

A LABORATORY SIMULATION EXPERIMENT OF HYDROTHERMAL PROCESSES ON MARS.

Yuhang Zhou and Alian Wang, Dept Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, MO, 63130, USA (yuhang@levee.wustl.edu) (alianw@levee.wustl.edu)

Hydrothermal processes on Mars: It has been suggested that hydrothermal process may have been active in the history of Mars [1]. This concept is supported by three lines of evidences: (1) widespread evidences of volcanic activity on Mars; (2) high levels of WEH (water-equivalent-hydrogen) found in two large equatorial regions on Mars (ODY_NS) [2]; (3) The ground ice excavated by meteorite impacts as observed by MRO_HiRISE and confirmed by MRO_CRISM [3]. Heat from volcanic activity interacting with ground water or ice could produce hydrothermal activity. The first surface confirmation of hydrothermal activity on Mars was made by Spirit, through exploration around the Home Plate area in Gusev Crater [4]. Amorphous silica and variety of sulfates were identified there and could be produced as secondary minerals by hydrothermal activity.

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 of the minerals and mineral assemblages, we designed a set of hydrothermal simulation experiments in laboratory under well controlled environmental conditions. This abstract describes the chemical and mineralogical characters of starting basalt and mineralogical characters of first set of experimental products.

Laboratory Hydrothermal Simulation Experiment: Different from previous studies [5,6,7,8], our experiments has two characters: (1) the use of an oxygen-poor environment: a dry CO_2 200 (purity 99.9%) environment (>1 atm); (2) the use of three temperature ranges to separate the produced secondary minerals.

The experiment was conducted in three steps: (1) to react basaltic sand with acidic fluids (H_2SO_4 : HCl in 4:1 molar ratio) with four different densities (5, 10, 15, 20%) and at two fluid to sand (2:1 and 10:1) ratio 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; (5) to evaporate the residual fluid at room T.

Every step of the experiment except (5) was conducted in a dry CO_2 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. There are 20 vials of samples reacted at different conditions, that produced about one hundred samples, including reaction residues from 90°C experiments, precipitated solids from 50°C brines and the decanted

fluids, and evaporated minerals from residual fluid at room T.

The starting material is basaltic rock HP003, whose chemical composition (including compositional zoning) and surface morphology have been studied by EMP analysis. This sample was collected from a recent PuuOo flow of the Kilauea volcano in Hawaii. For our experiment, a piece of HP003 was crushed, ground, and sieved. The basaltic sand with size $250 \mu\text{m} < d < 850 \mu\text{m}$ was used.

Chemistry and mineralogy of the starting Basalt:

We made EMP analysis on a polished HP003 basalt chip. The piece of sample was put in epoxy, polished with a smallest of $5 \mu\text{m}$ abrazone. Then the sample was carbon-coated and sent to make EMP analysis. The result of EMP analysis shows that HP003 includes great amount of glass, pyroxene, and plagioclase. Olivine was not report in EMP analysis, yet rare olivine has been observed with Raman measurements. The basalt is rich in Ca, Na, Fe, Mg, Al and Ti. We calculated the feldspar stoichiometry in the system An-Ab-Or based on EMP analysis, which shows an enrichment in anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (71%), albite $\text{NaAlSi}_3\text{O}_8$ (28%), and poor in orthoclase KAlSi_3O_8 (0.5%). In addition, the pyroxene stoichiometry in the system Wo-En-Fs was calculated. It shows a large proportion of enstatite $\text{Mg}_2\text{Si}_2\text{O}_6$ (55%), greater than wollastonite $\text{Ca}_2\text{Si}_2\text{O}_6$ (30%), and than ferrisilite $\text{Fe}_2\text{Si}_2\text{O}_6$ (15%).

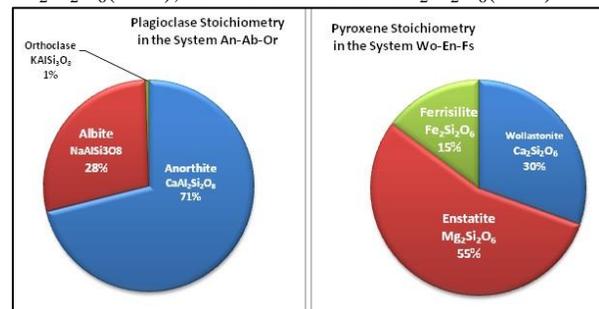


Figure 1. Plagioclase in starting HP003 basalt expressed in stoichiometry of the system An-Ab-Or (left); Pyroxene in HP003 expressed in stoichiometry of the system Wo-En-Fs.

Mineral identifications in starting basalt were first made by using a KOSI HoloLab5000 Raman spectrometer, with ~ 9mW of 532 nm laser power at the sample in a condensed beam of 6 μm diameter. Two types of measurements were made: first is a series of point-checking measurements on individual grains, at the spots selected on the basis of morphology, such as particle shape, color, and surface texture; second is a 200-points Raman mapping using automatic point-count mode, The purpose of second measurement was to identify as many mineral phases as possible. Many

different mineral phases has been identified in the starting HP003 basalt, including feldspar, pyroxene, hematite (Fe_2O_3), magnetite (Fe_3O_4), tridimite (SiO_2), anatase (TiO_2), rarely olivine [$(\text{Mg,Fe})_2\text{SO}_4$] and Perovskite(CaTiO_3).

