EXPERIMENTAL INVESTIGATION OF CALCIUM MINERALS IN A VENUS SIMULATED ENVIRONMENT. S. T. Port[1], A. R. Santos[2], 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 of Venus is approximately ~460°C and ~95 bar of pressure with an atmosphere mostly composed of CO_2 with trace abundances (120-180 ppmv) of SO_2 [1]. This extreme environment promotes chemical interactions with the Venusian surface that are not well understood. Of particular interest is SO_2 due to its relatively high abundance and reactivity with several common elements [2-5].

SO_2 gas is present in volcanic environments on Earth, and its interactions with minerals have been explored through modeling and experimentally in conditions present near or in volcanic vents and eruption plumes [6-9]. One common outcome of these reactions is the formation of $CaSO_4$ (anhydrite) when calcium is present in the mineral [6-9]. Although this conclusion is presented in numerous papers, the kinetics of these reactions are not well documented, and very little investigations have been completed at conditions present on Venus.

Knowledge on these chemical reactions has implications for the past and current state of Venus. For example, some models have suggested that Venus may have hosted liquid water on its surface in the past [10]. This scenario implies that minerals such as hydrous silicates may have formed at that time [11-12]. In order to determine if these minerals could still exist on Venus today, several experiments were completed on tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$) and phlogopite ($KMg_3AlSi_3O_{10}(OH)_2$) at simulated Venus conditions [11,13]. They concluded that these minerals will not decompose over geologic timescales at the surface and may still be present [11, 13]. However, those experiments were only completed in CO_2, therefore exposure to SO_2 may have an effect on their stability.

The Venus Emissivity Mapper (VEM), which will fly on both VERITAS and EnVision, has the ability to glean the bulk composition of the surface by observing the transition metal content (particularly FeO) [14-15]. Under Venusian conditions calcium diffuses through basalt to the surface to react with CO_2 and SO_2. This changes the bulk composition of the surface resulting in a detectable decrease in emissivity from orbit [14]. However, further experiments investigating the reaction rate and the reactions' limiting factors are important in understanding how quickly the thickness of the weathered layer changes over time and how this would affect the emissivity.

Our goal for this project is to investigate the interactions between several calcium bearing minerals and SO_2 to constrain the reaction rate, but also to determine how different crystal lattices may affect these rates. Each of the selected minerals for this project were created under different formation processes (igneous, metamorphic, sedimentary) and exhibit different crystal structures that will affect their interaction with SO_2.

Methods: Experiments will be completed using Thermogravimetric Analysis (TGA). The TGA is similar to a vertical tube oven with the addition of a built-in scale to record changes in the sample's mass in real time (Figure 1). This data, as well as the temperature, will be automatically collected and saved every few minutes by a computer.

Figure 1: TGA (left) used for these experiments. The temperature and the gas flow are monitored on the right.

We selected five different minerals for these experiments. Calcite ($CaCO_3$) was chosen as a starting point and to validate the experimental apparatus because it is known to react with SO_2 to form $CaSO_4$ in simulated Venus conditions [2-3]. Wollastonite ($CaSiO_3$) was selected since it is a calcium silicate mineral and because past modeling suggested that wollastonite and calcite could buffer the CO_2 in the atmosphere [16]. Anorthite ($CaAl_2Si_2O_8$) was selected because it is the calcium endmember of feldspar and is common in igneous rocks [17]. Grossular ($Ca_3Al_2(SiO_4)_3$) was chosen because it is a nesosilicate and forms in metamorphic conditions [17]. Our last mineral is tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$) because it has a different silicate structure and the results can be compared to past experiments [11,13]. As mentioned previously, it has been exposed to simulated Venus conditions, but only in CO_2.

The five selected minerals will be polished then cleaned in an ultrasonic bath (Table 1). The samples will be hung in the center of the tube with gold wire. The samples will be tested in two different gases: high purity CO_2 and CO_2/1.5% SO_2. The former gas will be used during control experiments and the data will be compared with experiments completed in the latter gas. Since these experiments will be completed in ambient pressure, the high SO_2 abundance is to expose the samples to the same molecular number density of SO_2 as at the surface of Venus [2]. Preliminary experiments will be completed at 460°C, the approximate average lowland temperature of Venus [18]. Experiments are currently planned to last 1, 2 and 3 weeks. The completion of longer experiments will be dependent on the preliminary results.

After the experiments the surface of the samples will be analyzed using Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS). Next, the samples will be milled using a Focused Ion Beam (FIB) to create a trench. Using SEM and EDS we will observe the cliff face to investigate the morphology and chemistry within and near the surface of the minerals. Additional analysis will be completed using X-ray Photoelectron Spectroscopy (XPS) to provide additional data on chemical changes at the surface and shallow subsurface, and future samples may be examined with Transmission Electron Microscopy (TEM).

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: Minerals that will be investigated during this project.

Summary: Using the instruments discussed above we will be able to observe the thickness of any secondary mineral layers, the depth of the reaction front, and the interchange of elements in this region. Additionally, we will have data on the change in mass of the sample in real time. This information will be combined to calculate the samples' reaction rates with SO_2 at simulated Venus conditions.

Our results will inform on the mechanisms by which calcium interacts with SO_2 to form secondary minerals. Our time series experiments will be useful in understanding if reaction rates are constant over time, or if rates slow as the reaction progresses. Lastly, we will investigate the extent that the crystal structure may affect the reaction rates with the atmosphere of Venus. Combined, this will inform on which minerals are stable over long durations under the continual exposure of the Venusian atmosphere at the surface, thus illuminating which minerals, if once present on Venus, may still exist within rocks. If a future Venusian lander drills into the surface and finds the thickness of a weathering rind, the combined data may be used to help constrain the age of the surface.

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