STABILITY OF METAL SULFIDES ON VENUS. S. T. Port, A. C. Briscoe, and V. Chevrier, University of Arkansas, Fayetteville, AR, 72701; (saraport@email.uark.edu)

Introduction: Venus' atmosphere is a concoction of sulfur gases in such forms as SO_2, H_2SO_4, COS, S_2, S_2O, and SO_x [1-3]. The large variety of sulfur species indicates its importance in the Venusian environment. Interactions between the atmosphere and the surface are expected, however the lack of information on the composition of the surface prevents the determination of sulfur source and sinks [2-5]. Our goal was to determine possible mineralogical sources of sulfur on Venus, and to observe the effects of various sulfur gases on these minerals.

We selected three different minerals for this study: galena (PbS), pyrrhotite (Fe_7S_8), and metacinnabar (HgS). Pyrrhotite was chosen because it is speculated to be one of the most abundant sulfur minerals on Venus [4]. Calculations have shown that the oxidation of pyrrhotite would release COS [4]. Galena is the most common lead mineral on Earth and is known to release SO_2 when oxidized [6-8]. Galena and pyrrhotite have also been suggested as the source of the high radar reflective signal seen on the mountains of Venus [4,9]. Metacinnabar is temperature sensitive, and would only be stable in cooler regions of Venus i.e. the mountain tops [10]. Cinnabar, the low temperature/pressure polymorph of metacinnabar, is the most common mercury mineral found on Earth, and both sulfur and mercury are known to be released during volcanic eruptions [10-11]. The Pioneer probe also detected trace levels of mercury in the atmosphere of Venus [12].

We then placed these minerals in environmental conditions similar to Venus to observe if the minerals changed in some way, and if any gases were released. This will help us better characterize the surface of Venus and the sulfurous gases found in the atmosphere.

Methods: One gram of the three pre-ground samples purchased from VWR were tested in one of three different gas mixtures, in one of three different temperatures, and tested in either an oven or a sealed chamber. The three gas mixtures were selected based on the composition of the Venusian atmosphere. Our control environment was pure CO_2, as Venus' atmosphere is comprised of 96.5% CO_2. The two other environments contained CO_2 with traces amounts of sulfur bearing gases, both of which are found on Venus: 100 ppm of SO_2 in CO_2 or 100 ppm of COS in CO_2. The temperature and pressure greatly vary with altitude, thus the minerals were tested in three different temperature/pressures on Venus: 460°C/95 bar (lowland), 425°C/75 bar (frostline), and 380°C/45 bar (highland). The frost line condition is the altitude where the surface of Maxwell Montes starts to become radar reflective. To assess the effects of pressure and a sealed environment on the minerals, experiments were completed in the Lindberg Tube Oven (ambient pressure) as well as the Cassiopeia Chamber (high pressure). Each experiment lasted a total of 24 hours before the samples were removed to be analyzed. The samples' mineralogy was determined using XRD.

Results: Our oven results for pyrrhotite showed troilite (FeS) formed in the highlands, and the formation of magnetite (Fe_3O_4) at the frost line. Lowland condition experiments resulted in the formation of hematite (Fe_2O_3) and mikasaite ($Fe_2(SO_4)_3$). In pure CO_2 chamber experiments minor traces of troilite were found in the highland and lowland conditions. Pyrrhotite tested in the oven in CO_2/ SO_2 gas resulted in pyrrhotite, hematite, troilite, magnetite, and pyrite (FeS_2) in the highland condition. Meanwhile, pyrrhotite, troilite, and hematite were found in the sample treated at the lowland conditions. Frost line experiments have not been completed at this time. In the oven experiments in CO_2/COS, pyrrhotite, pyrite, and hematite were found in the highlands. In the frost line experiments, hematite, mikasaite, as well as maghemite (Fe_2O_3) were found in the sample. Experiments completed in the lowland conditions resulted in hematite and mikasaite.

	460°C/1 bar (lowlands)	425°C/1 bar (frost line)	380°C/1 bar (highlands)
Oven	Hematite (Fe_2O_3) Mikasaite ($Fe_2(SO_4)_3$)	Magnetite (Fe_3O_4) Pyrrhotite (Fe_7S_8)	Pyrrhotite (Fe_7S_8) Troilite (FeS)
	460°C/95 bar	425°C/75 bar	380°C/45 bar
Chamber	Pyrrhotite Troilite	-----	Pyrrhotite Troilite

Table 1: Results for pyrrhotite experiments completed in the oven and the chamber in pure CO_2. Results are listed in order of peak match percent.

