SUPERCRITICAL VERSUS GASEOUS CO_2: MINERALS UNDER SIMULATED VENUS SURFACE CONDITIONS. E. J. Merchak[1], S. T. Port[2], V. F. Chevrier[1], [1]University of Arkansas, Fayetteville AR 72703, [2] NASA Postdoctoral Program Fellow, NASA Glenn Research Center, Cleveland, OH 44135. (ejmercha@uark.edu)

Introduction: CO_2 makes up 96.5% of Venus' atmosphere and exists in different phases at different altitudes due to the varying temperature and pressure [1]. In the lowlands the temperature and pressure, approximately 740K and 90 bar, causes the CO_2 to be a supercritical fluid; meanwhile, the CO_2 in the highlands remains gaseous [2]. We experimentally examine the effects that the two states of CO_2 have on various surface minerals using a Venus simulation chamber at the University of Arkansas. Our goal is to determine if the supercritical state influences the chemical reactions occurring between the surface and the atmosphere, as well as identify the resulting secondary minerals or parageneses.

Venus' exact surface composition remains unknown; however, we will be using minerals previously hypothesized to be present on the surface through mission data and previous modeling. These groups include minerals that can be found in basalts (olivine, pyroxenes, and feldspars), with a special focus on the mineral wollastonite.

Basaltic minerals will be examined due to the observation of shield volcanos, which are generally formed from basaltic lava flows, on Venus by the Venera and Vega missions through remote sensing [3]. These missions also used X-ray Fluorescence and/or Gamma Ray spectrometry to measure elemental abundances and the results suggested a basaltic surface composition [4]. Although we do not know the exact chemical composition of the surface, our samples include olivine ($(Mg,Fe)_2SiO_4$) and pyroxenes (endmembers enstatite-ferrosilite ($(Mg,Fe)SiO_3$) due to their presence in basaltic rock on Earth [5]. The two pyroxene endmembers listed have different stabilities under Venus conditions and further characterization will be completed in our experiments [6].

Wollastonite ($CaSiO_3$) has been proposed to buffer the atmosphere of Venus and we will explore this reaction in our experiments [7]. We will verify if this buffer is a possible reaction pathway and if the state of CO_2 effects this reaction.

The final group of minerals are those found in igneous rocks, specifically feldspars orthoclase ($KAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) [8]. Modeling on the stability of igneous minerals on Venus has been completed and our experiments can be used to corroborate those results [9].

Methods: To investigate the effects of supercritical CO_2 we will utilize both a Venus simulation chamber and a Lindberg tube oven. The Venus chamber seen in Figure 1, nicknamed the Cassiopeia chamber, is a 500 mL chamber made of stainless steel 316. This chamber can replicate the harsh conditions found on Venus' surface, both lowlands and highlands. After the chamber is filled with our chosen atmosphere, the heater is turned on and the pressure increases until it reaches our desired conditions. After reaching Venus' surface conditions the sample is left to react with the atmosphere for two weeks.

Figure 1: Venus Simulation Chamber (Cassiopeia chamber) is located at the center in a holder. The heating sleeve is towards the bottom left, and the pressure gauges are located at the top of the system.

To prepare our samples, each mineral sample is ground using an alumina-ceramic pulverizing dish and sieved to <63 microns to ensure uniformity. One gram of each sample is placed in a ceramic bowl that is positioned in the center of the chamber. The chamber is then sealed before the air is removed using a vacuum pump. After flushing the system for a couple minutes with CO_2, the chamber is filled to ~34 bar. This pressure at room temperature will result in ~95 bar at 460°C, Venus' lowlands conditions. We will also complete experiments at 45 bar and 380°C for the highland conditions. A computer monitors and records the interior temperature and pressure throughout the duration of the experiment.

Simultaneously, an identical sample is reacted in the Lindberg tube oven. This oven is heated to the same temperature as the chamber, but the gas is continuously flowing through the tube at ambient pressure, which maintains CO_2 in a gaseous state. With these two experimental set ups we can then compare the reactions that occurred in gaseous CO_2 versus supercritical CO_2.

Samples are analyzed prior to and after each experiment using X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Electron Dispersive Spectroscopy (EDS). XRD enables us to distinguish any changes to the mineralogy or crystal structure as a result of the experiment. Meanwhile, changes to the sample can be visibly observed using SEM, and EDS can be used to determine changes to the sample's elemental composition.

