EXPERIMENTAL INVESTIGATION OF APATITE VOLATILE EXCHANGE ON VENUS. A. R. Santos[1], T. Kremic[1], L. M. Nakley[1], D. M. Vento[1], K. Phillips[1], A. H. Treiman[2], F. M. McCubbin[3], [1]NASA Glenn Research Center, 21000 Brookpark Rd., Cleveland, OH 44135, [2]Lunar and Planetary Institute, USRA, 3600 Bay Area Boulevard, Houston, TX 77058, [3]NASA Johnson Space Center, Mailcode XI2, 2101 NASA Parkway, Houston, TX 77058, USA. (alison.r.santos@nasa.gov)

Introduction: Volatiles are known to be important to several aspects of planetary evolution, from atmospheres to the development of internal structure and melt generation [1]. Thus, volatiles likely are important to the explanation of why Venus and Earth evolved down two drastically different paths [e.g., volatiles are important to plate tectonics, 2]. Real samples and measurements from Venus are key to addressing this question, however, until such data are acquired, we rely on currently available simulation chambers to begin to assess reactions and processes that likely occur on Venus in order to build our understanding of required measurements and possible models.

The major magmatic volatiles on Earth include H_2O, CO_2, S, Cl, and F [3], and these volatiles have been found to influence magma behaviors from melting point to viscosity. On the Earth's surface, these compounds also have profound influence as atmospheric gas species and participate in the hydrosphere and chemical weathering. The Venusian atmosphere is a dense, complex mixture containing the aforementioned volatiles and more, and this gas mixture, combined with a surface temperature of 460 ºC and pressure of 96 bars, suggests an interesting and unique set of surface-atmosphere interactions on this planet. There are many points to address when considering planetary volatiles, but a place to start is with material that would be involved with multiple parts of the planetary system (e.g., mantle, atmosphere, crust). Crustal minerals fill this role, as many of them form as products of igneous magmatism (sampling mantle), exist as part of the crust (crust), and participate in weathering processes (atmosphere, hydrosphere).

The most widespread volatile-bearing mineral is apatite, nominally ($Ca_5(PO_4)_3$(F,Cl,OH)), which has been proposed to occur on Venus [4]. The compositions of apatites have been used to constrain the volatile contents of planetary melts and mantles [e.g., 5-6]. Although chemical compositions of Venusian minerals are not known yet, these studies demonstrate that apatite can be an important volatile reservoir in rocky bodies and monitor of the compositions of volatile phases. Apatite can accommodate a wide range of volatile—bearing substitutions The apatite X-site is commonly filled by OH^-, F^-, and/or Cl^-, but other species including CO_3^{2-}, S_2^-, Br^-, and vacancies can be present too

[7]. SO_4^{2-} CO_3^{2-} can also substitute for the PO_4^{3-} group. Gas molecules related to these anions have all been detected in Venus' atmosphere [8], and thus are available to interact with apatite on the Venusian surface.

Apatite may have an additional important role on Venus. Treiman et al. [4] proposed that Cl-apatite could be the ferroelectric material [9] responsible for the distinctive pattern of high and low radar reflectance (e.g., Magellan SAR) on near-equatorial Venusian highlands. Chlorapatite is the likely ferroelectric material because it is electrically polar (i.e. not centrosymmetric, because the large Cl^- anions don't fit in a centrosymmetric site [10]), and because its polarity can be reversed by an applied electric field (the Cl^- anions are displaced). Apatite is a common accessory mineral in all igneous rocks, as fluorapatite, and so should be present at Venus' surface. Venus' atmosphere contains significant HCl, so that chemical interaction between fluorapatite and Venus's atmosphere could produce chlorapatite. The morphologically youngest volcanoes on Venus do not show the chlorapatite ferroelectric radar pattern [4], which suggests that chlorapatite forms over time, at geologically slow rates.

Due to these two important potential roles for apatite on Venus, we are conducting experiments in order to examine the alteration behavior of apatite in a simulated Venus atmosphere at expected Venus surface conditions.

Methods: *Samples.* The prediction of Treiman et al. calls for fluorapatite to be converted to chlorapatite through interaction with the atmosphere. Fluorapatite is a common naturally occurring apatite on Earth and other planetary bodies [7], and can be reasonably assumed to occur on Venus [4]. We selected two naturally occurring terrestrial apatites for this study. One apatite sample, AP2.1, is a small, light blue, anhedral crystal. The second sample, AP1.1, is a large, euhedral, greenish yellow, single crystal of Durango apatite. The crystal appears to be fractured and contain small inclusions of a reddish mineral, possibly an iron oxide.