When galena was tested in the oven in pure CO_2, galena and anglesite ($PbSO_4$) were found at all three tested temperatures, and lanarkite ($Pb_2(SO_4)O$) was found in the frost line and lowland temperatures. Galena was also tested in the chamber in pure CO_2. Galena and litharge (PbO) were found in the highlands, meanwhile only galena was found in the lowlands. The CO_2/SO_2 experiment in the oven revealed galena and anglesite to be present at all three temperatures, while lanarkite appeared only in the lowland temperature. In the CO_2/COS experiment galena and anglesite were present at all three temperatures.

Metacinnabar was tested in both the oven and the chamber. When metacinnabar was tested in the oven in pure CO_2 the sample was completely vaporized. Experiments completed on metacinnabar tested in the chamber resulted in a solid sample in both the highland

and lowland conditions. However, the exact composition was not analyzed. When metacinnabar was tested in the oven in CO_2/SO2 the sample was only present in the cooler, highland conditions. When completed in CO_2/COS a sample was present in the highland experiment, however it was not metacinnabar, but cinnabar.

	460°C/1 bar (lowlands)	425°C/1 bar (frost line)	380°C/1 bar (highlands)
CO_2/SO_2	Galena (PbS) Anglesite ($Pb(SO_4)$) Lanarkite ($Pb_2(SO_4)O$)	Galena Anglesite	Galena Anglesite
	460°C/1 bar	425°C/1 bar	380°C/1 bar
CO_2/COS	Galena Anglesite	Galena Anglesite	Galena Anglesite

Table 2: Results for galena experiments completed in the oven. Experiments completed in the CO_2/ SO_2 mix are found in the top row, experiments completed in the CO_2/COS mix are found in the bottom row. Results are listed in order of peak match percent.

Discussion: The general trend of the pyrrhotite experiments in the oven is stability of pyrrhotite in the highlands, magnetite and maghemite in the frostline condition, and hematite in the lowland conditions. A similar trend, though not directly correlated to temperature, was found in previous experiments [13]. Troilite appeared in the highland to frost line conditions because troilite is a 1:1 ratio of iron to sulfur; thus as the temperature increase, and sulfur vaporizes, the ratio approaches 1:1. Mikasaite was also present in several experiments. Though mikasaite is rare on Earth, it is found near coal gas [14]. Pyrite formed in the low temperature, mixed gas experiments. When pyrrhotite is exposed to an oxidizing environment, iron diffuses to the surface to bond with oxygen to create an iron oxide. This in turn creates a sulfur rich layer under the boundary layer, where pyrite can form [15]. Underneath this layer is the untouched pyrrhotite layer [15]. The formation of iron oxides is expected to release several gases such as S_2, CO, and COS [13]. More experiments will need to be completed in the frost line conditions to determine the likelihood that it is the source of the high radar reflective signal.

On Earth, anglesite normally forms via the interaction between galena and oxygen. This reaction involves the creation and utilization of SO_2 [7]. However, another possible reaction is the formation of anglesite through the interaction between galena and CO_2. This reaction would also release CO, a gas found on Venus. Lanarkite forms from the interactions between anglesite and galena, and this reaction can be seen in our experiments where lanarkite is only present after anglesite forms [7]. This reaction can also release SO_2. Lead oxide can be produced from the interaction between galena and CO_2 and release either COS, or CO and S_2. Due to the similar results at all tested altitudes on Venus, galena does not appear to be a likely source of the radar reflective signal. If a type of lead sulfide is the source, it would form from some unknown interaction that cannot be properly recreated with the initial conditions used here.

Metacinnabar was instable in all CO_2 experiments completed in the oven, but was more stable in the chamber. The pressure, and the sealed environment most likely facilitated its stability. The presence of metacinnabar in the CO_2/ SO_2 experiment revealed that the sulfur in the gas contributed to its stability.

Conclusion: Pyrrhotite showed instability in the oven and produced numerous iron oxides. Pyrrhotite showed better stability in the chamber and longer timescales experiments will be completed to observe if this trend continues. Over the course of the experiments galena was still the main component of the sample. Longer experiments may answer the question on its stability. Interactions between galena and the atmosphere could be one possible source and sink of SO_2 and CO. In the metacinnabar experiments, metacinnabar showed better stability in the chamber. This is because the sealed chamber prevented any metacinnabar from escaping, therefore as it sublimated it equilibrated with the gas phase in the chamber.

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