An Investigation of Metal Sulfides as the Source of the Low Emissivity Anomaly on the Highlands of Venus

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An Investigation of Metal Sulfides as the Source of the Low Emissivity Anomaly on the Highlands of Venus

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Space and Planetary Sciences

by

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December 2019
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Dissertation Director

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Julia Kennefick, PhD
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__________________________________________
Adriana Potra, PhD
Committee Member
Abstract

Since its detection in the 1960s the source of the unusual radar emissivity signal seen on several highlands on Venus has long eluded researchers. Researchers have determined that a mineral with a high dielectric constant could explain the signal. Using a Venus simulation chamber, we experimentally investigated this enigma to build upon the candidate mineral list that has been compiled over the last several decades. We tested the stability of 8 different minerals and elements at two to three different temperature/pressure regimes in three different gas mixtures meant to simulate the conditions found on Venus for a period of no less than 24 hours. These samples included: Bi/Te/S, Bi₂S₃/Bi₂Te₃, Bi₂S₃/3Te, Pb, PbO, PbS, PbSO₄, and Fe₇S₈. The temperature/pressure regimes simulate the conditions found in the average lowlands, 460°C/95 bar, 4.5 km above the planetary radius, 425°C/75 bar, and 11 km above the planetary radius, 380°C/45 bar. The three tested gases were 100% CO₂, 100 ppm of COS in CO₂, and 100 ppm of SO₂ in CO₂. Samples were analyzed via XRD (X-ray Diffraction) and on occasion SEM/EDX (Scanning Electron Microscope/Energy-Dispersive X-ray spectroscopy) or XPS (X-ray Photoelectron Spectroscopy). Additional studies were completed at Okayama University in Japan where we modeled the effect of surface temperature on SO₂ abundance and the elevation of the critical altitude (where the emissivity changes) if the source mineral was pyrite (FeS₂).

Our Bi/Te/S mixture experiments resulted in the formation of numerous minerals but tetradymite (Bi₂Te₂S) formed in every tested condition. Our lead experiments revealed that PbS and lead carbonates can form in the highland condition. Pyrrhotite was stable at all tested conditions. Our modeling results verified that surface temperature, SO₂ abundance, and the critical altitude are all closely correlated.

The data collected in this project can be used to better understand the near surface environment on Venus. It provides information on the surface-atmosphere reactions that occurs due to the different gases and temperatures/pressures on Venus. Most importantly, our data
expands upon the mineral candidate list and identifies which minerals are stable and could perhaps explain the anomalous radar signal.
Acknowledgements

The research completed in this project was funded by NASA Solar System Workings grant #NNX15AL57G. Additional funding was acquired from National Science Foundation: East Asia Pacific Summer Institutes program, the Japan Society for the Promotion of Science (JSPS), and by the Sturgis International Fellowship.

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I would like to thank my undergraduate researchers, Austin Chase Briscoe and Alec Fitting for their assistance in the lab.

A special thank you to Travis Garmon and Luis Morales for their helpful discussions, and Rachel Slank and Ellen Czaplinski for their assistance in preparing some of the chapters.

I also greatly appreciated the use of the Arkansas Nano & Bio Materials Characterization Facility at the University of Arkansas which houses the MRD, Versaprobe, and the SEM/EDX used during this project. I would like to thank the faculty that work there (Dr. Andrian Kuchuk, Dr. Mourad Benamara, and Dr. Betty Martin) for all their help and kind words. I really enjoyed my time there.

I would also like to thank the High Density Electronics Center (HiDEC) for allowing me to use their Rigaku XRD which was used to analyze several of my pyrrhotite samples. A special
thank you to faculty at Los Alamos National Lab (Dr. Sam Clegg, Adriana Reyes-Newell, Dr. Nina Lanza, and Dr. Patrick Gasda) for analyzing my pyrrhotite samples using the ChemCam.

Lastly, I would like to express my gratitude to all the reviewers for their invaluable insight and commentary on my papers.
Dedication

To my loving and supportive family as well as all my friends who helped and supported me during my time at Stony Brook University and The University of Arkansas. Thank you to my grandmother who ignited my love of science and my father who fostered it.
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Chapter 2:

1.0 Introduction

1.1 The Radar Reflective Anomaly on Venus

The surface of Venus has been studied since as early as the 1960s and has been observed by Earth based observatories, numerous orbiters, and several landers. The thick atmosphere of Venus is comprised of a plethora of gases that strongly absorb light in numerous wavelengths leaving very few atmospheric windows. As a result, the surface of Venus was originally observed by Earth observatories and Venus orbiters in long wavelengths, between 8-17 cm (Marov and Grinspoon, 1998; Tyler et al., 1991; Taylor, 2014). These observations revealed an unusual characteristic on the surface of Venus; very radar reflective\(^1\) regions on the highlands.

The first known mention of this characteristic was discovered through ground-based observation (\(\lambda=12.56\) cm) completed by Goldstein (1965). He found evidence of two radar reflective regions on Venus that were attributed to very rough terrain on the surface. In 1976 researchers at Arecibo Observatory (\(\lambda=12.6\) cm) observed a radar bright region they named Maxwell and asserted that the brightness was indicative of very rough terrain (Campbell et al., 1976).

New evidence of radar anomaly was obtained after the insertion of Pioneer Venus (\(\lambda=17\) cm) into Venus’ orbit in 1978 (Pettengill et al., 1982; Masursky et al., 1980; Ford and Pettengill 1983). Initial data determined that the mean reflectivity of the surface of Venus was 0.12, while a radar reflective region known as Theia Mons was as high as 0.28 (Pettengill et al., 1982). It was

\(^1\) Over the course of this dissertation emissivity and reflectivity will be used interchangeably. The two are associated with one another through the equation \(e=1-p\)', where \(e\) is emissivity and \(p\) is reflectivity. Thus, high reflectivity is equivalent to low emissivity and vice versa (Ford and Pettengill, 1983).
later reported that the average lowland reflectivity is approximately 0.15, meanwhile the highlands average is much higher, around 0.6 (Pettengill et al., 1996).

The Magellan orbiter ($\lambda=12.6$ cm), which was launched in 1989, was designed to expand and improve upon past radar maps by increasing its coverage and observing the surface in higher resolution (Saunders et al., 1990). This enhanced data set allowed researchers to study the radar anomaly with higher precision and assisted them in pinpointing its starting altitude and the change in reflectivity/emissivity versus altitude (Klose et al., 1992; Gilmore et al., 2017). The radar anomaly was found on several, but not all, mountains and highlands (Fig. 1). The elevation at which it manifests is different based on the highland (Klose et al., 1992; Arvidson et al., 1991), and there is no correlation with latitude or longitude. Many of these highlands also exhibit a sudden transition from radar bright back to radar dark at higher elevations, meanwhile others such as Maxwell Montes show a more gradual change (Brossier et al., 2019; Treiman et al., 2016; Arvidson et al., 1994; Shepard et al., 1994; Klose et al., 1992). Maat Mons is particularly

![Emissivity map of Venus obtained by Magellan. Areas of low emissivity are in purple and coat several well-known mountains and mountain ranges (circled in black). The regions circled in black include Alta Regio, Beta Regio, Ovda Regio, Thetis Regio, Danu Montes, and Maxwell Montes. Maxwell Montes, Ovda Regio, and Maat Mons are labeled in the figure.

Figure 1: Emissivity map of Venus obtained by Magellan. Areas of low emissivity are in purple and coat several well-known mountains and mountain ranges (circled in black). The regions circled in black include Alta Regio, Beta Regio, Ovda Regio, Thetis Regio, Danu Montes, and Maxwell Montes. Maxwell Montes, Ovda Regio, and Maat Mons are labeled in the figure.](https://astrogeology.usgs.gov)
perplexing because it is the second tallest volcano on Venus, yet there is no correlation between elevation and reflectivity/emissivity (Klose et al., 1992; Treiman et al., 2016). It is possible that the source of the radar bright region develops over time and that the surface of Maat Mons has not matured enough to produce the signal (Klose et al., 1992).

Several theories have emerged on the possible cause of the radar bright regions. Campbell et al. (1976) voiced that the surface may be very rough, however Maxwell’s roughness is not much different from Fortuna Tessera and their emissivity is distinct from one another (Tyler et al., 1991). Pettengill and Ford (1993) suggested that decimeter sized voids could create the unknown signal, however a mechanism to produce such voids is needed (Brackett et al., 1995). Tryka and Muhleman (1992) suggested that dense rock mixed in a low loss soil matrix could cause scattering and produce the signal, but they did not discuss why it would only be present in the highlands (Klose et al., 1992; Brackett et al., 1995).

Table 1: Summary of some minerals and elements that have been hypothesized to be the source of the radar anomaly in the highlands of Venus.

