The Stability of Metal Sulfides under Venusian Surface Conditions and their Relation to the Sulfur Cycle. S. T. Port and V. Chevrier, University of Arkansas, Fayetteville, AR, 72701; (saraport@email.uark.edu)

Introduction: Sulfur has been known to be a major component in the Venusian atmosphere since the late 1970s when its ultraviolet spectrum was first analyzed [1-3]. The bulk of sulfur found in the atmosphere is in the form of such compounds as SO_2, H_2SO_4, and COS, among many others [1-3]. Scientists have since been working to uncover a probable geochemical sulfur cycle to explain the sources and sinks of sulfur [1-6]. This work intends to investigate the effects of metal sulfides in Venusian conditions and to observe if they play a role in the sulfur cycle.

Past chemical equilibrium calculations theorized that pyrite (FeS_2) and pyrrhotite (Fe_7S_8) may be the most common sulfur minerals on the surface of Venus [6]. Recent experimental research demonstrated that pyrite is stable in simulated Venus conditions, but weathering may result in complete decomposition after a few thousand years [7, 8]. Experimental and theoretical research has shown that due to its slow rate of oxidation large masses of pyrrhotite could exist for millions of years on the surface of Venus [7]. Pyrrhotite is also of interest because it may be a source of COS, and on Venus there is evidence of increasing concentrations of COS with decreasing altitude [6, 9].

Galena (PbS) was chosen for this study because approximately 1.4 mg/kg of lead is known to exist in the crust on Earth, and the primary source of lead on Earth is found in galena [10-12]. Since Earth and Venus are very similar in origin and density the elemental percentages are assumed to be very similar. Also of note, some studies have indicated that the oxidation of galena can release SO_2 [12]. Other experiments have found that galena commonly oxidizes into anglesite ($PbSO_4$), but may back react to form lead and SO_2 [13, 14].

Metacinnabar (HgS) was also added to the study because of the abundance of mercury on Earth, approximately $8.5*10^{-2}$ mg/kg [10]. Though recent mission have found no evidence of its existence, mercury clouds were once theorized to exist if mercury was completely degassed from the crust [15]. The two most common types of HgS are cinnabar, which is trigonal, and metacinnabar, which is cubic [16]. We selected metacinnabar as opposed to cinnabar for this research because metacinnabar is stable in higher temperatures [16]. Metacinnabar is also a very stable mercury mineral and has found to be thermodynamically favorable [17].

Methods: Galena (PbS), pyrrhotite (Fe_7S_8), and metacinnabar (HgS) were each studied under simulated Venusian conditions to observe any changes to the samples. Two grams of each sample was placed in a Lindberg Tube Oven at three different temperatures corresponding to different altitudes on Venus: 460°C (0 km), 425°C (4.5 km), and 380°C (11 km). Each mineral was also exposed to one of three different gas mixtures: pure CO_2, 100 ppm of SO_2 in CO_2, or 100 ppm of COS in CO_2. Each experiment lasted a total of 24 hours after which the samples were removed and weighed. The samples were then analyzed via X-Ray Diffraction using the MRD to determine if there were any compositional changes to the sample.

Results: The galena experiment completed in 380°C was mostly stable, but some anglesite ($Pb(SO_4)$) formed. In both the 425°C and 460°C experiments anglesite formed once again, but also some lanarkite ($Pb_2(SO_4)O$) was present. There was no mass change over the course of the experiments (Table 1a).

In the pyrrhotite experiments troilite (FeS) formed when it was heated to 380°C, yet when the sample was heated to 425°C troilite was not present, but some magnetite (Fe_3O_4) was. When the sample was heated to 460°C the sample fully turned into troilite and hematite (Fe_2O_3). No mass change was detected between the start and the end of the experiments (Table 1a).

All metacinnabar experiments completed in pure CO_2 resulted in a complete vaporization of the entire sample. However when metacinnabar was tested in the CO_2/SO_2 gas mixture the sample was present after the experiment. There was no mineral change, however 1.5 g of the sample was lost. When metacinnabar was tested in the CO_2/COS gas mixture the entire sample morphed into cinnabar (HgS). There was also a loss of 1.25 g of the sample (Figure 1, Table 1b).

