

**WEATHERING OF HAWAIIAN BASALTS UNDER SULFUR-RICH CONDITIONS: APPLICATIONS TO UNDERSTANDING SURFACE-ATMOSPHERE INTERACTIONS ON VENUS.** M. C. McCanta<sup>1</sup>, M.D. Dyar<sup>2</sup>, L. T. Elkins-Tanton<sup>3</sup>, A. H. Treiman<sup>4</sup>. <sup>1</sup>Geology Dept., Tufts University, Medford, MA 02155; <sup>2</sup>Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075; <sup>3</sup>Dept. of Earth, Atmos. & Planet. Sci., M.I.T., Cambridge, MA 02139; <sup>4</sup>Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston, TX, 77058.

**Introduction:** There are only a few constraints on the elemental composition and mineralogy of Venus' surface and subsurface, but these are critically needed to test models of surface evolution and weathering based on understanding of the physics and chemistry of Venus' crust and atmosphere. Three sets of XRF major element analyses from the Venera and Vega landers all suggest the presence of basaltic rock types along with variable amounts of sulfur, either primary or secondary from atmospheric interactions. Modeling of these results by various workers [e.g., 1,2] has provided the ground-work and experimental context for distinguishing the contributions of chemical weathering reactions in an attempt to see through the geochemical overprinting to infer primary igneous rock compositions and mineralogy. The key to understanding Venus geology is to work backwards from the elemental and mineralogical compositions of surface-altered rocks to understand both the weathering products (and from them, rock-atmosphere interactions) and the rock type(s) from which they form.

The atmospheres of Venus and Earth are of dissimilar compositions. Notably, the atmosphere of Venus contains a significant amount of sulfur [3]. Therefore, it is expected that surficial weathering in the presence of SO<sub>2</sub>-rich atmosphere will be an important process on Venus. To study the gas-rock interactions likely active on the surface of Venus a natural analogue would be advantageous, however, this type of weathering is fairly unusual terrestrially. In this study we present data on basalts weathered under high-SO<sub>2</sub> conditions from the Big Island of Hawaii as a terrestrial analog for surface conditions on Venus.

Since March 19, 2008, there has been renewed activity in the Halemaumau crater, previously the site of eruptions in the 1920's. The recent events have included significant releases of SO<sub>2</sub>-rich gas at rates of ~700 tonnes per day [4], with highly concentrated emissions containing up to 600 ppm SO<sub>2</sub> [5]. The samples studied here were collected directly downwind and in the path of the gas plume. We present SEM, XRD, and spectroscopic data on the mineralogy of these altered basalts, to lend insights into sulfur weathering of the Venusian surface.

Table 1. BHVO-1 Composition*	
Wt.% Oxide	
SiO <sub>2</sub>	49.94
TiO <sub>2</sub>	2.71
Al <sub>2</sub> O <sub>3</sub>	13.80
FeO	8.58
Fe <sub>2</sub> O <sub>3</sub>	2.82
MgO	7.23
MnO	0.17
CaO	11.40
Na <sub>2</sub> O	2.26
K <sub>2</sub> O	0.52
P <sub>2</sub> O <sub>5</sub>	0.27
Sum	99.70
* <a href="http://minerals.cr.usgs.gov/geo_chem_stand/basalt/bhvo1.html">http://minerals.cr.usgs.gov/geo_chem_stand/basalt/bhvo1.html</a>	

**Methods and Samples Studied:** Bulk rock samples were obtained courtesy of staff at the Hawaii Volcano Observatory from distances of 100-150m S-SE of the Halemaumau overlook in late March of 2010. Samples are friable vesiculated basalts with yellowish white coatings in vesicles and in varying thicknesses upon the surface. Some samples contain fresh black basaltic material, whereas others are altered throughout, with only alteration phases evident (one sample was so altered

that it was completely amorphous to XRD). The primary composition of these samples is shown in Table 1 (USGS standard BHVO-1).

For XRD analysis, chunks containing both basalt and alteration material were powdered by hand. Samples were analyzed by Actlabs using a Panalytical X'Pert Pro diffractometer equipped with a Cu X-ray source. X-ray conditions included 40 kV voltage, 40 mA current, 4-80° 2θ range in 0.02° steps at 1s/step. The divergence slit was fixed at a 1° angle, the receiving slit size was 0.2 mm, and the sample was rotated at 1 rev/s.

For SEM analysis, whole samples were gold or carbon coated to allow inspection of surface alteration. Some samples were also encased in epoxy and sliced to make thick sections to facilitate observation of alteration textures and compositions. Analyses were done at Tufts University using a JEOL 6300 scanning electron microscope and the Revolution software package for data reduction.

**Results:** XRD output from the six samples analyzed is shown in Table 2. Basalt components (pyroxene and plagioclase) are still present in some samples, but all samples show significant alteration to mostly sulfates. Two samples contained small amounts of anatase, which is likely an alteration product of the primary igneous Fe-Ti oxides (Table 1). Cristobalite was found in sample H10-7; it could be either primary (as the end-product of high temperature, lower pressure crystallization) or secondary (formed by either

vapor phase deposition or devitrification of volcanic glass). The remaining phases are all sulfate alteration products: gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), anhydrite ( $\text{CaSO}_4$ ), and natroalunite ( $\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$ ).