<table>
<thead>
<tr>
<th>Mineral/Element</th>
<th>Composition</th>
<th>Ref.</th>
<th>Mineral/Element</th>
<th>Composition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germanium</td>
<td>Ge</td>
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<td>Chlorapatite</td>
<td>(Ca₅(PO₄)₃Cl)*</td>
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<td>Tellurium</td>
<td>Te</td>
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<td>-</td>
<td>WO₃*</td>
<td>6</td>
</tr>
<tr>
<td>Pyrite</td>
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<td>2</td>
<td>Altaite</td>
<td>PbTe</td>
<td>6</td>
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<tr>
<td>Pyrrhotite</td>
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<td>3</td>
<td>Clausthalite</td>
<td>PbSe</td>
<td>6</td>
</tr>
<tr>
<td>Galena</td>
<td>PbS</td>
<td>4</td>
<td>Stibnite</td>
<td>Sb₂S₃</td>
<td>6</td>
</tr>
<tr>
<td>Bismuthinite</td>
<td>Bi₂S₃</td>
<td>4</td>
<td>Antimonselite</td>
<td>Sb₂Se₃</td>
<td>6</td>
</tr>
<tr>
<td>Tellurobismuthite</td>
<td>Bi₂Te₃</td>
<td>8</td>
<td>-</td>
<td>(Pb(Ba,Sr,Ca))TiO₃*</td>
<td>7</td>
</tr>
<tr>
<td>Galenobismutite</td>
<td>PbBiS₄</td>
<td>4</td>
<td>-</td>
<td>K(Ta,Nb)O₃*</td>
<td>7</td>
</tr>
<tr>
<td>Rutile</td>
<td>TiO₂</td>
<td>3</td>
<td>-</td>
<td>Pb₂Bi(Ta,Nb)O₅*</td>
<td>7</td>
</tr>
<tr>
<td>Lillianite</td>
<td>Pb₂BiS₅</td>
<td>4</td>
<td>-</td>
<td>Pb(Nb,Ta)₂O₆*</td>
<td>7</td>
</tr>
<tr>
<td>Cannizarite</td>
<td>Pb₂Bi₅S₁₁</td>
<td>4</td>
<td>Hematite</td>
<td>Fe₂O₃</td>
<td>2</td>
</tr>
<tr>
<td>Cosalite</td>
<td>Pb₂Bi₅S₅</td>
<td>4</td>
<td>Magnetite</td>
<td>Fe₃O₄</td>
<td>3</td>
</tr>
<tr>
<td>Metacinnabar</td>
<td>HgS</td>
<td>5</td>
<td>Ilmenite</td>
<td>FeTiO₃</td>
<td>3</td>
</tr>
<tr>
<td>Coloradoite</td>
<td>HgTe</td>
<td>5</td>
<td>Perovskite</td>
<td>CaTiO₃</td>
<td>3</td>
</tr>
</tbody>
</table>

* indicates a ferroelectric mineral

References: 1 - Pettengill et al. (1996); 2 - Ford and Pettengill (1983); 3 - Fegley et al. (1992); 4 - Schaefer and Fegley (2004); 5 - Kohler et al. (2013); 6 - Brackett et al. (1995); 7 - Shepard et al. (1994); 8 - Kohler et al. (2014); 9 - Treiman et al. (2016)
Two other theories that gained traction among the community were: 1) it is related to the composition of the surface itself, or 2) something is depositing onto, and coating the surface. A list of candidate materials is displayed in Table 1. Garvin et al. (1985) had proposed that Fe-Ti-rich basalts could produce the signal, however Klose et al. (1992) rebuked it referencing that Venera data showed that the basalts at the surface are Fe poor. Moreover, an explanation for the presence of Fe-rich basalt at high altitudes, but not low altitudes, has not been discussed. Pettengill et al. (1988) theorized that perhaps a loaded dielectric could be the source, however in general a basalt would not contain enough -less than 9 vol %- of a conducting material (Klose et al., 1992). Greeley et al. (1991) proposed that aeolian sources could accumulate these high dielectric minerals, which would increase the volume percent.

Tyler et al. (1991) determined that Gula Mons, another mountain with high radar reflectivity, could be covered with a material that has a dielectric constant of 25 or greater, compared to Venus’ average value of 5. Updated calculations showed that in general the dielectric constant, $\varepsilon$, in the highlands is $>50$, with the surface of Maxwell Montes requiring a dielectric constant of $\sim 100$ (Pettengill et al., 1992; 1997). Furthermore, the imaginary component of the permittivity on Maxwell Montes is very large and has been calculated to be around $-i100 \pm i50$ (Pettengill et al., 1996; 1997).

The dielectric constant, $\varepsilon$, is the ratio of the permittivity and the permittivity of a vacuum. The permittivity is a measure of how well a material can transmit an electric field. It is a combination of a real and imaginary part where the real part represents how well the energy is stored and transmitted, and the imaginary part is how well it absorbs (dissipates incident) energy (Brodie et al., 2015; Treiman et al., 2016). Semiconductors can conduct well, although not as good as metals, so they exhibit a higher dielectric constant than rocks such as basalt (Treiman et al., 2016). The dielectric constant is inversely proportional to emissivity.
Pyrite (FeS$_2$) was proposed as a suitable candidate due to its high dielectric constant (Pettengill et al., 1982; Ford and Pettengill, 1983; Klose et al., 1992). Pyrite could originate from fresh magma upwelling to the surface or perhaps as a secondary mineral assemblage formed from the primary basalt interacting with the atmosphere (Ford and Pettengill, 1983; Klose et al., 1992; Pettengill et al., 1982). It was calculated that it would be unstable on Venus, but if there is a recurring process to remove the upper layer then it could be replenished (Ford and Pettengill, 1983; Pettengill et al., 1982). Electrically conducting pyrite can be mixed within the surface material to create a loaded dielectric capable of being radar reflective (Ford and Pettengill, 1983; Pettengill et al., 1988). Klose et al. (1992) calculated that the stability of pyrite was dependent on the oxidizing state of the surface, and if pyrite is stable it would only be so in the highlands.

Experimental work completed in the 1990s discovered that pyrite is thermodynamically unstable on Venus and will eventually oxidize into magnetite (Fe$_3$O$_4$) and then hematite (Fe$_2$O$_3$) via a several step process (Fegley et al., 1992; 1995; Fegley and Treiman, 1992; Hong and Fegley, 1997). Recent experiments on pyrite stability have been completed using the NASA Glenn’s Venus simulation chamber (GEER). Here Radoman-Shaw (2019) exposed pyrite to Venus lowland temperature/pressure conditions (470 ± 20°C and 92 ± 5 bar) and 9 Venus gases (CO$_2$, COS, SO$_2$, CO, N$_2$, H$_2$O, H$_2$S, HCl, HF) for 42 days. He found that pyrite is unstable and oxidizes completely to magnetite (Radoman-Shaw, 2019). However, arguments for its stability still persist since COS, S$_2$, and H$_2$S could stabilize pyrite, but their abundances have either not been measured or are not well constrained on Venus (Wood and Brett, 1997; Straub, 1993; Zolotov, 2018). Other recent experiments completed in simulated Venus conditions at the University of Toulouse and in NASA Goddard have evidence for pyrite formation and stability.

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2 In an abstract published in 1993 the authors stated that when the dielectric constant of pyrite was originally studied it wasn’t pyrite at all, but instead pyrrhotite. They claimed that the original assumption is incorrect, and pyrite may not be the source of the radar reflective signal. Subsequent research has not been completed on this topic since the author suddenly passed away the following year (Burns and Straub, 1993).
Berger et al., 2019; Kohler et al., 2015). This ongoing debate will most likely continue until a future lander analyzes the mineralogy of Venus.

In 1994 a different category of mineral was suggested as a cause for the source, not a semiconducting mineral, but a ferroelectric one. Shepard et al. (1994) and Arvidson et al. (1994) suggested the presence of a ferroelectric mineral. These minerals are paraelectric at all temperature except for the Curie temperature, which is dependent on the mineral. At this temperature the mineral becomes ferroelectric which causes a decrease in radar emissivity. A ferroelectric mineral would explain why some mountain ranges have an abrupt decrease and then a sudden increase in emissivity at higher altitudes (Fig 2) (Shepard et al., 1994; Arvidson et al., 1994; Treiman et al., 2016). Chlorapatite (Ca₅(PO₄)₃Cl) has been proposed as a possible ferroelectric mineral because it is a relatively common mineral found in basalts on Earth and transitions from paraelectric to ferroelectric at 675-775 K; which is between the temperature range on Venus (Treiman et al., 2016). However, experiments on the formation and stability of chlorapatite at Venus conditions have not been completed at this time.

In 1995 the theory of a mineral depositing onto the surface was first proposed. Brackett et al. (1995) postulated that volcanic outgassing can release metal halides or chalcogenides that could deposit onto the cooler highlands and coat the surface (Fig 3). Metal halides and chalcogenides such as Bi, Cu, Zn, Sn, Pb, As, and Sb, are also found in volcanic gases and near
volcanic vents on Earth. If these minerals have high dielectric constants there may be enough to cause surface scattering as seen by observation. They suggest that the failure of the Pioneer Venus probes at 12.5 km in altitude may have been due to these gaseous metal halides or chalcogenides that coated the probes and caused ion accumulation. Additionally, evidence of a possible low altitude haze between 1-6.4 km in altitude has been collected by the Pioneer probes, Venera 13, and Venera 14 and could be composed of metal halides or chalcogenides (Ragent and Blamont, 1980; Brackett et al., 1995; Grieger et al., 2003).

Evidence for tellurium as the source of the radar anomaly was first presented by Pettengill et al. (1996). Tellurium gas is released from volcanic vents on Earth, and a similar process may occur on Venus before it condenses on the cooler highlands. Tellurium also has the right conductivity to explain the signal. Calculations carried out by Pettengill et al. (1996) claimed that only 1 part in 10⁴ of tellurium would need to be outgassed from the crust and mantle to create the high reflectivity (low emissivity) material on the highlands. However, experiments completed on tellurium at Venus conditions in 99.95% CO₂ found that it is unstable and easily oxidizes into TeO₂ (Kohler et al., 2015). Schaefer and Fegley (2004) used chemical equilibria calculations to determine that tellurium does not condense at the frost line, but instead at an altitude of 46.6 km from the surface. Their data shows that >182 ppm of tellurium is needed in order to condense at the critical altitude of ~2.6 km, an abundance 60,000 times larger than the abundance on Earth.
The last element that was studied in greater detail was lead. Fegley et al. (1992) was the first to consider its possibility as the source of the radar anomaly when they calculated the stability of PbCO₃, a mineral with a semi-high dielectric constant. They studied its stability in relation to PbSiO₃ and PbSO₄ and found that PbCO₃ would be unstable everywhere on the surface of Venus. Brackett et al. (1995) also incorporated lead bearing minerals (PbS, PbF₂, and PbCl₂) with high dielectric constants into their calculations. Equilibria calculations completed by Schaefer and Fegley (2004) found that galena (PbS) can condense at 2.6 km in altitude, close to the critical altitude on Venus. There is one caveat; it only occurs when the lead abundance is less than the abundance found in Earth’s basaltic crust, however the abundance is still reasonable and is within the range found in basaltic meteorites (eucrites) (Schaefer and Fegley, 2004; Kitts and Lodders, 1998).