Samples were cut into smaller pieces for use in the experiment (Figure 1); AP2.1 was cut in half, while a slice perpendicular to the c-axis was cut from the AP1.1 crystal. A roughly rectangular piece was then cut from this slice, with the long axis of the rectangle parallel to the c-axis of the mineral.
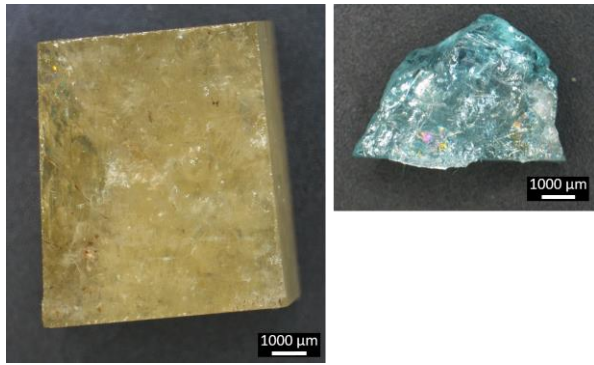
Figure 1: Images of the two apatite samples used in this study. Left: AP1.1, the c-axis is parallel to the face shown here, Right: AP2.1.

Experimental Conditions. The apatite samples will be exposed to a simulated Venus surface environment using the Glenn Extreme Environment Rig (GEER) located at NASA's Glenn Research Center (Figure 2). This apparatus has demonstrated the capability to sustain Venus surface conditions, including temperature, pressure, and atmosphere composition, for over a month [e.g., 11]. The conditions for this experiment are a temperature of 460 ℃, pressure of 93 bars, and an atmosphere consisting of CO_2 (96.5%), N_2 (3.5%), OCS (51 ppm), H_2O (30 ppm), CO (12 ppm), HCl (0.5 ppm), SO_2 (180 ppm), H_2S (2 ppm), and HF (2.5 ppb) [12]. While in GEER, the apatite samples will rest inside alumina trays. The experiment duration will be between 21 to 28 days. At the termination of the experiment, the temperature will be decreased to 150 ℃ over a period of days, at which point the atmosphere will be purged with nitrogen, then cooled to ambient pressure, again over a period of days. After extraction from the GEER vessel, the samples will be stored in desiccators to prevent or minimize reaction of the run products with the terrestrial atmosphere.

Analysis. Samples will be photographed and weighed upon removal from GEER. Examination under an optical microscope will be conducted, and uncoated samples will be examined under low-vacuum SEM to look for any surface changes. Samples will then be cut in half without water, polished without water, and examined again under SEM and EPMA to look for compositional gradients and reacted surface layers. The unreacted halves of the samples will be examined in the same manner to serve as baselines to compare against the Venus reactions.

Expected Results and Applications: Chlorapatite may be thermodynamically stable on the surface of Venus [4]. Based on measured diffusion coefficients [13], and the experimental temperature and duration, we expect Cl and F to diffuse fastest along the c axis, and a relatively thin layer of chlorapatite to form from the fluorapatite starting material (on the order of ~1 micron thickness).
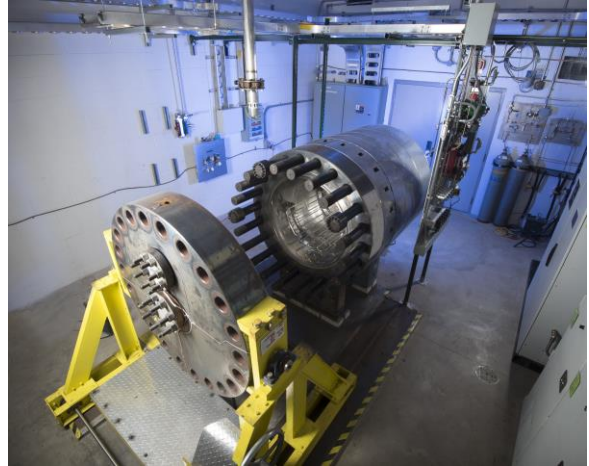

Figure 2: Glenn Extreme Environment Rig showing the interior of the experimental chamber. Image courtesy of Bridget Caswell/NASA GRC.

This experiment will serve as an initial assessment of the F-Cl exchange reaction proposed by [4]. Observation of a reaction layer at the surface of the apatite and/or diffusion of any volatile out of or into the mineral after 21 days will provide evidence for this process being possible on Venus, and will be grounds for continued study with longer duration experiments. These experiments will use samples with known crystallographic orientations (determined using XRD at NASA Glenn), and will build on the results of this first study to create a time series to examine the rates of the observed reactions. This information can then contribute to understanding volatile cycling between the atmosphere and crustal materials, and how interactions between these two parts of Venus led to the atmosphere and surface we observe today.

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