SURFACE-ATMOSPHERIC REACTIONS ON VENUS: EFFECT OF SUPERCRITICAL VERSUS GASEOUS CO_2

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: The surface of Venus is approximately 733K and 95 bar with an atmosphere mostly comprised of CO_2 (96.5%). [1]. The high surface temperature and pressure induces a phase transition from gaseous CO_2 in the highlands to a supercritical state towards the surface [2]. The effect this phase change has on the interactions with minerals on the surface is unknown. To study any potential effect on reaction rates we will experimentally examine chemical reactions between a variety of minerals and CO_2 both as a gas and as a supercritical fluid using a specially designed Venus environmental chamber.

Our first set of minerals will be olivine ($(Mg,Fe)_2SiO_4$) and pyroxenes (endmembers enstatite-ferrosilite ($(Mg,Fe)SiO_3$) because they are commonly found in basalts on Earth [3]. Basalts are of significant interest because remote sensing of some of the volcanos on Venus made by the Venera and Vega missions indicated shield volcanoes, which are typically composted of basaltic rock on Earth [4]. The missions used X-ray Fluorescence and/or Gamma Ray Spectrometry to measure abundances of elements at the surface, and the results indicated a strongly basaltic composition [4]. The endmember pyroxenes have different stabilities at Venus conditions which will be explored in these experiments [5]. Wollastonite ($CaSiO_3$)) will also be used because it has been proposed to buffer the CO_2 on Venus and we will be able to verify if it is a viable reaction pathway along with the effect, if any, that supercritical CO_2 has on the reaction rate [6].

We are also interested in testing two feldspars, orthoclase ($KAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$), in the chamber due to their presence in igneous rocks on Earth [7]. Some modeling on the stability of igneous rocks in Venus conditions has been completed, however, more experimental data is required to confirm the proposed reactions, as well as their kinetics [8].

Methods: In order to test the effects of Venus conditions on minerals, the experiments are completed in the Venus simulation chamber seen in Figure 1. The ideal gas law allows us to pressurize the CO_2 inside the chamber while simultaneously heating to the chosen temperature. After reaching Venus' surface conditions, the closed system is be left to react for up to two weeks.

Figure 1: Venus simulation chamber at the University of Arkansas. The pressure vessel is shown towards the middle with the heating sleeve to the left and pressure gauges on top.

The Venus simulation chamber is a 500 mL cylinder made of stainless steel 316 that was purchased from Parr Instruments in 2016. A computer monitors the internal pressure and temperature and records these values over the length of the experiment. An Agilent HP 6890 Gas Chromatograph (GC) has been added to the laboratory and will be used to analyze any changes to the atmosphere composition inside the chamber. In order to transfer gas from the chamber to the GC, a secondary chamber will be added to depressurize the gas in the chamber before it is injected into the GC. The GC is equipped with a thermal conductivity detector and flame photometric detector to detect sulfur-bearing gases (SO_2, COS and H_2S).

Before an experiment, the minerals are ground with an alumina-ceramic pulverizing dish and sieved to <63 microns to ensure uniform reaction between mineral grains. A gram of each mineral is measured and placed into a ceramic dish that is then added to the chamber.

The mineral samples are analyzed before and after the experiment with X-Ray Diffraction (XRD) and Electron Dispersive Spectroscopy (EDS). The XRD is used to detect structural changes in the crystal, while the EDS is used to determine the elemental changes that have occurred over the course of the experiment (Figure 2).

After the sample is added to the chamber and the vessel is sealed, the chamber is evacuated to 2 bar and flushed with CO_2. The chamber is then filled with CO_2 and heated until reaching surface conditions, 90 bar and 740 K for lowland conditions [2].

Alongside the chamber experiments, we run an identical experiment at ambient pressure conditions (to compare the effects of pressure at identical temperature). The sample is placed in a Lindberg tube oven at the same Venus temperature, but the atmosphere is at a constant flow of 1 bar of CO_2. This allows for a direct comparison of the interactions of gaseous versus supercritical CO_2 on minerals.

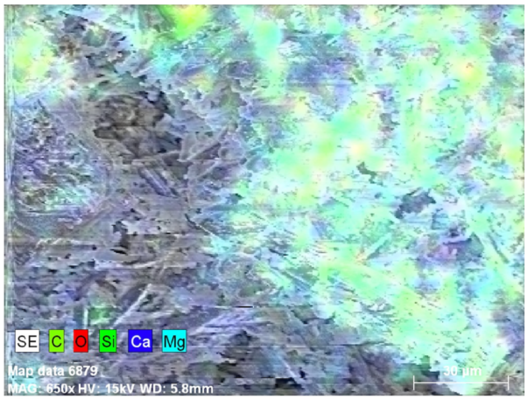

Figure 2: An EDS image of wollastonite before any treatment or experiment. Each color represents an element seen in the bottom left corner

Some minerals need additional treatment before being included in experiments as they are naturally occurring and contain contaminants. XRD showed that our wollastonite sample contains small amounts of calcite; it was removed by adding diluted HCl treatment until the sample did not exhibit any residual calcite in XRD. The remaining sample was then rinsed with DI water and baked until dry.

At this preliminary stage only experiments using untreated wollastonite have been completed. Wollastonite was tested for 6 days at Venus lowland conditions in the chamber and altered from a whiteish color to a dark grey (Figure 3). Further investigation of the sample is currently underway, and experiments using HCl treated wollastonite will begin shortly.

Figure 3: Untreated wollastonite sample before and after exposed to Venus conditions (460°C and 102 bar of CO_2 atmosphere) for 135 hours.

Significance of this Work: With the three upcoming missions to Venus, NASA's DAVINICI and VERITAS as well as ESA's EnVision, experimental data regarding surface-atmosphere interactions will be valuable. We will investigate the effect of the phase state of CO_2 on its interactions with surface materials. This will contribute to our understanding of reaction rates which may help constrain the age of Venus' surface. This is especially relevant as one of the goals of the upcoming missions is determining the age of the surface [9, 10].

The upcoming Venus missions have renewed interest in Venus experimental work and the results of our project will be helpful to those creating Venus simulation facilities. Our results will provide insight into which type of simulation equipment would best suit an institution's research goals. Our configuration to extract gas through a secondary chamber to inject into a GC could provide a blueprint for future chambers.

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References: [1] Fegley (2014) Venus. *Treatise on Geochemistry* 127-148. [2] Cordier et al. (2019) The Physical Origin of the Venus Low Atmosphere Chemical Gradient. *The Astrophysical Journal* 880 (2) [3] Papike (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)* [4] Surkov 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] Zolotov (2018) *Reviews in Mineralogy and Geochemistry*. 84**,** 351-392. [6] Nozette and Lewis (1982) *Science* 216. 181-183 [7] Klein (2007) The Manual of Mineral Science pp 548-554 [8] Klose and Zolotov, 1992 Lunar and Planetary Science Conference XXIII, 1992, pp. 699-700. [9] Freeman et al. (2016) VERITAS- a Discovery-Class Venus Surface Geology and Geophysics Mission [10] Ghail et al. 2020 Europlanet Science Congress The Science Goals of the EnVision Venus Orbiter Mission