It has been recently proposed that there are multiple mechanisms at work on Venus to explain the different radar anomaly patterns on the highlands. It is possible that a ferroelectric mineral coat several highlands, such as Ovda Regio, which would explain the very sudden decrease, and abrupt increase in radar emissivity. Meanwhile, Maxwell Montes is most likely covered by a semiconducting material which explains the lack of a sudden increase in emissivity at higher altitudes (Treiman et al., 2016).

The history behind the study of the low emissivity highlands is extensive, with many questions still left unanswered. A multitude of researchers have utilized numerous methods to better understand this odd phenomenon that has not been observed on any other planet in this solar system. Building upon this information and incorporating both new and old theories, we have set forth to try and experimentally determine the origin of the source of this unusual phenomenon.

1.2 Research background

1.2.1 Bismuth, Tellurium, and Sulfur

The first part of our research focused on mixtures of bismuthinite (Bi₂S₃), tellurobismuthite (Bi₂Te₃), bismuth, tellurium, and sulfur. All three elements are outgassed from volcanic plumes on
Earth (Table 2) which implies that they were likely outgassed on Venus at some point in its history. Our goal was to observe if a mixture of these minerals, as well as a mixture of bismuth, tellurium, and sulfur would preferentially form a mineral in the highland but not in the lowland conditions. Though several of these materials have been tested under Venus conditions, mixtures of minerals, which we believe more accurately represents conditions found in nature, have not been studied.

Bismuthinite was discussed by both Brackett et al. (1995) and Schaefer and Fegley (2004) regarding its volatility on Venus and its ability to be the source of the radar anomaly in the highlands. It can be a product of volcanism and also exhibits a high dielectric constant of 108 (Mizutani, 1966; Wolfe, 1938; Schaefer and Fegley, 2004; Lukaszcwicz et al., 1999). Calculations completed by Schaefer and Fegley (2004) found that if the bismuth abundance on Venus is similar to the abundance found in basaltic meteorites (eucrites), 4 ppb, then bismuthinite can condense at 2.6 km in altitude, the critical altitude, on the highlands of Venus (Schaefer and Fegley, 2004; Kitts and Lodders, 1998). Experiments completed in simulated Venus conditions have found that bismuthinite is stable when tested at both the lowland and highland conditions (Kohler et al., 2015). Thus, if it is the source a mechanism, such as the movement of volatiles from the lowlands

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (μg/m³)</th>
<th>Location</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te</td>
<td>0.001-0.089</td>
<td>Etna (Italy)</td>
<td>Aiuppa et al. (2003)</td>
</tr>
<tr>
<td>Te</td>
<td>0.001-0.134</td>
<td>Kilauea (USA)</td>
<td>Mather et al. (2012)</td>
</tr>
<tr>
<td>Te</td>
<td>0.11-0.19</td>
<td>Masaya (Nicaragua)</td>
<td>Moune et al. (2010)</td>
</tr>
<tr>
<td>Te</td>
<td>0.005-0.02</td>
<td>Stromboli (Italy)</td>
<td>Allard et al (2000)</td>
</tr>
<tr>
<td>Te</td>
<td>≤~0.15</td>
<td>Etna (Italy)</td>
<td>Milazzo (2017)</td>
</tr>
<tr>
<td>Te</td>
<td>≤~0.05</td>
<td>Vulcano (Sicily)</td>
<td>Milazzo (2017)</td>
</tr>
<tr>
<td>Te</td>
<td>≤~0.055</td>
<td>Copahue (Chile)</td>
<td>Milazzo (2017)</td>
</tr>
<tr>
<td>Te</td>
<td>≤~0.06</td>
<td>Japan</td>
<td>Milazzo (2017)</td>
</tr>
<tr>
<td>Bi</td>
<td>0.002-0.35</td>
<td>Etna (Italy)</td>
<td>Calabrese (2011)</td>
</tr>
<tr>
<td>Bi</td>
<td>~0.0001-0.010</td>
<td>Etna (Italy)</td>
<td>Milazzo (2017)</td>
</tr>
<tr>
<td>Bi</td>
<td>~0.001-1.0</td>
<td>Nyiragongo (Congo)</td>
<td>Milazzo (2017)</td>
</tr>
<tr>
<td>S</td>
<td>900-131,570</td>
<td>Etna (Italy)</td>
<td>Calabrese (2011)</td>
</tr>
<tr>
<td>S</td>
<td>16,000-93,600</td>
<td>Kilauea (USA)</td>
<td>Olmez et al. (1986)</td>
</tr>
</tbody>
</table>
to the highlands as proposed by Brackett et al. (1995), must exist to explain its abundance in the highlands and absence in the lowlands. Tellurobismuthite, a semiconductor, has also been tested by itself in Venus conditions and was found to be mostly stable, though minor amount of BiTe has been reported (Kohler et al., 2015).

Bismuth, tellurium, and sulfur can all be released via eruption plumes and outgassing (Aiuppa et al., 2003; Mather et al., 2012; Moune et al., 2010; Allard et al., 2000; Milazzo, 2017; Calabrese, 2011; Olmez et al., 1986), a phenomenon that if it does not occur today, once was prevalent on Venus (Wilson and Head, 1983; Basilevsky and Head, 2003; Ivanov and Head, 2011). Evidence of bismuth in Earth based volcanic plumes can be found near numerous volcanoes including Merapi volcano, Mount Etna, Nyiragongo, Nyamuragira, Kilauea, and la Fossa crater at Vulcano Island (Symonds et al., 1987; Milazzo, 2017; Hinkley et al., 1999). Calculations on the amount of bismuth outgassed per year on Earth vary from as low as 405 tons up to as high as 4000 tons (Hinkley et al., 1999; Lambert et al., 1988; Patterson et al., 1987) (Fig 4).

Tellurium is also a well-known element that is found near fumaroles and volcanic plumes, and recent studies have calculated that a mean of 98 ton/year is outgassed on Earth (Fig. 4) (Milazzo, 2017). The abundance of tellurium measured in the plumes of several locations on Earth...
have concentrations of around <0.003 to 0.15 μg/m³ (Fig 5). Tellurium has a fairly low melting point and thus has a high enrichment factor in plumes compared to the continental crust (Milazzo, 2017).

![Diagram showing atmospheric concentrations of tellurium](image)

Figure 5: Measured tellurium abundances emitted from several volcanoes on Earth (Milazzo, 2017).

Sulfur is a common element that is closely associated with volcanism. Due to its volatility, it can easily be found near fumaroles and eruption plumes (Patterson et al., 1987; Calabrese, 2011; Hinkley et al., 1999; Halmer et al., 2002). Samples collected in Kilauea have found that the amount of sulfur in the volcanic gas was 3.4*10⁶ times higher than the basalt (Olmez et al., 1986). Outgassing abundances on Earth have been calculated to be between 4.5*10⁶ and 17*10⁶ ton/year (Bluth et al., 1993; Patterson et al., 1987). In addition, sulfur is abundant on Venus in such compounds as SO₂ (150 ± 30 ppmv), COS (4.4 ± 1 ppmv), H₂S (3 ± 2 ppmv), S₈ (20 ppbv) (Zolotov, 2018). Thus all three elements should have sufficient reservoirs on Venus to account for their occurrence on the highlands of Venus.

1.2.2 Lead

The second objective of this project was to study the stability and effect of Venus conditions on several lead-based minerals. Lead is also a common element that is outgassed on Earth and recent calculations have suggested between 855 and 2500 tons is outgassed per year
(Fig. 4) (Hinkley et al., 1999; Patterson et al., 1987; Lambert et al., 1988). Lead minerals are also commonly found near terrestrial volcanic fumaroles (Toutain et al., 1990). Models have shown that lead bearing minerals can migrate from the lowlands to the highlands over several thousand to millions of years depending on the mineral (Brackett et al., 1995).

The first mineral we tested in this project was PbS because it has a high dielectric constant (205 at 1 MHz (Olhoef, 1979)) and was once discussed as a possible source of the radar anomaly (Brackett et al., 1995; Schaefer and Fegley, 2004), but experimental studies are needed because it has only been experimentally tested once (Kohler et al., 2014). Pb was selected to examine if carbon- or sulfur-bearing minerals formed when it was exposed to Venus gases such as CO₂, COS, and SO₂. Anglesite (PbSO₄) was chosen because it is one of the most common lead minerals on Earth, but its stability on Venus is unknown. Lastly, we incorporated PbO into our experiments because of the unfortunate contamination of PbO in our Pb sample. By exposing PbO to Venus conditions we can remove any error from our Pb results in case our resulting products were due to PbO.

1.2.3 Pyrrhotite

The stability of pyrrhotite (Fe₁₋ₓS) on Venus has been a subject of research since pyrite was first considered to be the source of the radar anomaly on the highlands (Fegley and Treiman, 1992; Zolotov, 1991; Barsukov et al., 1982; Treiman and Fegley, 1991). Pyrrhotite is one of the most common sulfides on Earth and is found in basaltic rocks (Fegley and Treiman, 1992; Treiman and Fegley, 1991). Pyrrhotite stability is closely tied to the abundance of COS and could be its source and sink (Fegley et al., 1995; Barsukov et al., 1982; Zolotov, 2018). It also has a high dielectric constant with past research placing it at greater than 81 (Parkhomenko, 1967; Rosenholtz and Smith, 1936). A pyrrhotite-pentlandite assemblage has also been suggested to explain some of the radar bright region found in the lowlands near impact craters (Burns and Straub, 1993).
Experiments completed in the 1990s proclaimed that pyrrhotite is unstable at all Venus conditions (Treiman and Fegley, 1991; Fegley et al., 1995). However, several researchers expressed doubt over their results because the tested vessel was not pressurized and also the sample/gas system was not allowed to react until equilibrium (Wood and Brett, 1997). Additionally, in the experiments completed by Treiman and Fegley (1991) the cylinder of CO$_2$ used may have been contaminated with O$_2$ (Straub, 1993). Furthermore, in the lowlands of Venus CO$_2$, SO$_2$, and COS are supercritical, which is not simulated in their experiments, and there is little data on the effect of supercritical fluids on pyrrhotite. However, recent experiments completed by Radoman-Shaw (2019) point to pyrrhotite instability; a further discussion on his results will be presented in Chapter 4.

