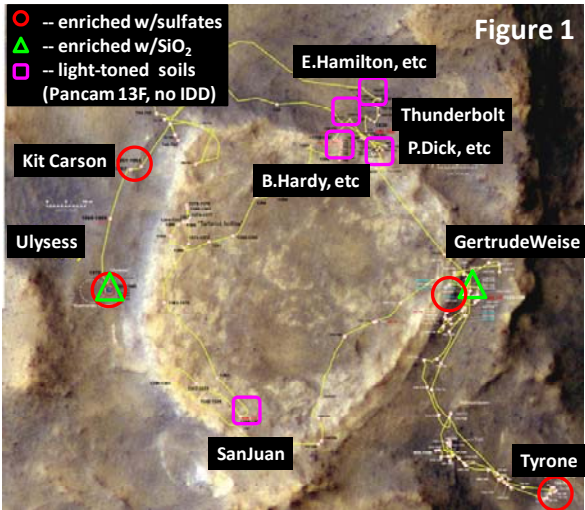


HYDROTHERMAL PROCESS ON MARS – MISSION OBSERVATIONS AND A LABORATORY SIMULATION EXPERIMENT, Z. X. Peng, Alian Wang, B. L. Jolliff, Department of Earth & Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University, St. Louis, MO, 63130 (alianw@levee.wustl.edu).

Hydrothermal process on Mars: Hydrothermal processes are suggested to have been active in the past on Mars [1]. This concept is generally supported by the widespread evidence of volcanic activity on Mars, and the high WEH levels (water-equivalent-hydrogen) found in two large equatorial regions on Mars [2]. Furthermore, the ground ice excavated by meteorite impacts observed by HiRISE and confirmed by CRISM on MRO [3] further supports the potential for ground ice beneath the surface regolith, especially during periods of high obliquity. Heat from volcanic activity interacting with ground water or ice could produce hydrothermal activity. The associated energy and dissolved compounds may have provided a favorable environment for microbial life forms on Mars.

The first surface confirmation of hydrothermal activity on Mars was made by Spirit, through exploration around the Home Plate area, south of Husband Hill in Gusev Crater [4]. In addition to morphological evidence, amorphous silica and variety of sulfates were identified (Fig. 1) as secondary minerals produced by hydrothermal activity [5,6,7]. They coexist at some locations (e.g. Ulysses), or occur at well separated sites (Tyrone and GertrudeWeise).



Laboratory Simulation Experiment: In order to gain a better understanding on the hydrothermally produced secondary minerals under Mars relevant atmospheric conditions, especially their precipitation sequences and the compositional and structural details as mineral assemblages, we designed a set of simulation experiments in laboratory under well controlled environmental conditions. Our experiments differed from previous

Table 1. Experiments at 90°C

starting solid	HP003 (250 μm < d < 850 μm)			
starting acid	H ₂ SO ₄ :HCl (4:1 molar ratio):H ₂ O			
fluid (acid-to-H ₂ O ratios)	fluid-to-sand ratios	duration @ 90°C (a total of 20 experiments)		
		5 vol%	2:1	3 days
10 vol%	2:1	1 day	3 days	10 days
		10:1	1 day	3 days
15 vol%	2:1	3 days	10 days	
		10:1	3 days	10 days
20 vol%	2:1	1 day	3 days	10 days
		10:1	1 day	3 days

studies [8,9,10,11] by (1) the use of an oxygen-poor environment; (2) the use of three temperature ranges to separate the secondary minerals. The experimental runs were just finished. We report in this abstract the experimental methods and some very preliminary results.

The general plan of this experiment was (1) to react basaltic sand with acidic fluids with different molar percentages at different sand-to-fluid ratios at 90°C; (2) to separate the fluids from the sand after 1, 3, 10 days reactions; (3) to allow precipitation to occur in the decanted fluids at 50°C; (4) to separate the precipitated solid; and (5) finally to evaporate the residual fluid at room T. Every step of this experiment, except for the last part of the last step, was conducted in a dry CO₂ environment (>1 atm). A variety of analytical methods including EMP, SEM, ICP-MS, Raman, XRD, NIR & MIR spectroscopy are planned to examine the initial, middle, and final reaction products.

Starting materials (Table 1): Basaltic sand HP003 was used as the starting solid sample, whose chemical composition (including compositional zoning) and surface morphology are to be studied by EMP and SEM analysis. This sample was collected from a recent Puu Oo flow of the Kilauea volcano in Hawaii. A piece of HP003 was crushed, ground, and sieved. The basaltic sand with size 250 μm < d < 850 μm was used to react with acidic fluids in this experiment. For each of twenty reactions at 90°C, 3 grams of basaltic sand was used, with weighing error < 1 mg (0.03%).

Diluted mixtures of sulfuric acid and hydrochloric acid (4:1 molar ratio) were used to react with the basaltic sand at 90°C. Initially, acidic solutions with 10 % and 20 % acid-to-H₂O volume ratios were used for twelve reactions. Eight reactions using 5 % and 15 % (acid-to-H₂O volume ratios) fluids were added later,

for the purpose of confirming an interesting experimental observation (discussed later). 2:1 and 10:1 fluid-to-sand volume ratios were used for each diluted acid. Reaction durations of 1 day, 3 days, and 10 days were used.