**Table 2. Minerals Identified by XRD Analyses\***

Sample	H10-4	H10-6	H10-7	H10-8	H10-9
Augite	34	5	n.d.	24	32
Plagioclase	45	n.d.	n.d.	16	51
Gypsum	6	72	84	56	6
Anhydrite	n.d.	23	n.d.	n.d.	n.d.
Natroalunite	15	n.d.	n.d.	n.d.	10
Cristobalite	n.d.	n.d.	10	n.d.	n.d.
Anatase	n.d.	n.d.	6	4	n.d.

\*Results expressed in semi-quantitative wt%. Note that one additional sample, H10-2, was composed of 100% X-ray amorphous material.

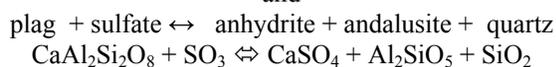
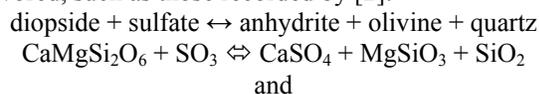
\*\*n.d. = not detected

SEM observations are consistent with the XRD data, and show the sulfates forming as euhedral to subhedral grains with  $\sim 1 \mu\text{m}$  diameters (Figure 1).

**Discussion:** The observed mineralogy is consistent with the assemblage predicted by [2], who simulated basalt weathering using SUPCRT, Thermocalc, and associated databases; these predicted the presence of anhydrite, plagioclase, pyroxene, quartz, cordierite, and hematite (see reactions below, from [1] and [2]).

The work of [6] shows the effects of acid fog deposition at Kilauea prior to the recent increases in gas output; they documented the presence of an alunite group sulfate (potentially jarosite) and amorphous silica rock coatings. They also reported the presence of a Ca-sulfate mineral as a minor constituent. Additionally, Mössbauer spectroscopy of those samples indicated the presence of minor amounts of hematite. The models of [6] suggest that at very low effective rock-to-water ratios, basaltic glass dissolution takes place, followed by evaporative precipitation of alteration phases in the order: amorphous silica, jarosite, gypsum.

**Relevance to the Surface of Venus:** Due to the high sulfur content of the Venusian atmosphere, alteration products high in sulfates are to be expected. However, by definition, all terrestrial basalt weathering reactions occur in the presence of water at a slow rate (relative to 93 bar, 740K conditions on Venus). Although there is believed to be small amounts of  $\text{H}_2\text{O}$  remaining in the Venusian atmosphere, water is unlikely to play a major role in Venus weathering reactions. This suggests that anhydrous reactions may be favored, such as those recorded by [2]:



On Venus, carbonate alteration phases might also be prevalent, but there is no terrestrial analogue that replicates those conditions.

If mineral assemblages like those measured in our Halemaumau samples were observed on Venus, it would be possible to back-calculate a range of major element abundances of the parent rock, in a manner similar to the work done (e.g. Fig. 4 in [6]). Our Halemaumau basalts thus provide a useful demonstration of how basalt alteration might be driven by  $\text{SO}_2$ -rich

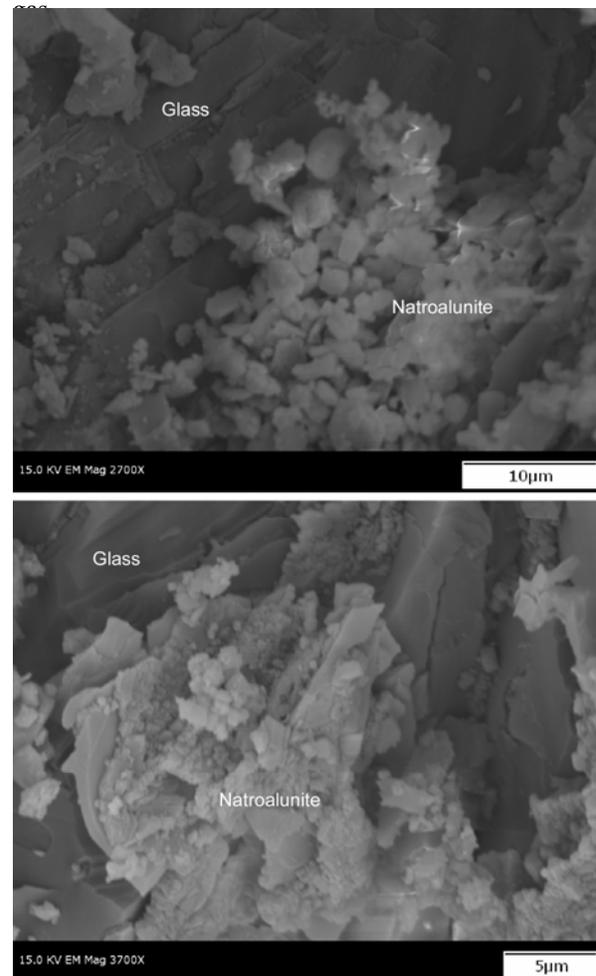


Figure 1. SEM images of sulfates growing on basaltic glass surface in sample H10-4. Sulfate phase is natroalunite.

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**References:** [1] Zolotov M. Yu. et al. (1997) *Icarus*, 130, 475-494. [2] Treiman A. H. and Schwenzer, S. P. (2009) *Venus Geochemistry: Progress, Prospects, and New Missions*, Abstract #2011. [3] Krasnopolsky and Parshev (1981) *Nature* 292, 610-613. [4] Hawaiian Volcano Observatory website: <http://volcanoes.usgs.gov/hvo/activity/kilaueastatus.php>. [5] Martin et al., 2009, *Eos*. [6] Schiffman P. et al. (2006) *Geology*, 34, 921-924.