

ROCK AND MINERAL WEATHERING EXPERIMENTS UNDER MODEL VENUS CONDITIONS.

D. C. Aveline¹, W. J. Abbey¹, M. Choukroun¹, A. H. Treiman², M. D. Dyar³, S. E. Smrekar¹, and S. M. Feldman¹.
¹Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109-8099, daveline@jpl.nasa.gov, ²Lunar & Planetary Institute, Houston, TX 77058, ³Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075.

Introduction. Chemical analyses of rock and regolith at the Venera and Vega landing sites [1] suggest that Venus' surface consists of basaltic rocks with variable amounts of S, either as a primary constituent or as a secondary product of atmospheric interactions. Starting with these chemistries, models of Venus mineralogy predict that the surface is composed of primary basaltic minerals, unreacted residual glass, and specific alteration minerals [2-4]. Because Venus surface conditions are challenging to replicate in the laboratory (ca. 92 bars and 735K, with an atmosphere of 96.5% CO₂, 3.5% N₂, and 150 ppm SO₂ and other gases), little experimental work has been done to confirm the modeled mineralogy. It is known that calcite (CaCO₃), likely an alteration product of Ca-bearing igneous Venusian minerals, reacts rapidly in Venus-like atmospheres at high temperature [2,3]. Diopside (pyroxene) and amphiboles decompose slowly on laboratory timescales [2,5-7]. Basalt glass reacts under pure CO₂ [8] and also under SO₂-bearing volcanic gases [9].

We describe here the initial experiments in a campaign to simulate weathering of likely Venus surface materials to understand changes in mineralogy that occur via interactions between basalts and the atmosphere. Our goal is to determine if and how primary igneous rocks have been weathered by the atmosphere, and to enable and corroborate backward models that will determine the primary rock compositions that were the starting point of Venus' geological evolution.

Venus Weathering System. We have built and tested a high-temperature pressure system (Fig. 1) designed to study the alteration of rocks under the atmospheric conditions on the surface of Venus. By boosting CO₂ and/or SO₂ gas densities higher than Venus' known partial pressures, the system can accelerate the geochemical reaction rates, and therefore simulate years of Venusian surface weathering within several days in the laboratory.

The weathering chamber is housed inside a custom oven that can provide uniform heating up to 1000°C. It includes feed-throughs for the gas lines and temperature probes, as well as a rigid support structure for the high pressure vessel. This compact chamber was designed to handle over 1000 bars at 460°C. It includes a 6" long cylindrical volume of 36 mL with three ports: gas inlet/outlet, thermocouple feed-through, and sample transfer port. A special sample holder assembly slides into the chamber and can hold multiple samples, including chips, powders and/or pressed pellets up to 13 mm diameter.



Figure 1. A photo of the Venus Weathering System assembled inside a fumehood showing the major components. The high pressure vessel is mounted inside the oven system.

Samples and Methods. Our weathering experiments utilized minerals and rocks likely to be primary and secondary phases on Venus' surface (Table 1).

Table 1. Samples Studied	
Calcite	Chihuahua, Mexico, Wards #49-5860
Calcite	synthetic powder, J.T. Baker #1294-01
Diopside	Fianarantsoa, Madagascar Wards #48E-5870
Diopside	Trinity Mtns, CA
Enstatite	Bamble, Norway, Wards #49-2125
Hedenbergite	Viliut, Russia
Hypersthene	Quebec, Canada
Dunite	Twin Sisters, WA
Anorthosite	Northern Ontario, Canada
Basalt glass	Hawaii, from M. Bullock

After loading the samples and sealing the chamber, the pressure vessel is purged with nitrogen gas and evacuated with a vacuum pump before being filled with pure SO₂ gas at a tank pressure of ~36 psi. We then close the gas inlet valve and heat the vessel to 460±2°C over about 2 h, driving the pressure up to ~70 psi. Pressure is monitored throughout a run duration of 4-5 days; it follows an exponential decrease due to a small leak. Our metric of interest is the overall inte-

grated pressure-time divided by the Venusian partial pressure of SO_2 , yielding a total exposure time denoted in equivalent Venus years. We have performed two main runs. The first run (1100 Earth days = 4.9 Venus years) included 3 chips of each of the 9 samples. The second run (equivalent to 3 Venus years) incorporated 5 powdered samples along with a pressed pellet of calcite and several calcite chips, which acted as controls in the experiments.

Analytical methods. An FEI (Philips) XL 30 environmental scanning electron microscope (ESEM), with an accelerating voltage of 20 keV and 264 μA beam current was used for secondary electron imaging. An EDAX Genesis energy dispersive X-ray spectrometer (EDS) in spot mode was used for elemental analyses. XRD used a Bruker AXS model D8 Discover X-ray diffractometer equipped with a General Area Detector Diffraction System; $\text{CuK}\alpha$ radiation ($\lambda = 0.1542 \text{ nm}$) was used to obtain powder XRD patterns. A Horiba Jobin-Yvon LabRam HR confocal microscope equipped with a Raman spectrometer was used to excite samples with a 532 nm Nd-YAG solid-state laser.

