THERMOGRAVIMETRIC ANALYSIS OF KEY MINERALS EXPOSED TO VENUS-LIKE GAS MIXTURES. W. H. H. Nealley[1], B. G. Radoman-Shaw[2], N. S. Jacobson[3], and R. P. Harvey[2], [1]Department of Physics, Case Western Reserve University, whn10@case.edu, [2]Department of Earth, Environmental, and Planetary Sciences, Case Western Reserve University, [3]NASA Glenn Research Center, 21000 Brookpark Road, Cleveland, OH 44135.

Introduction: The planet Venus is currently in a massive greenhouse state, with surface pressures nearly 90 times greater than Earth's and temperatures approaching 500°C. Chemical reactions between Venus' crust and atmosphere have been hypothesized to either maintain the greenhouse environment or modify it over the planet's history. Unfortunately, existing models are inconsistent with respect to the specific reactions that may be taking place and their relative importance. This makes it difficult to comprehensively model the origin and ultimate fate of Venus' greenhouse state.

Our group is conducting a broad experimental study that exposes key basaltic phases to Venus-like atmospheric chemistry and/or physical conditions on the premise that the exposure of new volcanic rock at the planet's surface would be a key driver of chemical reactions. Pyroxene- and feldspar-group minerals are key phases in our study as are olivine and glasses of basaltic and calc-alkaline compositions. Our goal is to identify key reactions that take place in these experiments and the secondary minerals they produce. This research is part of an ongoing project at NASA Glenn Research Center utilizing many sophisticated apparati including the Glenn Extreme Environment Rig (GEER). The apparatus serves as a high-fidelity simulation of the Venus atmosphere that includes accurate temperature, pressure, and gas composition to the parts per billion level.[1]

Atmospheric Buffering: Early theory about the regulation of the atmosphere's composition revolved around maintenance of the partial pressure of CO_2 through buffering reactions. Typically these invoked the exchange of divalent cations (Fe, Mg and Ca) between silicates and carbonates, either producing or consuming CO_2. The most commonly cited example was the exchange of Ca between calcite and wollastonite:

$$\underset{Calcite}{CaCO_3} + \underset{Quartz}{SiO_2} \rightarrow \underset{Wollastonite}{CaSiO_3} + CO_2 \quad (1)$$

However, recent evidence has conclusively shown that the CO_2 does not act as a buffer for this reaction in the Venus-surface conditions; this reaction proceeds to the right and is limited only by the availability of the reactants (2). In contrast, buffers do exist for SO_2, constituting 200ppm of Venus-atmospheric composition.[2]

$$\underset{Pyrite}{FeS_2} + CO_2 \rightarrow \underset{Magnetite}{Fe_3O_4} + SO_2 + CO \quad (2)$$

Despite being a minor component of the atmosphere, SO_2 is highly reactive and thus a key component that must be included in any study of the planet's surficial geochemistry.[3] Oxidizing reactions between the materials and the CO_2 and SO_2 gas species in the atmosphere are hypothesized to be the primary reactions that control the atmosphere.

Thermogravimetric Analysis: One method of studying how the minerals are altered under extreme conditions is to observe how their mass changes with exposure to varying temperatures and atmospheric chemistry. To measure this, thermogravimetric analysis (TGA) is used.

The TGA apparatus is a mass balance contained in a sealed vessel that tracks how an object's mass changes over a long period of time. The sample is hung from a platinum hook inside of a quartz tube. A gas of mixed CO_2 and SO_2 in Venus' atmosphere proportions (roughly 200 ppm SO2) flows through the tube and allowed to react with the sample. A furnace maintains Venus surface temperatures (470° C) at the sample location. For our experiments, after 120 hours of exposure, the sample is removed, photographed, and massed to compare to the same measurements taken prior to exposure.

Electron Microscopy: The most effective way of studying the changes in the mineral is by utilizing scanning electron microscopy (SEM). It is a non-destructive measurement technique that allows for the collection of both physical and chemical data (Fig. 1).

Following exposure, the sample is mounted to a SEM mount using two-sided carbon tape. It is then coated in 10nm of palladium to prevent the sample from charging during imaging.