Energy minimization computer models completed by Klose et al. (1992) stated that pyrrhotite stability depends on the oxidizing conditions found on the surface of Venus, and if the conditions on Venus were reducing enough for pyrrhotite to be stable, it would only be found in the lowland condition. Calculations have revealed that H$_2$S, S$_2$, and COS all have a strong

![Figure 6: Stability diagram of pyrrhotite, magnetite, pyrite, and hematite based on fCOS and fCO. The box represents possible Venus conditions and the lined box is the measured conditions on Venus. A) lowland condition b) highland condition. Pyrrhotite stability may be attained if the COS abundances on Venus is greater than measured. Future measurements of the COS abundance are needed to determine if it is consistent over time. Figure obtained from Zolotov (2018).]
influence on the stability of pyrrhotite (Fig. 6) (Fegley and Treiman, 1992; Zolotov, 2018). The abundance of all three is highly dependent on the state of the atmosphere. If the atmosphere is in equilibrium, the abundance of COS and $S_2$ should be greater than what has measured/calculated and thus pyrrhotite may be stable (Fig. 6) (Zolotov, 2018). Some ambiguity on the stability of pyrrhotite still remains, leaving room for future experiments to further address this issue.

2.0 Dissertation

2.1 Goals and Significance

The objective of this project was motivated by the lack of experimental research on uncovering the source of the radar anomaly on the highlands. Due to the rarity of many of the minerals on the candidate list, and the insufficient understanding of Venus gases (which are supercritical in the lowlands), thermodynamic models cannot accurately simulate the conditions and reactions that can occur on Venus. Thus testing the stability of minerals on the candidate list through experimental means was at the center of this dissertation.

We endeavored to modify the candidate list for the source of the radar anomaly by eliminating and/or adding minerals. Our initial step was to expose several minerals on the candidate list to different Venus environments to ascertain if any transformations occurred. If we produced a stable mineral, either the candidate or a new mineral as a result of weathering, in the highlands but not the lowlands then this mineral’s candidate status was reinforced. We also expanded the study to incorporate individual elements to examine if the minerals in the candidate list could form under Venus conditions.

Sulfur gases, in particular $SO_2$, play a vital role on the weathering process on Venus (Barsukov et al. 1980; Fegley and Treiman, 1992; Zolotov, 2018). Therefore, the incorporation of sulfurous Venus gases was crucial for these experiments because of their capability to influence minerals, particularly the sulfur-bearing ones that were selected for this study. The significance of
sulfur gas led to my internship in Japan where I aimed to understand how the surface temperature of Venus affected the SO₂ abundance, and thus the elevation of the critical altitude.

The unusual radar signal found on several highlands on Venus has long perplexed Venus researchers. Its unknown origin highlights our inadequate understanding of the geology of Venus and its surface weathering properties. Our results give us better insight on both. The completed experiments illustrate the surface-atmosphere chemical reactions that can occur on Venus. This is also significant because it addressed several goals set out by VEXAG according to their “2019: Venus Exploration Goals, Objectives, and Investigations” document. Specifically, it tackled Goal III.B which included gathering knowledge on local weathering, global weathering, and chemical interactions that can occur on Venus. Additionally, by determining possible sources of the signal, we can hypothesize the surface geology. For instance, the source may be a component of the surface, and weathering accumulated and/or altered the surface to produce the mineral. The minerals on our list are products of volcanism; they can be found in crystalizing magma or released as vapor into the atmosphere after an eruption. Thus, depending on the source it may reveal if volcanism played a vital role in its production. Volcanism may also explain its presence in highlands; perhaps the volatiles released from an eruption only condensed in the highlands due to their much cooler temperature.

The data collected here can also be applied in future mission planning to Venus. For instance, in a future mission the presence of lead, iron, bismuth, and tellurium minerals in both the lowlands and highlands should be studied. Analysis of several highland locations should be completed to determine if the radar anomaly in different locations is a result of the same mineral. Additionally, the temperature/pressure profile and COS and SO₂ abundance at different latitudes should be obtained since these factors affected the stability of some of the tested minerals.

The information presented in this dissertation have revealed misconceptions on some minerals, while reaffirming others on the candidate list. Very little experimental research has been completed on mineral stability on Venus, specifically with an emphasis on the highlands, thus this
project represents a significant step in the pursuit of the origin of the radar anomaly. Though much more work is still needed, and new data on the surface of Venus is vital, the outcome of this project assists in our understanding of the surface of this fascinating planet.

2.2 Dissertation Outline

This dissertation consists of an Introduction, Methods, four Chapters, and a Conclusion. The methods section summarizes all instruments used over the course of this dissertation, as well as the general methodology used in three of the four chapters. The first chapter will discuss the experiments and results of the exposure of bismuth, tellurium, and sulfur to Venus temperatures, pressures, and several Venus gases. It also examines the ability of bismuth, tellurium, and sulfur to explain the radar anomaly via a discussion on tellurium abundance and a transport mechanism to the highlands. This paper has just been accepted for publication in Icarus. The second chapter discusses the effect of Venus conditions on Pb, PbO, PbS, and PbSO₄. These experiments used a slightly different experimental procedure than the bismuth, tellurium, and sulfur experiments, and incorporated data obtained via X-Ray Photoelectron Spectroscopy (XPS). This paper is currently submitted to Journal of Geophysical Research, Planets. The third chapter investigates the stability of the controversial pyrrhotite at Venus conditions using the same experimental setup as Chapter 2 and has been submitted to Planetary and Space Science. The last chapter is in regard to research completed during my internship in Japan. Here my advisor and I studied the interaction between the atmosphere and surface of Venus through computer modeling. In particular, we were interested in observing how the surface temperature affected the SO₂ abundance in the atmosphere and the critical altitude assuming the radar anomaly mineral was pyrite.

3.0 Method

3.1 Instruments

Our experiments required the use of multiple different instruments to prepare, test, and analyze our samples. The majority of our samples came as powders, but some arrived in the form
of large crystalline chunks which were then ground down into a powder using a ring mill found at the University of Arkansas’ Geoscience Department. Afterwards they were run through a sieve (125 μm) in order to ensure that the powders all had a similar diameter.

Our samples were tested in the Venus simulation chamber purchased from Parr Instruments (Fig. 7). The chamber is a 500 mL cylinder composed of stainless steel 316. Attached to the head of the chamber is an inlet and outlet valve, an interior pressure gauge, electrical feedthrough, and a sapphire window. The outlet valve is also attached to a vacuum pump (not seen in figure) and pressure gauge. The chamber is sealed with a graphite gasket. The vessel contains an internal thermowell where the thermocouple resides, and the chamber is heated from the exterior via a heating sleeve. Venus pressure is attained through heating; as the chamber heats up to Venus temperature, the pressure increases with it. The chamber’s temperature and pressure are controlled and monitored through an external temperature-pressure controller purchased from Parr instruments. This controller is attached to a computer which collects data every second in real time (Fig. 8).

Figure 7: The Venus Simulation Chamber (Cassiopeia Chamber) located at the University of Arkansas W.M. Keck Laboratory for Planetary Simulations. a) and b) Blueprints of the chamber from Parr Instruments. c) The Venus Simulation chamber set up in the laboratory.
Figure 7 (continued)
The bulk of our analysis was completed using X-ray Diffraction (XRD) via the PANalytical's Materials Research Diffractometers (MRD) located at the University of Arkansas’ Nano & Bio Materials Characterization Facility. XRD is used to determine the mineralogy of a sample. An X-ray beam sent towards the sample is scattered due to the crystalline structure of the sample. The angle between the incoming and outgoing beam and the intensity of the interference pattern will inform us on the minerals or elements present in the sample. The 2θ scan range was between 15-85 degrees. We used CuKα radiation, 1.54 Å. The voltage was 45 kV and the counting time was 0.8 sec per step. The diffraction spectrum is then compared to a spectral database built into the X’Pert Highscore program in order to better ascertain the composition of the sample. This program was also used to determine the abundance of minerals/elements in the sample. One drawback is if the mineral is rare it will not have the Reference Intensity Ratio (RIR) value needed to calculate its abundance. Another drawback to the XRD method is that it cannot detect amorphous structures.

Samples were also occasionally analyzed using the FEI XL-30 Environmental Scanning Electron Microscope (SEM) and the Energy Dispersive X-ray (EDX). The EDX sends a beam of high energy electrons to the sample which excites the electrons and creates electron holes. These holes are then filled with electrons at higher energy levels which release X-rays which is measured by a detector. This data can be used to determine the elemental composition and its abundance in a sample. This method was used to verify if any of our samples contained specific elements. In addition, it detects the elemental composition of any amorphous phases found in a sample and can be used in tandem with the MRD.

The VersaProbe from Physical Electronics (PHI) was occasionally used for X-Ray Photoelectron Spectroscopy (XPS) analysis. Similar to the EDX, it can also be used to determine the elemental composition of a sample. Due to its analytical technique it is more powerful and more accurate than the EDX. A sample is hit with X-rays which excites and ejects electrons. Unlike the EDX, the XPS not only measures the ejected electron’s energy, but also the binding
energy to inform the user on the elemental composition and quantity present in the sample. A useful characteristic of the XPS is its ability to determine the elemental composition of the upper few nanometers of the sample which can be used to study such processes as adsorption. It can also detect the chemical state of an element, such as determining between sulfates and sulfides. The X-ray source used was a monochromated k-alpha ray from Al at 1486 eV. We used a pass energy of 117.4 eV for surveys and 58.7 eV or below for high resolution scans. The samples were exposed to a 2 kV/2 μA Ar+ beam for 30 seconds to 1 minute prior to analysis in order to remove atmospheric contamination.

