Opportunity rover at Meridiani has provided the first-ever data on salt beds on Mars. Previously, at the two Viking sites and at the Mars Pathfinder landing site, high levels of sulfates and other salts were found in the ubiquitous mobile layer of fine particles. Although this layer appears to be homogeneous in composition across Mars, its source remains a mystery. The thick sulfate beds at Meridiani evidently laid down by precipitation from a briny shallow martian lake or sea, hold some promise for understanding the origin of Mars' salty surface.

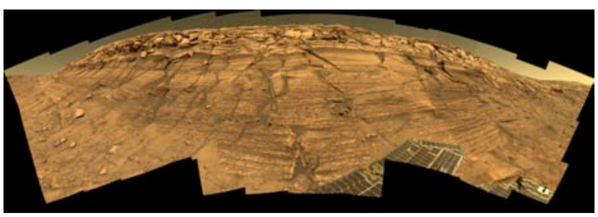


Figure 1. Burns Cliff as imaged by MER Opportunity Rover Pancam. Interior of Endurance crater wall at Meridiani Planum. Light-toned material at the top, all the way to the layered deposits near the bottom are high in sulfate salts.

Brines Simulation Facility: The Mars brines experimental apparatus (Fig. 2) has been designed to provide carefully controlled pressure, temperature, gas and liquid environments for up to 117 independent reaction vessels. The apparatus provides effective flow-through of reactant (Mars-analog) gas mixtures. The Mars brines experimental apparatus consists of 4 major subsystems, which work together to maintain precise environmental conditions. These 4 subsystems are: (I) 3 gloveboxes (with airlocks), for environmental isolation, stacked on top of each other; (II) the sample flask system for each glovebox, consisting of 36 Teflon flasks on gas circuits separate from the gloveboxes; (III) independent closed-loop temperature control systems for each glovebox; and (IV) independent pressure control systems for both the gloveboxes and the sample flask subsystems. The temperature and pressure conditions inside the glovebox and sample flask subsystems are computer-controlled, with extensive environmental data logging performed for the duration of the experiments. Within each of the three gloveboxes, the sample flask system contains two gas circuits: a Mars-analog gas system and an Earth air system, the latter for experimental controls. Individual 250 ml sample flasks contain 100 ml water and 50 g of rock, with the remaining volume given to head space gas. These flasks rest in holes within massive aluminum pallets, which provide a constant thermal environment for the flasks. The pallets are temperature-controlled by recirculating heaters/coolers through a heat exchange fluid maintained with an accuracy of ± 1.0°C). Tools and aliquot extraction supplies are passed into and out of the gloveboxes via airlocks.

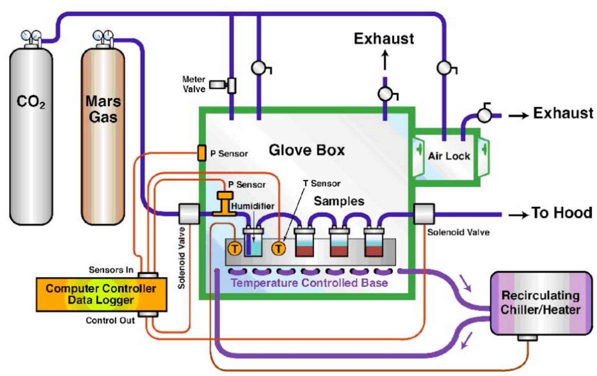
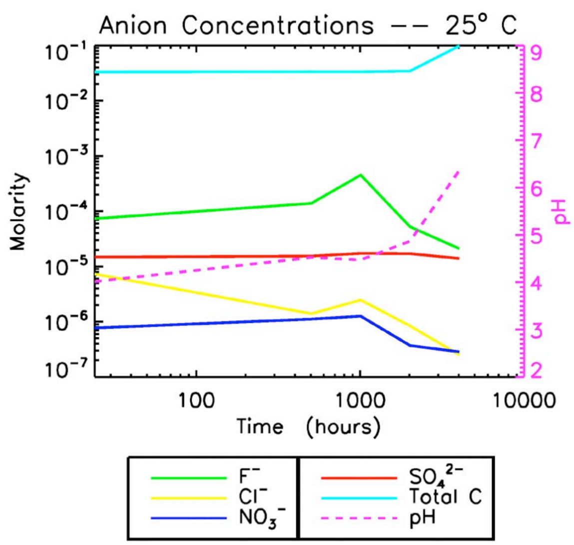


Figure 2. Schematic of the brines experiment apparatus. One of three gloveboxes is shown for clarity. 32 sample vessels containing purified water and Mars-analog rocks (or controls, see text) sit in machined impressions in a temperature-controlled aluminum pallet. A closed-loop pressure sensor/solenoid valve system feeds synthetic Mars atmosphere into the daisy-chained sample containers, at a slightly higher pressure than the glovebox CO_2.

