REACTIVITY OF CALCIUM-BEARING MINERALS UNDER SIMULATED VENUS CONDITIONS. S. T. Port[1], A. R. Santos[2], D. Lukco[1], T. Kremic[1], G. W. Hunter[1], [1]NASA Glenn Research Center, 21000 Brookpark Road, Cleveland, OH 44135, [2]Department of Earth and Environmental Sciences, Wesleyan University, Middletown, CT 06459; (sara.port@nasa.gov)

Introduction: The surface conditions on Venus are approximately 460°C and 95 bar under an atmosphere composed of a myriad of volcanic gases [1]. A planet's atmosphere and its surface are interconnected and can exchange various elements present in the environment. Thus, knowledge of surface-atmosphere interactions is critical for understanding the current and past environment of Venus. Additionally, the Venus Emissivity Mapper (VEM), which will be on the EnVision and VERITAS missions, will collect emissivity data of the surface of Venus, which can be used to determine the presence and relative abundance of FeO in the surface rock [2-3]. However, as minerals react with the atmosphere they may weather and form a reaction coating, and it is currently unclear how this would affect the orbital emissivity signature. Experiments investigating reaction kinetics are critical for interpreting mission data and understanding the history of Venus's surface and atmosphere.

The focus of this project is to investigate calcium-bearing minerals exposed to Venus-relevant conditions since calcium has been well documented to react with SO_2, a gas with an abundance of 120-180 ppmv in the atmosphere of Venus [1, 4-7]. We will study various minerals that have formed in different geologic settings to examine the effect different crystal lattices and bonding environments may have on reaction rate.

Methods: A series of experiments are being conducted using Thermogravimetric Analysis (TGA) (Fig. 1). The approach is that a mineral (Table 1) is hung in the TGA and is exposed to one of two different temperatures (460°C or 700°C) in one of two different gases (99.99% CO_2 or CO_2 with 1.5% SO_2) for 6 or 12 days. All samples are cut to a cube-like shape and polished to 0.5 µm with diamond paste. The temperature and mass of the sample are recorded by a computer in real time over the duration of the experiment. The 700°C temperature was chosen to increase the amount of reaction in the experimental timeframe. A gas mixture of CO_2 with 1.5% SO_2 was selected to provide the same molecular number density of SO_2 at 1 bar as would be present at Venus pressures of 95 bar [4]. Depending on the results experiments may be run for longer periods of time.

At the end of the experiment the sample is cooled in argon gas before being stored in an N_2 purge box. The samples are first analyzed (uncoated) with X-ray Photoelectron Spectroscopy (XPS). Several of the samples were also sputtered for varying lengths of time to analyze the chemistry a few angstroms beneath the surface. The samples are then coated with platinum and cut into using a Focused Ion Beam (FIB) (gallium source) in order to produce a trench to determine the depth of the reaction rind. Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) are used to analyze the texture and qualitative chemistry of the sample surface and the interior within the trench. EDS analysis was completed using the AZtec software. All purchased minerals were also analyzed by X-Ray Diffraction (XRD) at the start of the project to confirm the mineralogy and identify any other minerals present in the sample.

Figure 1: The TGA used to complete the experiments.

Mineral	Chemical Composition
Calcite	$CaCO_3$
Wollastonite	$CaSiO_3$
Grossular	$Ca_3Al_2(SiO_4)_3$
Anorthite	$CaAl_2Si_2O_8$
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$

Table 1: The minerals to be investigated during this project.

Results: At present, only a handful of experiments have been completed with more planned to be completed by the VEXAG workshop (Table 2).

Mineral	Temp	Gas	Time
Calcite	460°C	CO_2/SO_2	6 days
Calcite	700°C	CO_2	5 days
Calcite	700°C	CO_2/SO_2	5 days
Wollastonite	460°C	CO_2/SO_2	6 days
Tremolite	460°C	CO_2/SO_2	6 days

Table 2: Experiments that have been completed thus far.

The calcite that was heated to 460°C in CO_2/SO_2 did not undergo any noticeable physical changes at the surface. However, XPS analysis revealed 15.1 at% of sulfur at

the surface, which dropped to 10.6% after the top 500Å was removed by sputtering for 5 minutes. Analysis of the binding energy reveals that the sulfur is present as sulfate. After the experiment carbonate is not present at the surface but is present at depth. EDS analysis of the cliff wall confirms that sulfur decreases with increasing depth.