3.2 Methodology

A total of 8 different minerals/mixtures were studied in this project (Table 3). Several minerals/elements were already on hand while others needed to be purchased. Bismuth granules (99.8% purity) and sulfur powder were two such element that were already present in the lab. The bismuth was purchased from Mallinckrodt. The manufacturer of the sulfur is unknown, but the XRD detected 100% S8. Tellurium powder (99.5% purity), Bi2Te3 powder (99.98% purity), Bi2S3 powder (99.9% purity), Pb powder (99%), and PbSO4 powder (99.999%) were all purchased from Alfa Aesar. PbO (99.9%) was purchased from Acros Organics and is <10 microns. Fe7S8 was purchased from Ward’s Science, and the mineral chunks came from Galax, Virginia. PbS was purchased from VWR as large, crystalline chunks sourced from Mexico and Colorado. All samples were reanalyzed with XRD and occasionally XPS and SEM/EDX to confirm their composition.

The initial step of our experiments was to grind our samples in the ring mill and run them through a sieve to ensure that the samples were of equivalent diameters. At the start of each experiment all samples were less than 125 microns. Each of the experiments consisted of one gram of the sample. The only samples that did not follow this pattern were the Bi/Te/S mixtures. Our Bi/Te/S mixture experiments consisted of three different mixtures. We studied a 1:1 molar ratio of Bi2Te3 and Bi2S3, a 1:3 molar ratio of Bi2S3 and Te, and a 1:1:1 molar ratio of Bi, Te, and S.
To start an experiment the sample was placed within the chamber and the chamber was fully sealed using a torque wrench. The chamber was then placed in vacuum (20 ± 15 mbar) before the gas to be used in the experiment was set to 60 psi for several minutes to flush out any unwanted terrestrial gases. Assuming ideal conditions, the ideal gas law was used to calculate the initial pressure by knowing the initial temperature and the desired final temperature and pressure. Thus, once the chamber has been flushed for several minutes, it was resealed and filled to the calculated initial pressure before a heating sleeve was attached to the chamber. The final temperature was then set on the temperature/pressure controller. The chamber took between 30-45 minutes before it reached the desired temperature/pressure.

The samples were tested in one of two or three different temperature/pressure conditions and in one of three different gas compositions. The three different temperature/pressure conditions correlate to three different altitudes on the surface of Venus. We tested 460°C/95 bar, 425°C/75 bar, and 380°C/45 bar. The first condition is the average lowland condition, the second condition is found right above where the emissivity decreases on Maxwell Montes, 4.5 km above datum, and the third condition is found at the top of Maxwell Montes, 11 km above datum. Subsequent experiments omitted testing the condition at 4.5 km because there were no observable differences in the samples collected between this and the lowland condition.

The average initial temperature was 22.65°C ± 3.11°C and the average initial pressure for the highland experiments was 19.09 bar ± 0.76 bar, mid-altitude was 32.78 bar ± 0.38 bar, and the lowland experiments was 38.36 bar ± 1.60 bar. The average final temperature for the highland condition experiments was 381.56°C ± 1.33°C, the mid-altitude was 424.97°C ± 0.71°C, and lowland conditions was 460.03°C ± 1.01°C. The average pressure over the course of the experiments for the highland condition was 42.11 bar ± 0.72 bar, the mid-altitude condition was 70.06 bar ± 3.73 bar, and the lowland condition was 90.25 bar ± 1.25 bar.
Figure 8: The temperature and pressure within the Venus Simulation Chamber over the course of 72 hours as recorded by the temperature-pressure controller. This experiment was testing the condition in the highlands, so the chamber was set to 380°C and the desired pressure was 653 psi. Although the pressure was ~7 psi (0.48 bar) higher than expected, the chamber exhibits significant stability in temperature and pressure.
The three tested gases were 99.99-99.999% CO₂, 100 ppm of SO₂ in CO₂, and 100 ppm of COS in CO₂. Pure CO₂ was chosen since Venus’ atmosphere consists of 96.5% CO₂. The CO₂ cylinders used for the Bi/Te/S experiments were 99.99% pure, and experiments using the Pb minerals and the pyrrhotite were 99.999% pure. The purity of the 99.999% CO₂ cylinders were measured by AirGas and were tested for O₂+Ar+CO (<1.0 ppm), THC (<1.0 ppm), H₂O (<3.0 ppm), and N₂ (<5.0 ppm). The 99.99% CO₂ cylinders (which were also used for the mixed gas) were tested for H₂O (<10 ppm), hydrocarbons (<10 ppm), N₂ (<70 ppm), and O₂ (<20 ppm). The COS was 97% pure and was tested for CS₂ (<300 ppm), CO₂ (<1.7 ppm), N₂ (<0.2 ppm), and H₂S (<0.8 ppm). The SO₂ was 99.98% pure. Even though the abundance of COS is roughly 0.25 to 16 ppmv at <36 km (Pollack et al., 1993; Marcq et al., 2005; 2008; 2017), due to the limiting gas abundance as set by the gas company, we could not include less than 100 ppm of a gas into the cylinder. In addition, SO₂ and COS are corrosive, thus special regulators were purchased to use them. However, these regulators were not high output regulators, therefore we could not simulate pressures found in the lowlands of Venus and so the mixed gases were only used in highland experiments.

All experiments lasted between 24 to 96 hours. At the end of each experiment the gas in the chamber was vented while it was still hot, and then the chamber was placed in vacuum (20 ± 15 mbar). It was then flushed with N₂ at 60 psi for several minerals before it was filled with 20 bar of N₂ and cooled down, a process which takes approximately 5 hours. After the chamber was cooled to room temperature, the sample was removed and analyzed. For the bismuth, tellurium, and sulfur experiments the samples were originally cooled down in the tested experiment’s gas and not N₂. In subsequent experiments they were cooled down in N₂, however no noticeable changes in the final samples were visible between the two cooling down methods.
Table 3: A summary of all tested minerals/elements in all tested gases, temperatures, and pressures completed during this project.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Temperature/Pressure</th>
<th>Gases</th>
</tr>
</thead>
</table>
| Bi$_2$Te$_3$/Bi$_2$S$_3$  
Bi$_2$S$_3$/3Te  
Bi/Te/S          | 380°C/45 bar         | 99.99% CO$_2$                              |
|                   |                      | 100 ppm of SO$_2$ in CO$_2$                |
|                   |                      | 100 ppm of COS in CO$_2$                   |
|                   | 425°C/75 bar         | 99.99% CO$_2$                              |
|                   | 460°C/95 bar         |                                            |
| PbS               | 380°C/45 bar         | 99.999% CO$_2$                            |
| Pb                |                      | 100 ppm of SO$_2$ in CO$_2$                |
| PbO               |                      | 100 ppm of COS in CO$_2$                   |
| PbSO$_4$          | 460°C/95 bar         | 99.999% CO$_2$                            |
| Fe$_7$S$_8$       | 380°C/45 bar         | 99.999% CO$_2$                            |
|                   |                      | 100 ppm of SO$_2$ in CO$_2$                |
|                   |                      | 100 ppm of COS in CO$_2$                   |
|                   | 460°C/95 bar         | 99.999% CO$_2$                            |

4.0 References


Chapter 2

Investigation into the Radar Anomaly on Venus: The Effect of Venus Conditions on Bismuth, Tellurium, and Sulfur Mixtures

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1.0 Abstract

The source of the unusually high radar reflectivity signal found on the highlands of Venus is hypothesized to be caused by a mineral with a high dielectric constant. We propose that this source could be a combination of tellurium, sulfur, and bismuth. All three elements are commonly outgassed in terrestrial eruption plumes and thus are likely to be found on Venus. To test our hypothesis, we used a Venus simulation chamber and studied the stability of various tellurium, bismuth, and sulfur mixtures at Venus temperatures and pressures and in atmospheres of CO₂, 100 ppm SO₂ in CO₂, or 100 ppm COS in CO₂. When mixed together bismuth, tellurium, and sulfur phases preferentially formed tetradymite (Bi₂Te₃S). The remaining minerals that formed in each experiment strongly depended on the initial mixture. For instance the Bi₂S₃/Bi₂Te₃ mixture experiments resulted in the original minerals as well as BiTe at hotter temperatures, meanwhile the Bi/Te/S mixture produced Bi₂S₃ and occasionally Bi₂Te₃, Bi(S,Te), and Bi₄(S,Te)₃ depending on the temperature/pressure. There is evidence that COS, but not SO₂, affected the stability of some minerals. Due to the presence of these elements in volcanic gases we propose that they can be present in the highlands and can, at least in part, account for the high radar reflectivity signal on the highlands.

2.0 Introduction

Since the 1960s, ground based and orbiter data have unveiled radar bright regions located on the mountain tops of Venus. It wasn’t until 1978 when NASA’s Pioneer orbiter began to image
the surface that the extent and the unique brightness of these regions was realized (Ford and Pettengill, 1983; Masursky et al., 1980; Pettengill et al., 1982). The Magellan spacecraft determined a mean global emissivity of 0.845 (reflectivity=0.15), with values in the highlands reaching as low as 0.3-0.4 (reflectivity=0.6) (Pettengill et al., 1992; Shepard et al., 1994). Emissivity and reflectivity are related via the equation $e=1-p'$ where $e$ is emissivity and $p'$ is reflectivity, thus low emissivity corresponds to high reflectivity (Ford and Pettengill, 1983).

The high radar reflective regions are only found on certain mountain ranges and begin at different elevations (Arvidson et al., 1991; Klose et al., 1992). The critical altitude, where reflectivity begins to increase, varies from between 2.49 km (above the planetary radius of 6051.0 km) on Sapas Mons and 4.75 km on Maxwell Montes (Klose et al., 1992). There is no correlation between the latitude/longitude and the formation of these radar reflective regions. Some volcanoes, such as Maat Mons, do not exhibit a relationship between reflectivity and elevation. It is possible that this is due to its very young surface, thus the low emissivity signal has not had enough time to manifest (Klose et al., 1992).