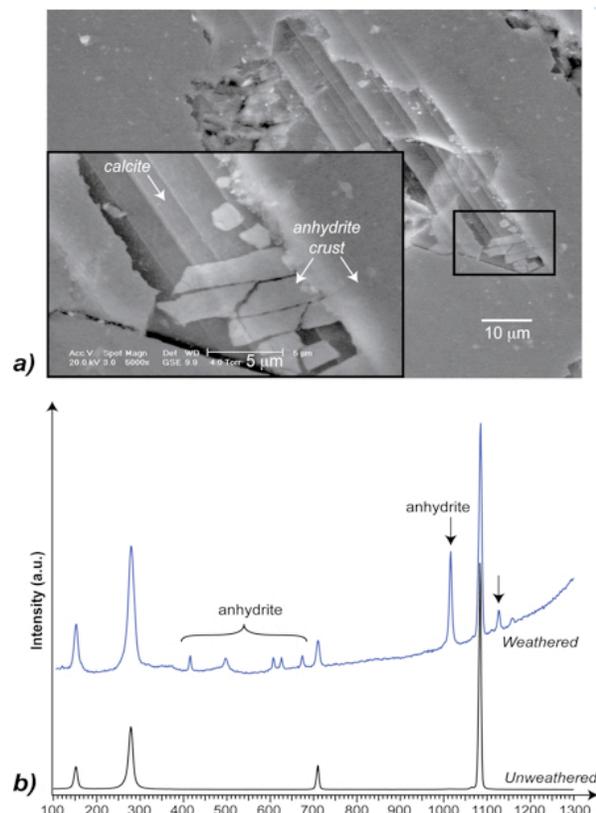


Figure 2. Results obtained on calcite (Iceland spar) surface. a) ESEM photographs showing development of a thin anhydrite crust confirmed by EDS. b) Raman spectra of starting and weathered calcite. The anhydrite signature is weak except in crevices (shown) and on pressed calcite pellets.

Results. Of the materials investigated, calcite reacted the most rapidly. A crust of anhydrite formed on all calcite surfaces (Fig. 2), and S was present throughout. EDS, Raman and XRD all confirm the presence of anhydrite in the reacted calcite, as expected [2,3,9]. Powders and pressed pellets exhibited more anhydrite in XRD and Raman than chips because there was greater surface area available for reaction.

On calcite chips, the anhydrite crust has a weak signature in Raman, whereas EDS shows no residual calcite. X-rays used for EDS have a very small penetration depth (10-100 nm depending on the material's absorption), whereas the green photons of the Raman laser beam have a typical penetration depth of $\sim 5 \mu\text{m}$. The strong signature of anhydrite in EDS vs. weak in Raman suggests an anhydrite crust with a thickness of ~ 100 -1000 nm, consistent (within its large uncertainty) with the rate law for calcite \rightarrow anhydrite determined at higher T and lower $P(\text{SO}_2)$ by [2].

The diopside, basaltic glass, and anorthosite samples all showed some surface uptake of S (1-2% overall, but up to 4-5% in cracks and crevices, detected by EDS). S levels in dunite were barely above detection limits. For these minerals, reaction times were likely too short to allow for sufficient reaction to form detectable new mineral phases.

New weathering experiments are being conducted on the samples listed in Table 1 using longer Venus-equivalent durations. Results will be compared with those of McCanta et al. [9], who found augite, plagioclase, gypsum, anhydrite, natroalunite, cristobalite, and anatase in basalts weathered under high- SO_2 conditions from Halemaumau crater on the Big Island of Hawaii. High temperatures on Venus' surface will likely not allow for the formation of hydrated minerals [10], but anhydrous equivalents of the sulfates are expected. Results will be presented at this meeting.

Acknowledgments: This work was carried out at the California Institute of Technology Jet Propulsion Laboratory (JPL) under a contract with NASA. We thank JPL for support via Research and Technology Development funding Copyright 2011. All rights reserved. Government sponsorship acknowledged.

References: [1] Barsukov V.L. (1992) Venusian Igneous Rocks. In *Venus Geology, Geochemistry, and Geophysics* (eds. V.L. Barsukov, A.T. Basilevsky, V.P. Volkov, and V.W. Zharkov). Univ. Arizona Press, 65-176. [2] Fegley B. Jr. & Prinn R.G. (1989) *Nature* 337, 55-58. [3] Zhong Q. (1995) *Thermochimica Acta* 260, 125-136. [4] Treiman A.H. (2010) *Intl Venus Conf. Aussois*, Abstr. 05-02. [5] Johnson N.M. & Fegley B.Jr. (2000), *Icarus* 146, 301-306. [6] Johnson N.M. & Fegley B.Jr. (2003) *Icarus* 164, 317-333. [7] Johnson N.M. & Fegley B.Jr. (2003) *Icarus* 165, 340-348. [8] Treiman A.H. & Allen C.C. (1994) *Lunar Planet. Sci.* XXV, 1415-1416. [9] McCanta, M. et al. This conference. [10] Zolotov M.Y. et al. (1997), *Icarus* 130, 475-494.