The samples were imaged at several points on their surfaces with energy dispersive spectroscopy (EDS) data being taken at each of these points. The EDS data produce a spectrum that allows the composition of the sample to be analyzed. If any chemical changes have occurred on the surface, they will be apparent in the EDS analysis. For comparative purposes, unexposed

samples from the same groups were also imaged and had spectra taken of them. These samples acted as a control group since the samples that went into the TGA could not be imaged beforehand. Any deviations from the surface structure or chemistry observed in the exposed samples would be strong evidence that the sample is reacting.

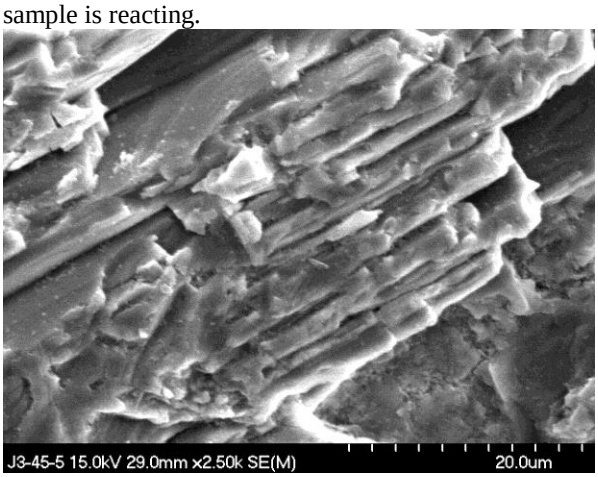

Fig. 1. 2500x magnification image of Enstatite after it had been exposed in the TGA; the sample shows signs of weathering resulting in structural breakdown and fracturing.

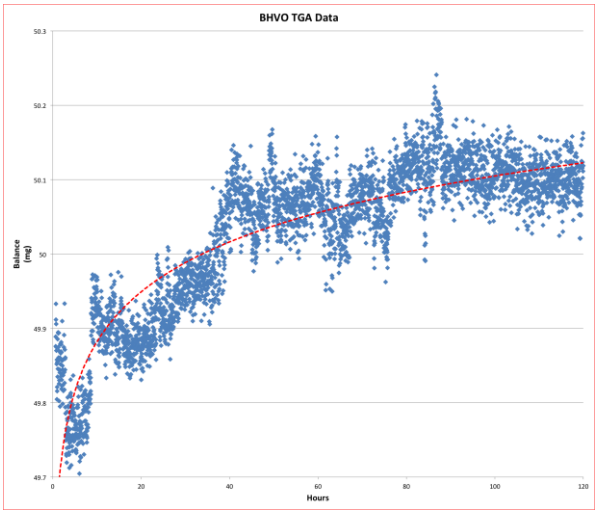

Fig. 2. TGA data from the first successful experiment that involved synthetic BHVO glass; the mass can be observed to increase as sulfates form on the surface of the material.

Preliminary Results: The exposed pyroxenes, feldspars, and olivines have all shown signs of mass-loss during exposure. The loss in mass is likely due to oxidation reactions occurring at the surface. The material being oxidized is then carried away by the flowing gas. It is possible that carbonates are forming as well, but the mass added in this deposition is significantly less than the mass removed by the oxidation.

Unlike the minerals mentioned above, the glasses exposed always increased in mass (Fig. 2). When examined under SEM, obvious crystals could be observed growing out of the amorphous glass background. EDS analysis of the sample revealed that sulfur was being deposited on the surface. Even though the crystals were too small to be analyzed individually with EDS, it can be deduced that the increased sulfur signal is due to sulfur within these crystals.

So far, the only glass sample exposed successfully is BHVO-2. It is a standard reference glass that consists of a homogenized and remelted Hawaiian basalt. This glass was provided to us by the United States Geological Survey and contains most of the naturally occurring elements including sulfur at the parts per billion level.[4] Our initial results suggest that a labile species within the glass (probably Na) is migrating to the chip surface to form sulfates with the S and O in the flow gas.

Future Work: Although early runs showed clear trends, the data was noisy. We have begun a second round of TGA runs on the same materials with reduced noise that will allow us to make more detailed conclusions about the chemical reactions involved, including preliminary rates. These will be compared to thermodynamic models produced by the program FactSage to help draw relevant conclusions regarding these reactions and the history of Venus' climate.

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