The first theory on the origin of the reflective regions to emerge was that it was due to surface roughness (Campbell et al., 1976; Masursky et al., 1980; Pettengill et al., 1980). However it was quickly dismissed because regions of similar roughness had different reflectivities, and the magnitude of brightness could not be explained solely by surface roughness (Masursky et al., 1980; Pettengill et al., 1982; Tyler et al., 1991). Three competing theories on the source of the radar reflective regions are high dielectric mineral inclusions within the surface material (Pettengill et al., 1982, 1988; Shepard et al., 1994), weathering of the surface creating a secondary mineral (Klose et al., 1992), or some high dielectric material is depositing onto, and coating the surface (Brackett et al., 1995; Schaefer and Fegley, 2004). The mountain ranges would need to have a material with a dielectric constant of $\varepsilon/\varepsilon_0 \pm \varepsilon_0$, compared to Venus’ average surface dielectric constant of 4.0 ± 0.5, in order to explain the source (Pettengill et al., 1996). The $i$ indicates the
imaginary component of the permittivity which signifies the amount of incident radar energy that is lost in the material (Brodie et al., 2015; Treiman et al., 2016).

Among these theories we pursued the last one, the theory of a mineral depositing onto the highlands. Minerals with volatile metals were first explored as a possible source by Brackett et al. (1995). They asserted that volcanic outgassing could release metal halides and chalcogenides with high dielectric constants which could migrate towards the much cooler highlands and coat the surface. Metal halides and chalcogenides are found in volcanic gases and near volcanic vents on Earth (Brackett et al., 1995). Possible evidence for their existence on Venus can be seen in the Pioneer probe data, where there was an unknown electrical anomaly at 12.5 km above the surface that could have been caused by an atmospheric haze of metal halides or chalcogenides (Brackett et al., 1995).

The focus of our research was to determine the stability of mixtures of Bi$_2$S$_3$, Bi$_2$Te$_3$, and Bi, Te, and S under Venus conditions. These elements and minerals were selected due to their high dielectric constants and several have been suggested or were a part of non-experimental studies. Tellurium (Te) has been theorized because of its high dielectric conductivity and because gaseous tellurium could deposit onto the cooler mountaintops (Lin et al., 2016; Pettengill et al., 1996). Bismuthinite (Bi$_2$S$_3$) is a semiconductor (Benattou et al., 2017; Yang et al., 2013) and has a high dielectric constant, 108 at 720 K measured at 30 GHz (Lukaszewicz et al., 1999). Additionally, it has been found near fumaroles (Mizutani, 1966; Wolfe, 1938), and will condense at 2.6 km on Venus assuming the abundance of bismuth is similar to that of basaltic meteorites (eucrites), 4 ppb (Kitts and Lodders, 1998; Schaefer and Fegley, 2004). We elected to study the mineral tellurobismuthite (Bi$_2$Te$_3$) as it is a semiconductor used in thermoelectric devices (Han et al., 2017; Kim et al., 2013; Nassary et al., 2009).

Bismuth, sulfur, and tellurium have been detected in volcanic gases and fumaroles on Earth. Currently their abundances on Venus are unknown, however because the early solar
System material was believed to be well mixed, and due to the similarities between the bulk compositions of Earth and Venus, these elements are likely present on Venus (Chambers, 2004; Rubie et al., 2015; Treiman, 2009).

Bismuth (Bi) has been found in volcanic plumes in Merapi volcano, Mount Etna, Nyiragongo, Nyamuragira, Kilauea, and la Fossa crater at Vulcano Island (Hinkley et al., 1999; Milazzo, 2017; Symonds et al., 1987). Measurements of volcanic gas from fumaroles in Merapi volcano in Indonesia have detected bismuth concentrations to be as high as 490,000 times the abundance of bismuth found in the surrounding magma (Symonds et al., 1987). Based on volcanic emission of sulfur, approximately 4,000 tons of bismuth is outgassed from volcanism on Earth every year (Patterson et al., 1987), though some have estimated much less, around 405 to 1,500 tons (Hinkley et al., 1999; Lambert et al., 1988). These values are plotted against tellurium and sulfur emission abundances in Figure 1.

![Figure 1: Estimated terrestrial emission abundances of tellurium, bismuth, and sulfur in tons/yr. The values are from measurements obtained from the vicinity of several volcanos on Earth. The data was obtained from Lambert et al. (1988), Milazzo (2017), Hinkley et al. (1999), and Halmer et al. (2002)](image-url)
Tellurium has been detected in volcanic plumes and fumaroles at concentrations of around \(<0.003 \text{ to } 0.15 \, \mu g/m^3\) on Earth, with an estimate outgassing of 98 tons/year (Milazzo, 2017) (Fig 1). Thermodynamic models of Venus completed by Schaefer and Fegley (2004) calculated that tellurium condenses at 46 km, well above the critical altitude. Other experimental studies found that tellurium oxidizes into TeO$_2$ under Venus conditions (Kohler et al., 2015). Nonetheless we believed that further experiments were needed to study tellurium and its interaction with bismuth and sulfur.

For our experiments we chose to study mixtures between bismuth, tellurium, and sulfur because mixtures are common on Earth, and due to their low melting temperature, Venus' elevated temperatures and pressures may facilitate the formation of Bi/Te/S minerals (Cook et al., 2007). The stability of Bi$_2$S$_3$ and Bi$_2$Te$_3$ at Venus temperatures/pressures in a CO$_2$/SO$_2$ atmospheric mixture have been tested separately in the past and were found to be stable in both the highland and lowland conditions (Kohler et al., 2015). However, a mixture between the two has not been studied before, and it is possible that when mixed together different phases may form depending on the environmental conditions. We also chose to test a Bi$_2$S$_3$/3Te mixture to observe if tellurium could replace the sulfur in Bi$_2$S$_3$. Lastly, we sought to study the minerals that were most likely to form if pure bismuth, tellurium, and sulfur were mixed together at Venus temperatures and pressures.

It has been over 30 years since a probe was sent to the surface of Venus and collected the chemical composition of the atmosphere and the elemental composition of the surface. In addition, no data on the environmental conditions in the highlands has ever been collected, thus the lack of new data requires a non-in situ approach. Computer modeling is one such method that can be used to better understand the surface, however to our knowledge there still does not exist a software that simulates thermodynamic reactions in supercritical CO$_2$. In addition, these models use thermodynamic databases that do not contain values for minerals at Venus conditions,
particularly for these uncommon phases. This justifies the need for experimental research in order to better grasp the surface-atmosphere interactions that can occur on Venus.

### 3.0 Methods/Materials

An overall summary of all tested conditions can be found in Table 1. We purchased five different samples to complete our experiments. We used bismuth granules (99.8% purity), tellurium powder (99.5% purity), Bi$_2$Te$_3$ powder (99.98% purity), Bi$_2$S$_3$ powder (99.9% purity), and sulfur powder. The tellurium, Bi$_2$Te$_3$, and Bi$_2$S$_3$ powders were purchased from Alfa Aesar. The bismuth powder was purchased from Mallinckrodt. The sulfur powder was already present in the lab, and though the manufacture’s name is unknown, XRD analysis verified that it is pure S$_8$. All samples were crushed then sieved to less than 125 microns. We combined these powders into three different mixtures: 1:1 molar ratio of Bi$_2$S$_3$/Bi$_2$Te$_3$, 1:3 molar ratio of Bi$_2$S$_3$/Te, and a 1:1:1 molar ratio of Bi, Te, and S.

Each of the samples were tested in the Venus simulation chamber (Cassiopeia Chamber, available at the University of Arkansas W.M. Keck Laboratory for Space and Planetary Simulations), constructed by Parr Instruments, at Venus temperatures and pressures. Each sample was tested in one of three different temperatures/pressures as well as one of three different atmospheric chemistry environments. The temperatures/pressures were determined based on the altitude that we aimed to simulate: 0 km/95 bar/460°C, 4.5 km/75 bar/425°C, and 11 km/45 bar/380°C. This range was selected to study the effects of the hottest and coolest regions on these minerals. Furthermore, our goal was to test the hypothesis that a mineral would be stable in the highlands but not in the lowlands. We chose the mid-elevation condition because this is where the radar reflectivity changes on Maxwell Montes (Treiman et al., 2016). The relationship between temperature/pressure and altitude was taken from the Venus International Reference Atmosphere (VIRA) (Seiff et al., 1986).
The three different atmospheric compositions were 100% CO$_2$, CO$_2$ with 100 ppm of SO$_2$, and CO$_2$ with 100 ppm of COS. CO$_2$ is the most prominent gas on Venus and comprises 96.5% of the atmosphere. The abundance of SO$_2$ has been determined to be around 130 ± 50 ppm on Venus (Bézard et al., 1993; Marcq et al., 2008). The abundance of COS varies greatly with estimates below 36 km being from 1 ppmv to 20 ppmv (Marcq et al., 2005; Marcq et al., 2006; Marcq et al., 2008; Pollack et al., 1993). All gases were bought pre-mixed from Airgas. Our tested COS abundance was much larger than estimates on Venus because of the limitations on gas mixtures (minimum of 100 ppm of a gas in a cylinder). The mixed gases were only used in the highland (380°C/45 bar) experiments due to the maximum pressure limit of the specially designed regulators used for corrosive gases.

Table 1: A summary of all tested experimental conditions. All experiments lasted 24 hours.