Preliminary Work: Wollastonite was exposed to lowland conditions for 10 days and the XRD spectra are displayed in Figure 2. The XRD data is still under analysis, but some of the peak changes are discernable. For instance, some graphite flakes from a broken gasket (Figure 3) fell onto the chamber sample and this is visible in the spectra as a wider peak (indicating two peaks) around 2θ = 26°. In the chamber spectra, peaks originally present at 2θ = 28° and 49° have disappeared. After the oven experiment new peaks appeared at 2θ = 36°, 48°, 64.5°. We plan to examine the samples using SEM/EDS to assist in identifying the unknown peaks.

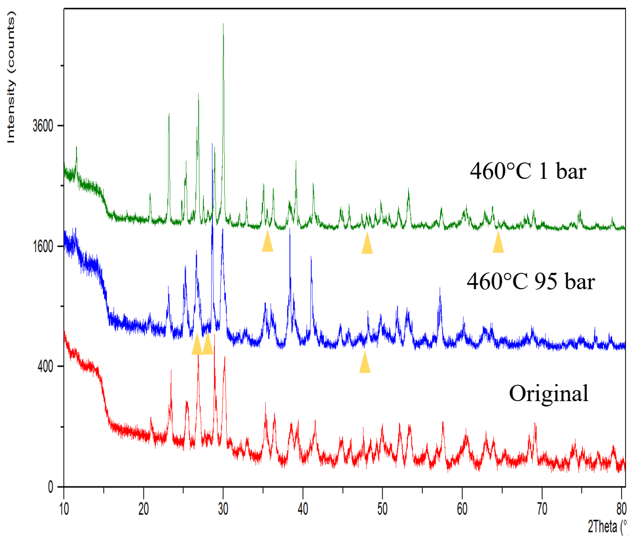

Figure 2: XRD spectra of wollastonite before the experiment (red), after exposure in the tube oven (green) and after exposure in the chamber (blue).

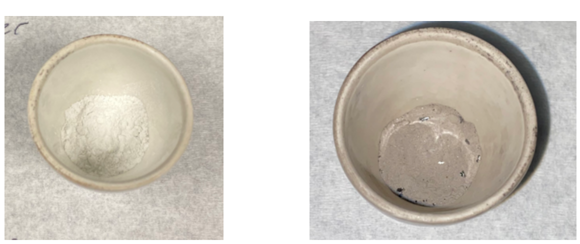

Figure 3: Wollastonite sample before (left) and after (right) reacting in the Venus simulation chamber for 10 days. The gleaming particles in the right sample are pieces of the graphoil gasket in the chamber that flaked into the ceramic bowl.

Significance of this Work: Venus research is becoming increasingly important due to the three announced Venus missions: DAVINCI and VERITAS from NASA, and EnVision from ESA. One of the goals of the missions is to constrain the age of Venus' surface, thus more data is required to understand mineral weathering and reaction rates under the relatively corrosive environment [10,11]. This is especially true of understanding the effects of the different phases of CO_2, supercritical and gaseous, on chemical reactions. The potential differences could alter how we date the Venusian surface in the highlands versus the lowlands. Weathering effects could be different based on the mineral, so it is crucial to understand how they react individually with the two phases of CO_2. Any experimental data obtained will assist in the planning stages of these upcoming missions along with successful data interpretation.

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References: [1] Fegley, B. (2014) Venus. *Treatise on Geochemistry* 127-148. [2] Cordier, D. et al. (2019) The Physical Origin of the Venus Low Atmosphere Chemical Gradient. *The Astrophysical Journal* 880 [3] Alexander T Basilevsky and James W Head 2003 Rep. Prog. Phys. 66 1699 [4] Surkov, Y. et al. (1984) New Data on the Composition, Structure, and properties of Venus Rock Obtained by Venera 13 and Venera 14. *Journal of Geophysical Research* 89(S02) [5] Papike, J. (2005) Comparative Planetary Minerology; Valence State partitioning of CR,Fe,Ti and V Among Crystallographic Sites in Olivine, Pyroxene, and Spinel from Planetary Basalts. *American Mineralogist 90 (2-3)* [6] Zolotov, M. Yu. (2018) *Reviews in Mineralogy and Geochemistry*. 84**,** 351-392. [7] Nozette, S. and Lewis, J. (1982) *Science* 216. 181-183 [8] Klein, C. (2007) The Manual of Mineral Science pp 548-554 [9] Klose, K. and Zolotov, M. Yu., 1992 Lunar and Planetary Science Conference XXIII, 1992, pp. 699-700. [10] Freeman, D. et al. (2016) VERITAS- a Discovery-Class Venus Surface Geology and Geophysics Mission [11] Ghail, R. et al. (2020) Europlanet Science Congress. The Science Goals of the EnVision Venus Orbiter Mission