Mineralogy of reaction residues from 90°C experiments by laser Raman spectroscopy: We have conducted laser Raman measurements on the 20 reaction residual solid samples from 90°C experiments. After the removal reaction fluid (post 1, or 3, or 10 days' experiments), the residual solid was washed with DI water twice and dried in air. On each of 20 samples, 10-20 point-checking Raman measurements and a 200 points Raman mapping were made. Under a optical microscope, the mineral grains in these samples can be divided into two groups, with dark or light color respectively. The dark colored grains are normally unreacted basaltic sand, mainly plagioclase, pyroxene and anatase. All the dark color grains from 20 experiments are coated with small granular white crystals. The white crystal grains have different shapes, either elongated, or rectangular, or needle shape. Raman ID indicated that these light colored crystals are the secondary minerals produced in the reaction at 90°C. A large amount of these crystals are Ca-sulfates, with the most common phases to be gypsum, and bassanite. We also found anatase (TiO_2), Mg- and Fe-sulfates and some other minerals whose Raman spectra yet to be assigned. For some of un-identified phases, additional XRD measurements were made. Figure 2 list the mineral phases identified using Raman spectroscopy and XRD in the reaction residues from the 20 experiments with different acid density (from 5% to 20%), acidic to sand ratio (2:1 or 10:1), duration of reactions (1 day, 3 days or 10 days).

Discussion about results: The major secondary minerals of all 20 experiments at 90°C are gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and anhydrite (CaSO_4). Gypsum distinguishes itself from bassanite or anhydrite with a strongest Raman spectrum from SO_4 mode found at 1008 cm^{-1} , and double peaks from H_2O mode at 3406 , and 3494 cm^{-1} , while bassanite and anhydrite have their strongest SO_4 mode peaks at 1015 , 1017 cm^{-1} respectively. It is important to notice that gypsum exist only in the reaction residues from the experiments with 5% acid density, as well as from a few short duration (1-3 days) experiments with 10% acid density. We did not observe gypsum either in the reaction residues with 10% acid density of long duration (10 days) or from any experiment with 15% and 20% acid density. Oppositely, bassanite (and possible anhydrite) are observed in all 20 experimental products. There seems a trend of finding Ca-sulfates with lower hydration degree from the experiments with higher acid density, or those with lower acid density but longer reaction duration. This trend is obviously

resulted from the decreasing of water activity in those reactions. Apparently, the hydration degree of Ca-sulfates is not dependent on fluid-to-rock ratio.

| sample # | acid density | acidic : rock | at 90C | pyroxene | feld | gypsum | anhy/bass | anatase | alunogen |
|----------|---------------|---------------|---------|----------|------|--------|-----------|---------|----------|
| 0 | Original Sand | | | * | * | | | | |
| 1 | 5% | 2:1 | 3 days | * | * | * | * | * | * |
| 2 | | | 10 days | * | * | * | * | * | * |
| 3 | | 10:1 | 3 days | * | * | * | * | * | * |
| 4 | | | 10 days | * | * | * | * | * | * |
| 5 | 10% | 2:1 | 1 day | * | * | * | * | * | * |
| 6 | | | 3 days | * | * | * | * | * | * |
| 7 | | | 10 days | * | * | * | * | * | * |
| 8 | | 10:1 | 1 day | * | * | * | * | * | * |
| 9 | | | 3 days | * | * | * | * | * | * |
| 10 | | | 10 days | * | * | * | * | * | * |
| 11 | 15% | 2:1 | 3 days | * | * | * | * | * | * |
| 12 | | | 10 days | * | * | * | * | * | * |
| 13 | | 10:1 | 3 days | * | * | * | * | * | * |
| 14 | | | 10 days | * | * | * | * | * | * |
| 15 | 20% | 2:1 | 1 day | * | * | * | * | * | * |
| 16 | | | 3 days | * | * | * | * | * | * |
| 17 | | | 10 days | * | * | * | * | * | * |
| 18 | | 10:1 | 1 day | * | * | * | * | * | * |
| 19 | | | 3 days | * | * | * | * | * | * |
| 20 | | | 10 days | * | * | * | * | * | * |

Figure 2 mineral phases identified using laser Raman spectroscopy and XRD in reaction residual solid from 20 experiments reacting acidic fluid with basaltic sand at 90°C in CO_2 atmosphere.

Another trend of observation is that other hydrous sulfates started to appear in the reaction residues of the experiments with acid density great than 10%, especially those of 15% and 20% acid density. Alunogen [$\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$] is one of the most commonly seen phase, appearing with a 993 cm^{-1} Raman peak position. We have identified a few hydrous Mg-sulfates, i.e., epsomite, and a few hydrous Fe-sulfates, i.e., coquimbite. It appears that a higher variety of cations get released from original HP003 basalt with increasing acid density produced the secondary minerals with more variety of cations.

Anatase is a mineral phase identified in the original basaltic sand. It stays in the reaction residues from all 20 experiments, which is a firm demonstration of the structural resistance of this phase in acidic environment (up to 20% acid density with fluid-to-sand ratio 10:1). This observation is consistent with the enrichment of Ti in the white-tone soil at Gertrude Weise site (at Gusev) [4] which were interpreted to be hydrothermal origin.

Further work: to accomplish the mineral phase ID of precipitation solids at 50°C (CO_2 atmosphere) and the evaporation solids at room T is critical to gain the general understanding of whole process.

Acknowledgement: This work was partially supported by NASA Mars Fundamental Research Project NNX10AM89G (AW) and by the Chinese Scholarship Council (YHZ). We want to thank the help given by Ms. Y. L. Lu and Mr. Paul Carpenter in Raman, IR, and XRD laboratories.

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