When calcite was heated to 700°C in CO_2/SO_2 the sample exhibited distinct secondary assemblages on the surface (Fig 2). EDS analysis detected sulfur on the surface which progressively decreased with increasing depth. Additionally, voids were observed in the cliff wall of the sample (Fig 3). These voids were not present after calcite was heated to 460°C. XPS analysis was not completed on this sample.

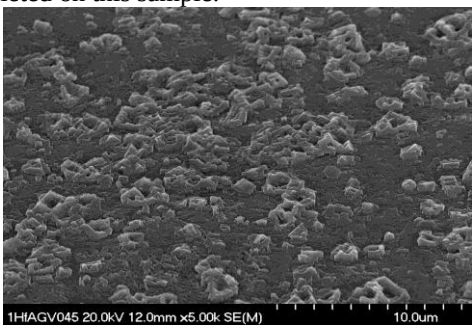

Figure 2: The surface of calcite after it was heated to 700°C in CO_2/SO_2 for 6 days.

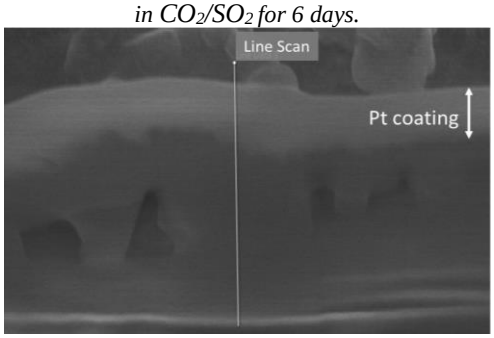

Figure 3: Calcite after it was heated to 700°C in CO_2/SO_2 for 6 days. Voids are present in the cliff wall of calcite.

Calcite was also exposed to 99.99% CO_2 at 700°C to isolate the effects of SO_2. After exposure, the surface appeared unchanged, and no voids were observable in the cliff wall cut into the sample. XPS analysis was not completed on this sample.

After wollastonite was heated to 460°C in CO_2/SO_2 the surface of the sample did not appear to be physically altered, nor were voids detected in the cliff wall. The EDS detected sulfur at the surface, but the peak is only slightly visible above the noise. The XPS detected 6.1 at% at the surface which decreased to 1.6 at% after moving the top 200 Å from the surface. It has been hypothesized that CO_2 in the atmosphere of Venus is buffered by wollastonite to form calcite, however no evidence of calcite has been detected [2]. Future experiments with wollastonite in 99.99% CO_2 are planned and may elucidate on this potential reaction.

At present the tremolite experiment (460°C CO_2/SO_2) has only been examined with XPS. The tremolite, which began a pale white/grey, developed dark/black patches during the experiment (Fig. 4). The darker regions had 4.1 at% of sulfur at the surface while the white areas only had 2.6 at%. After removing the top 200 Å from the dark regions the sulfur abundance dropped to 1.1 at%. The patches are likely due to uneven chemical interactions with the simulated Venus conditions owing to different mineral inclusions. XPS analysis indicates the presence of a sulfate, but no carbonate. Further investigation using SEM and EDS are currently underway.

Figure 4: Tremolite before (left) and after (right) the experiment.

Conclusions: Calcite is reactive with SO_2 and will produce $CaSO_4$ at the surface, but the reaction is slower at 460°C compared to 700°C. Wollastonite and tremolite are less reactive to SO_2, and less sulfur were detected at the surfaces. Longer experiments will be completed to observe the thickness of the reaction rind over time. This information combined with the dimensions of the sample and the known change in mass will be used to constrain the reaction rate.

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References: [1] Zolotov, M. Y. (2018) *Reviews in Mineralogy & Geochemistry*, 84, 351-392. [2] Dyar, M. D., et al. (2021) *Icarus*, 358, 114139. [3] Helbert, J. et al. (2021) *Science Advances*, 7, 3. [4] Fegley, B. and Prinn, R. G. (1989) *Nature*, 337, 6202, 55-58 [5] Radoman-Shaw B. G. (2019) *Exposure of Basaltic Materials to Venus Surface Conditions using the Glenn Extreme Environment Rig (GEER)*. Case Western Reserve University. [6] Berger G. et al. (2019) *Icarus, 329*, 8-23. [7] Reid, R. B. et al. (2021) *LPSC LII* Abstract# 1293.