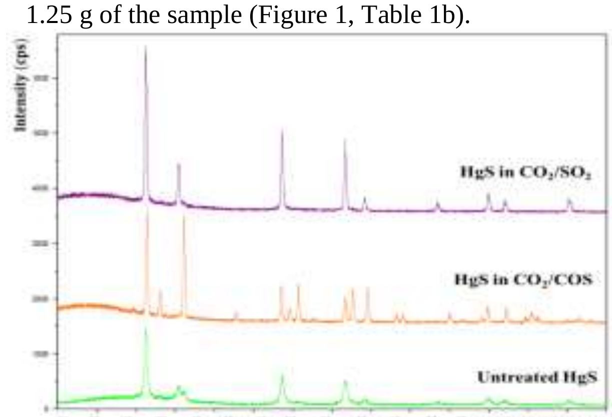

Figure 1: XRD results of the metacinnabar experiments. Untreated metacinnabar is graphed at the bottom, followed by metacinnabar heated in CO_2/COS, followed by metacinnabar heated in CO_2/ SO_2.

Table 1: a) Mineralogical results of the galena and pyrrhotite experiments completed in pure CO_2 b) Mineralogical results of the metacinnabar experiments completed in pure CO_2, 100 ppm of SO_2 in CO_2, and 100 ppm of COS in CO_2. Dashed

lines represent experiments that have not yet been completed. Results are listed in order of how well the spectra matched the XRD database.

a)

	460°C	425°C	380°C
Galena (PbS)	PbS $Pb(SO_4)$ $Pb_2(SO_4)O$	PbS $Pb(SO_4)$ $Pb_2 (SO_4)O$	PbS $Pb(SO_4)$
Pyrrhotite (Fe_7S_8)	Fe_2O_3 FeS	Fe_7S_8 Fe_3O_4	Fe_7S_8 FeS

b)

	460°C	425°C	380°C
CO_2 (100%)	None	None	None
CO_2 100ppm SO_2	----	----	HgS (metacinnabar)
CO_2 100ppm COS	----	----	HgS (cinnabar)

Discussion: The stability of HgS seems to correlate with the presence of sulfur in the atmosphere. When sulfur was not present, then metacinnabar completely vaporized. When sulfur was present in the form of SO_2 metacinnabar was present, however when it was in COS the entire metacinnabar sample converted into cinnabar. Experiments completed by [16] found that when metacinnabar is heated and allowed to cool to room temperature the result is cinnabar [16]. Therefore the true result of this experiment cannot be settled without an in situ analysis of the sample. At this time it cannot be determined why cinnabar was not found in the CO_2/SO_2 experiment. All of the metacinnabar experiments did lose mass, but currently we cannot determine what was lost, though we speculate that it was mercury which has a lower boiling temperature than sulfur [10]. It may be that the SO_2 does not stop the vaporization of metacinnabar, only prolongs it.

Galena oxidized as it was heated in CO_2 and only became more oxidized at higher temperatures. As it was heated anglesite was the predominant oxidized mineral followed by lanarkite at higher temperatures. Both of these minerals have been known to materialize in the presence of oxygen [13, 18]. At this time it cannot be determined if any SO_2 was produced as a byproduct in the experiment.

Pyrrhotite was found to be unstable at high temperatures. The instability of pyrrhotite was first made apparent after the lowest temperature experiment (380°C) resulted in troilite. The cause is due to the increasingly larger Fe/S ratio as the sulfur continually vaporized [7]. At 425°C the pyrrhotite reacted with the CO_2 thus forming magnetite. The 460°C experiment resulted in the formation of troilite and the oxidation of magnetite into hematite [7]. These experimental results are nearly identical to the results found in [7]. Though the oxidation of pyrrhotite is thought to release COS, it cannot be confirmed at this time.

Conclusion: The pyrrhotite experiments resulted in a succession of chemical reactions with an end result of hematite and troilite. Galena was found to oxidize at all temperatures and may oxidize further during longer experiments. Metacinnabar is unstable in pure CO_2, but is surprisingly stable in CO_2/SO_2. The results show that metal sulfides in pure CO_2 generally result in oxidation. Though Venus' atmosphere is mostly made up of CO_2, sulfur compounds are a major part of the atmosphere too, and based on the metacinnabar experiments in the mixed gases, galena and pyrrhotite may react in unforeseen ways when heated in the mixed sulfur gases.

Future Work: Both galena and pyrrhotite will be tested in the oven once more, but this time exposed to the mixed gases of 100 ppm of SO_2 in CO_2 and 100 ppm of COS in CO_2. The full set of metacinnabar experiments will also be completed. All minerals, temperatures, and gas composition combinations will also be tested in the Venus Simulation Chamber located at the University of Arkansas. The chamber is vital to our experiments because it can simulate the temperatures and the corresponding pressures found on Venus, thus enhancing the experiments. A gas chromatograph will also be attached to the Venus chamber to ascertain if the gas composition changed over the course of the experiments.

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