Experimental Procedure: Samples of Kilauea basaltic glass were ground, sorted, and mixed with doubly distilled water. The slurries were placed in a 1 bar environment 25°C in order to represent conditions within the martian subsurface where brines might reside.

Anion concentrations were determined to ppb levels using a Dionics 4500I Ion Chromatograph (IC) using EPA 300 protocols. Cations were also determined at ppb levels with an ARL 3410 Plus Inductively Coupled Plasma/Atomic Emission Spectrometer (ICP/AES), following the EPA 6010 protocol. Controls of two types are also performed during the experiment: (a) chambers with fluid and Mars-analog minerals with Earth atmosphere in the headspace, and (b) chambers with fluid, no rock, but with Mars-analog gas in the headspace.

Results: The experiments began on April 7, 2004 and will continue for one year. To date, aliquots at 1, 21, 42, 84 and 168 days have been extracted. The primary anions in solution are carbonate, fluoride and sulfate, in the range of 1e-5 to 0.1 moles/liter after 6 months. Cation concentrations are similar, with contributions from calcium, magnesium, sodium and iron. A dramatic increase in pH is seen after about 1000 hours. We interpret this to be a strong alkaline buffering effect due to the basaltic glass, in spite of the largely CO_2 headspace gas. Although iron continues to increase in concentration after this, most other cations such as calcium, magnesium and sodium begin to decline in abundance. Fluoride and the smaller amounts of chloride and nitride also decrease in abundance after the increase in pH at 100 hours. Sulfate remains at a very low abundance (1e-5 moles/liter) throughout the first 6 months of the experiment.



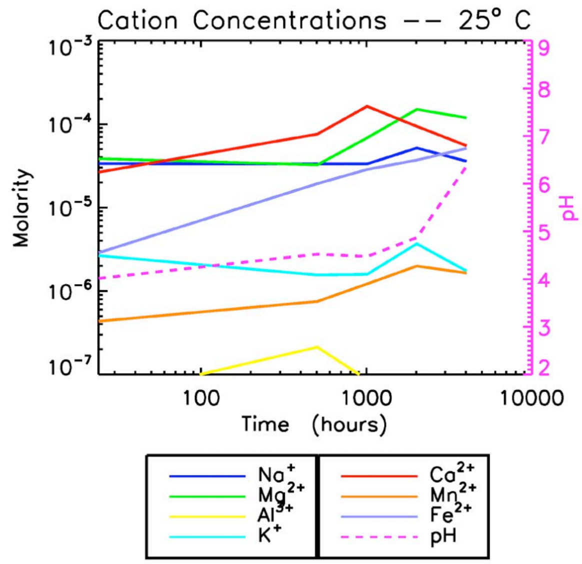


Figure 3. Anion and cation molar concentrations in dilute Mars-analog brines formed under a present-day synthetic Mars atmosphere and using basaltic glass obtained from Kilauea in December 2002. The top plot shows the results for anion concentrations as a function of time obtained at 25°C, the bottom one shows cation concentrations at 25°C. The dashed line and right hand axes show solution *p*H.

Conclusions: Fractionation of ions into solution from basaltic glass under Mars-like conditions is strikingly unlike that obtained by incubating an SNC-derived mineralogy under similar conditions [2]. To our surprise, ionic content is about an order of magnitude lower than obtained with the SNC-like minerals. Iron concentrations, however, are several orders of magnitude higher from the basaltic glass, and increasing. Sulfates and chlorides are low, while solution *p*H is rising to values of about 6.4 after 6 months. In the future we will investigate how mixing models that use our laboratory results from SNC-derived minerals and the present basaltic glass results may explain mobile ion content in soils analyzed by Mars Pathfinder and the two MER rovers.

References: [1] McSween H.Y. (1985) *Reviews of Geophysics, 23,* 391-416. [2] Bullock M.A. et al. (2004) *Icarus, 170,* 404-423. [3] Bullock M.A. and Moore J.M. (2004) *GRL, 31,* L14701.