<table>
<thead>
<tr>
<th>CO$_2$</th>
<th>CO$_2$/COS</th>
<th>CO$_2$/SO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowlands:</td>
<td>Mid-Alt:</td>
<td>Highlands:</td>
</tr>
<tr>
<td>460°C</td>
<td>425°C</td>
<td>380°C</td>
</tr>
<tr>
<td>95 bar</td>
<td>75 bar</td>
<td>45 bar</td>
</tr>
<tr>
<td>Bi$_2$S$_3$Bi$_2$Te$_3$</td>
<td>Bi$_2$S$_3$Bi$_2$Te$_3$</td>
<td>Bi$_2$S$_3$Bi$_2$Te$_3$</td>
</tr>
<tr>
<td>Bi$_2$S$_3$/3Te</td>
<td>Bi$_2$S$_3$/3Te</td>
<td>Bi$_2$S$_3$/3Te</td>
</tr>
<tr>
<td>Bi/Te/S</td>
<td>Bi/Te/S</td>
<td>Bi/Te/S</td>
</tr>
</tbody>
</table>

One gram of the mixture was placed in a long ceramic crucible before being inserted into the chamber. The crucibles are boat shaped with dimensions of 6 cm x 1 cm x 0.6 cm and are open above. The sample was inserted first, and then the chamber was flushed out with CO$_2$ followed by the gas for the chosen experiment. Once the chamber was successfully purged, the chamber was heated via a heating sleeve. In order to get the desired temperature and pressure we used the Ideal Gas Law to determine the initial pressure needed to end at the final pressure based on the initial and final temperatures. Since the gas is not ideal, several trial runs were completed in order to determine the best initial pressure to get the closest to the desired final pressure. The chamber takes between 30 to 45 minutes until it reaches the correct temperature. The experiment lasted 24 hours, then the sample was allowed to cool down to room temperature.
(about 5 hours) before it was removed. The sample was then analyzed with X-Ray Diffraction (XRD) using a PANalytical's Materials Research Diffractometers (MRD) located at the University of Arkansas. The 2theta scan range was between 15-85 degrees, the voltage was 45 kV, and the counting time was 0.8 sec. All data was collected in ambient conditions. The program X'Pert Highscore was used for analysis of the peaks.

4.0 Results

We used X'Pert Highscore to determine the composition of the samples, however due to the rarity of many of the minerals a reference intensity ratio (RIR) value is not available which prevented us from ascertaining the modal abundance of each phase. All results are displayed in Table 2. The experiments were completed multiple times and some of the minerals/elements were not present at the end of every experiment.

Our Bi$_2$S$_3$/Bi$_2$Te$_3$ mixture experiments formed Bi$_2$Te$_2$S in every tested condition. Almost every experiment still had evidence of Bi$_2$S$_3$ and Bi$_2$Te$_3$, excluding the experiment completed in CO$_2$/COS, which did not have any Bi$_2$S$_3$. The formation of BiTe was also observed, but only in the mid-elevation and lowland condition experiments. Our Bi$_2$S$_3$/3Te mixtures had very similar results in every experiment, specifically it always contained Bi$_2$S$_3$, Bi$_2$Te$_2$S, and Te. Bi$_2$Te$_3$ was the only new mineral in this scenario and formed only in the lowland condition experiments. Our Bi/Te/S results were the most inconsistent, with different minerals forming in each experiment. The only two minerals that formed in every tested condition were Bi$_2$Te$_2$S and Bi$_2$S$_3$. XRD spectra for select experiments are displayed in Figure 2.

Data pertaining to the mass loss of these experiments are displayed in Figure 3. The change in mass of the samples was collected for each experiment, unfortunately there were several instances where we were unable to directly measure the weight. This is due to the gas insertion method which, because high output regulators were used, could blow some of the sample out of the crucible resulting in mass loss. Regarding the Bi$_2$S$_3$/Bi$_2$Te$_3$ mixtures we can
conclude that these experiments lost very little mass when compared to all other mixtures and experiments tested in pure CO$_2$. On the other hand, when it was tested in the highland condition in CO$_2$/COS the mass loss percent is significantly more, 10 ± 3.3% compared to 3.6% when tested in the same condition but in CO$_2$.

In the Bi/Te/S experiments the largest mass loss was observed in the critical altitude and lowland condition experiments. In fact, overall these experiments lost the most mass compared to all the experiments completed in this project. This confirms the volatility of these elements which results in more mass loss at higher temperatures. Additional evidence is observed by a thin, silver residue coating the top of the chamber which only occurs after the critical and lowland condition experiments and is likely tellurium and perhaps bismuth. A similar coating was seen after the Bi$_2$S$_3$/3Te experiments in the lowland condition. Overall temperature/pressure has a stronger effect on mass loss than the composition of the gas.

Table 2: Summary of all the XRD results obtained during this project. The minerals and elements are not listed in any particular order.

<table>
<thead>
<tr>
<th>Mineral Mixtures</th>
<th>CO$_2$</th>
<th>CO$_2$/COS</th>
<th>CO$_2$/SO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lowlands: 460°C 95 bar</td>
<td>Mid-Alt: 425°C 75 bar</td>
<td>Highlands: 380°C 45 bar</td>
</tr>
<tr>
<td>Bi$_2$S$_3$/Bi$_2$Te$_3$</td>
<td>Bi$_2$Te$_2$S Bi$_2$S$_3$ Bi$_2$Te$_3$ BiTe</td>
<td>Bi$_2$Te$_2$S Bi$_2$S$_3$ Bi$_2$Te$_3$ BiTe</td>
<td>Bi$_2$Te$_2$S Bi$_2$S$_3$ Bi$_2$Te$_3$ BiTe</td>
</tr>
<tr>
<td>Bi$_2$S$_3$/3Te</td>
<td>Bi$_2$Te$_2$S Bi$_2$S$_3$ Bi$_2$Te$_3$ Te</td>
<td>Bi$_2$Te$_2$S Bi$_2$S$_3$ Bi$_2$Te$_3$ Te</td>
<td>Bi$_2$Te$_2$S Bi$_2$S$_3$ Bi$_2$Te$_3$ Te</td>
</tr>
<tr>
<td>Bi/Te/S</td>
<td>Bi$_2$Te$_2$S Bi$_2$S$_3$ Bi$_2$Te$_3$ Bi$_4$Bi$_4$(S,Te)$_3$ Bi(S,Te) Bi$_4$Te$_3$</td>
<td>Bi$_2$Te$_2$S Bi$_2$S$_3$ Bi$_2$Te$_3$ Bi$_4$Bi$_4$(S,Te)$_3$ Bi(S,Te) Bi$_4$Te$_3$</td>
<td>Bi$_2$Te$_2$S Bi$_2$S$_3$ Bi$_2$Te$_3$ Bi$_4$Bi$_4$(S,Te)$_3$ Bi(S,Te) Bi$_4$Te$_3$</td>
</tr>
</tbody>
</table>
Figure 2: XRD spectra of selected experiments completed in pure CO$_2$. The spectrum at the very bottom is the control, the one above is when it was heated to 380°C/45 bar, followed by when it was heated to 425°C/75 bar, and then when it was heated to 460°C/95 bar. Te= tellurium, Bi= bismuth, S= sulfur, T= tetradymite (Bi$_2$Te$_2$S), Tb= tellurobismutite (Bi$_2$Te$_3$), Bs= bismuthinite (Bi$_2$S$_3$), Ts= tsumoite (BiTe), IN= ingodite (Bi(Te,S)), J= joséite (Bi$_4$(S,Te)$_3$) a) Bi$_2$S$_3$/Bi$_2$Te$_3$ experiments b) Bi$_2$S$_3$/3Te experiments c) Bi/Te/S experiments
Figure 2 (continued)

Figure 3: Relative mass loss for a) experiments completed in pure CO$_2$ b) experiments completed in the highland (380°C/45 bar) condition. The mass loss of several experiments was not collected due to sample spillage.
Figure 3 (continued)

5.0 Discussion

5.1 Effect of CO$_2$ Gas

The results from the Bi$_2$S$_3$/Bi$_2$Te$_3$ experiments demonstrate a preferential formation of Bi$_2$Te$_2$S in all experiments. Bi$_2$Te$_2$S likely forms via the following reaction pathway:

$$\text{Bi}_2\text{S}_3 + 2\text{Bi}_2\text{Te}_3 = 3\text{Bi}_2\text{Te}_2\text{S} \quad (1)$$

Meanwhile in the lowland and intermediate temperature experiments BiTe was also present in the sample (Fig. 2a and 4b). It is likely forming as a result of the loss of some sulfur via the interaction:

$$2\text{Bi}_2\text{S}_3 + 4\text{Bi}_2\text{Te}_3 = 12\text{BiTe} + 3\text{S}_2 \quad (2)$$

We suggest this reaction pathway because BiTe is only produced in the Bi$_2$S$_3$/Bi$_2$Te$_3$ experiments. The only other instance where BiTe formed is in the Bi/Te/S experiments completed at 460°C/95
bar, but this reaction mechanism is very different because we start with individual elements which can more easily react with one another and thus facilitate its formation. We also tested the stability of Bi$_2$S$_3$ and Bi$_2$Te$_3$ separately in the lowland condition in CO$_2$ and found both were stable, which indicates that BiTe cannot form from one mineral. The loss of sulfur is also supported by the mass loss of 2% in the 425°C/75 bar experiment. When heated to 460°C/95 bar we only lost 0.02 %, however since we do not know the final abundance of BiTe, the reaction may still be occurring but producing very little BiTe. In addition, we were only able to measure the mass loss in one experiment, so its precision is unknown. The very low mass loss in both conditions defends the theory that reaction 1 is favored. Unfortunately, thermodynamic values do not exist for BiTe so this reaction cannot be verified via modeling. This reaction only occurs in hotter temperatures, lowland and critical altitude, thus the temperature/pressure somehow facilitates its formation. CO$_2$ does not appear to have any direct interaction with Bi$_2$S$_3$/Bi$_2$Te$_3$. The preference of reaction 1, and the lack of free elements in the original mixture, which could be lost at hotter temperatures, explains why so little mass is lost in these experiments compared to all other mixtures completed in CO$_2$.