Experimental setup: a major difference of our experiment from other laboratory studies is the use of CO₂ atmospheric conditions maintained for the reaction at 90°C, precipitation at 50°C, and evaporation at room T. We built an environmental chamber to provide a CO₂ atmospheric environment for set up the initial experiment at 90°C and for sample transitions between different temperatures. The chamber was sealed and then flushed by dry-CO₂ 200 (purity 99.9%). A 40 SCFM flow of CO₂ was maintained during each experimental step to maintain a positive CO₂ pressure (>1 atm) in the chamber.

We used 30 ml PFA vials to contain basaltic sand and acidic fluid during 90°C reactions. PFA is a material similar to Teflon that has an excellent resistance to strong acid at high temperature. Inside of the environmental chamber that is actively purged with dry CO₂, seven of these 30ml vials (with six experiment vials and one blank vial containing acidic fluid only) were placed in a 1000 ml reaction container also made of PFA. Each of 30 ml reaction vials was loosely capped to prevent excessive evaporation of acidic fluid at 90°C (especially for those with a 2:1 fluid-to-sand ratio). An infilling gas valve was installed on the cap of 1000 ml PFA reaction container to allow dry CO₂ gas to fill the container for at least 5 minutes before sealing. We used one reaction container for each of four concentrations of acidic fluid (i.e., 5%, 10%, 15%, and 20% acid-to-H₂O volume ratios).

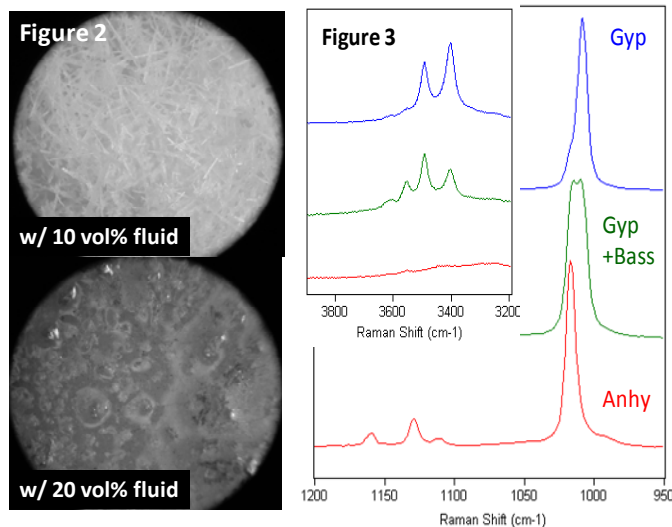
Two ovens, one at 90°C for reaction and one at 50°C for precipitation, were used. Silica sand was used as a thermal media to keep the temperature homogeneity, also to reduce the temperature fluctuation during the sample transitions.

Experimental Procedure: From the basalt-acid reaction containers at 90°C, individual reaction vials were removed after 1 day, 3 days, and 10 days. The top clear fluid in each vial was decanted into two glass vials. The glass vials were capped and then transferred to another container for precipitation. This precipitation container (~800 ml) was also filled with CO₂ (>1 atm) in the same way as for those reaction containers, and was stored at 50°C for 3-5 days. Finally, the top liquid in each precipitation vial was decanted and pipetted into another glass vial, which was set at room temperature in a third large container (loosely capped and actively purged with dry CO₂) to achieve the total evaporation. The leached basaltic sand from each of 90°C reactions and the precipitated solid from each of 50°C precipitation experiments were washed three

times with DI water (of similar temperature), and then set to room temperature in a CO₂-purged container to dry. The rinse liquids were collected and set to dry in open air.

Observations at early stages: We have observed a difference in the form and amount of precipitation at 50°C from the reactions with acidic fluids at different acid-to-H₂O ratios. For example, the precipitation from reactions using 10% acid-to-H₂O volume-ratio fluid has a much coarser grain size and a much higher quantity than those from reactions using 20 vol% fluid (Fig. 2a). In order to confirm this result, eight reactions using 5 vol% and 15 vol% acidic fluids were added, and a similar difference confirmed the first observation (Fig. 2).

Through a preliminary Raman analysis of reaction products (Fig. 3), we found a difference in the hydration state of Ca-sulfates formed during the reaction of basaltic sand with acidic fluids of different acid-to-H₂O ratios. Anhydrite (CaSO₄) was formed in the reaction with 20 vol% fluid, whereas all three types of Ca-sulfates, including gypsum (CaSO₄·2H₂O) and bassanite (CaSO₄·0.5H₂O) were formed in the reaction with 10 vol% fluid. This result was not affected by the fluid to sand ratio (2:1 or 10:1).



Future works: We are currently analyzing the products from these experiments. More results will be reported at the conference.

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References: [1] Carr, *Water on Mars*, 1996; [2] Feldman et al., *JGR*, 2004; [3] Byrne et al., *Science*, 2009; [4] Squyres et al., *Science*, 2006; [5] Squyres et al., *Science*, 2008; [6] Yen et al., *JGR*, 2008; [7] Wang et al., *JGR*, 2008; [8] Tosca et al., *JGR*, 2004; [9] Tosca et al., *JGR*, 2008; [10] Tosca et al., *EPSL*, 2006; [11] Golden et al., *JGR*, 2005; [12] Hurowitz et al., *Am. Minerals*, 2006.