When Bi$_2$S$_3$/3Te was tested at 380°C/45 bar in CO$_2$ the final sample contained Te, Bi$_2$S$_3$, and Bi$_2$Te$_2$S (Fig 2b and 4a). The likely reaction pathway of Bi$_2$Te$_2$S is:

$$\text{Bi}_2\text{S}_3 + 2\text{Te} = \text{Bi}_2\text{Te}_2\text{S} + \text{S}_2 \; (g)$$ \hspace{1cm} (3)

Since only two moles of tellurium is being used in this equation it also explains the excess of tellurium at the end of the experiments. When heated to 460°C/95 bar Bi$_2$Te$_3$ also appears in the sample (Fig 2b and 4b). This product likely forms from the replacement of sulfur in Bi$_2$S$_3$ by tellurium. At this temperature tellurium is a liquid which increases the reaction and diffusion rate allowing for the production of Bi$_2$Te$_3$. Bi$_2$Te$_3$ also formed in the Bi/Te/S experiments, but the formation mechanism is probably different since the starting material is composed of pure elements and not minerals. During lowland temperature experiments sulfur and minor amounts
of tellurium are also outgassed from the sample. Evidence for sulfur loss is observed by the deposition of sulfur in the chamber after the experiments. Evidence for tellurium outgassing was obtained from the observation of a silvery residue that thinly coated the interior of the chamber.

This residue only appeared in experiments involving pure tellurium, and thus is likely a fine layer of tellurium. The loss of sulfur and tellurium would explain the large mass loss of the sample tested in the lowland conditions, 0.338 g ± 0.002, a 19.7 ±0.3% decrease in mass. This result aligns with our expectation that free elements are more likely to leave the sample at elevated temperature/pressures.

In the experiments that started with a mixture of Bi/Te/S a larger selection of minerals formed as a result of the elements being unbounded. Bismuth and tellurium are liquid at all Venus temperatures (Klement et al., 1963; Lide, 2010; Stishov and Tikhomirova, 1966) and sulfur is a liquid at all Venus temperatures and pressures (Ferreira and Lobo, 2011), thus all the elements can easily interact with one another. In the CO$_2$ experiment at highland

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**Figure 4:** Ternary diagram summarizing the final solid products of this study completed in pure CO$_2$ a) experiments completed at 380°C/45 bar b) experiments completed at 460°C/95 bar.
temperature/pressure the samples were composed of minerals and elements that have been observed in other experiments, such as Bi$_2$Te$_2$S, and Bi$_2$S$_3$, (Fig 4a). However when the mixture was heated to the hotter condition, 460°C/95 bar, we formed even more minerals as well as solid solutions (Fig 4b). We even occasionally have leftover elements, such as bismuth, but it only appeared in one experiment. In fact, many of the minerals listed in the table only appeared in one experiment. The inconsistent results in our samples is due to the formation of a melt consisting of all three elements interacting with one another. In addition hotter temperatures resulted in the loss of more sample, likely from the displacement of sulfur and tellurium, and perhaps even bismuth onto the chamber walls. Therefore it is impossible to determine the formation mechanism of these minerals and which minerals are the most likely to manifest if we start with these pure elements on Venus.

5.2 Effect of Mixed Gases

Unlike in the experiments involving Bi$_2$S$_3$/ Bi$_2$Te$_3$ in CO$_2$, Bi$_2$S$_3$ was not found in the experiments involving CO$_2$/COS. It can be concluded that CO$_2$/COS has an effect on the sample, although the details of the chemical process occurring during the experiments is currently not well understood. Conversely, according to our observations there is no perceptible evidence that CO$_2$/COS interacts with the Bi$_2$S$_3$/3Te mixture since Bi$_2$S$_3$ is still present at the end of the experiments. Thus, the apparent absence of Bi$_2$S$_3$ is due to the overall chemical interaction of the initial sample mixture (Bi$_2$S$_3$/ Bi$_2$Te$_3$) and CO$_2$/COS. In the Bi$_2$S$_3$/ Bi$_2$Te$_3$ experiments the CO$_2$/COS mixture likely interacts and breaks down the Bi$_2$S$_3$. Next, either the Bi$_2$S$_3$, or some unknown product from the previous interaction, reacts with Bi$_2$Te$_3$ to form Bi$_2$Te$_2$S. However in the Bi$_2$S$_3$/3Te experiment the tellurium seems to prevent the full decomposition of Bi$_2$S$_3$. Future experiments will need to be completed with CO$_2$, COS, and Bi$_2$S$_3$ to determine the reaction mechanism. The Bi$_2$S$_3$/ Bi$_2$Te$_3$ experiments in CO$_2$/COS also resulted in a higher mass loss percent, approximately 10.1 ±3.3 %, compared to when this mixture was tested in CO$_2$, 3.6%. The higher mass loss points to
the loss of sulfur, observable by the increase in the Bi/S ratio during the experiment. The CO\textsubscript{2}/SO\textsubscript{2} mixture appeared to have little effect on the sample since the end results were identical to when it was tested in pure CO\textsubscript{2}.

In the Bi\textsubscript{2}S\textsubscript{3}/3Te mixture experiments completed in both mixed gases (CO\textsubscript{2}/COS and CO\textsubscript{2}/SO\textsubscript{2}), the results are the same compared to when it was completed in pure CO\textsubscript{2} at 380°C/45 bar. However based on the results of the Bi\textsubscript{2}S\textsubscript{3}/Bi\textsubscript{2}Te\textsubscript{3} experiments CO\textsubscript{2}/COS does have an effect on Bi\textsubscript{2}S\textsubscript{3}, and may cause it to dissociate. Since we currently cannot quantify our results, we cannot determine how much Bi\textsubscript{2}S\textsubscript{3} is lost during the experiment and thus verify its instability. The CO\textsubscript{2}/SO\textsubscript{2} mixture has little to no visible effect on this mixture over the course of the 24 hour experiments.

In the Bi/Te/S mixtures in CO\textsubscript{2}/COS we formed Bi\textsubscript{2}Te\textsubscript{2}S, Bi\textsubscript{4}Te\textsubscript{3}, and Bi\textsubscript{2}S\textsubscript{3}. Omitting pure elements that were occasionally present at the end of the experiments, all of the products can be found in the experiments that were completed in pure CO\textsubscript{2} except for Bi\textsubscript{4}Te\textsubscript{3}. Due to the plethora of minerals that form in the Bi/Te/S experiments this result is likely not related to the COS gas and instead simply a mineral that can form when all three elements interact at Venus conditions. In fact, the formation of Bi\textsubscript{4}Te\textsubscript{3} only occurred in one of the CO\textsubscript{2}/COS experiments. For the Bi/Te/S experiments in the CO\textsubscript{2}/SO\textsubscript{2} mixture we formed Bi\textsubscript{2}S\textsubscript{3}, and Bi\textsubscript{2}Te\textsubscript{2}S. The end products of each sample completed in each of the gases in the highland condition are similar, therefore it is unclear if the mixed gases have any role on the formation of these minerals.

5.3 Stability of Bi\textsubscript{2}S\textsubscript{3}, Bi\textsubscript{2}Te\textsubscript{3}, and Bi\textsubscript{2}Te\textsubscript{2}S

The fugacity of tellurium (f\textsubscript{Te2}) and the fugacity of sulfur (f\textsubscript{S2}) directly affect the formation of bismuth, tellurium, and sulfur bearing minerals (Afifi et al., 1988; Kong et al., 2015). As one would expect, in systems that have less sulfur, but more tellurium, tellurium minerals such as BiTe, Bi\textsubscript{2}Te\textsubscript{3} and Bi\textsubscript{4}Te\textsubscript{3} are more common (Cook and Ciobanu, 2004; Gu et al., 2001; Hassan and Roberts, 2017; Sejkora et al., 2009). Though Bi\textsubscript{2}Te\textsubscript{2}S contains sulfur, it is commonly found in
these systems as well (Cook and Ciobanu 2004; Gu et al., 2001; Hassan and Roberts, 2017; Jian et al., 2014; Sejkora et al., 2009). Systems with a higher $f_{S_2}$ tend to form $\text{Bi}_2\text{S}_3$, $\text{Bi}_4(\text{S,Te})_3$, and $\text{Bi}_2\text{Te}_2\text{S}$ (Cepedal et al., 2006; Ciobanu et al., 2010; Shimazaki and Ozawa, 1978). In nature, minerals with compositions of $\text{Bi}_2(\text{Te,Se,S})_3$, particularly $\text{Bi}_2\text{Te}_2\text{S}$ and $\text{Bi}_2\text{Te}_3$, are the most common due to their simple structure and so are preferentially formed depending on the availability of sulfur (Cook et al., 2007).

To better understand the effect of $f_{\text{Te}_2}$ and $f_{S_2}$ on the stability of bismuth, tellurium, and sulfur bearing minerals on Venus we created a mineral stability figure based on Afifi et al., (1988), but used different thermodynamic values and calculated it for Venus temperatures (Fig 5). The thermodynamic values we used were collected from Faure (1998), Robie and Hemingway (1995), Vaughan and Craig (1978), and the National Institute of Standards and Technology (NIST) JANAF thermochemical tables (Chase, 1998). Though thermodynamic values for $\text{Bi}_2\text{Te}_3$ and $\text{Bi}_2\text{S}_3$ are readily available, no values currently exist for any other Bi/Te/S bearing mineral, including $\text{Bi}_2\text{Te}_2\text{S}$. Since the formation of $\text{Bi}_2\text{Te}_2\text{S}$ is central to our project we have calculated the $\text{Bi}_2\text{Te}_2\text{S}$ stability field by using the ideal mixing model using an interaction between $\text{Bi}_2\text{Te}_3$ and $\text{Bi}_2\text{S}_3$ via Eq (1). The calculated $\text{Bi}_2\text{S}_3/\text{Bi}_2\text{Te}_2\text{S}$ and $\text{Bi}_2\text{Te}_3/\text{Bi}_2\text{Te}_2\text{S}$ lines are nearly identical, so the stability box for $\text{Bi}_2\text{Te}_2\text{S}$ is small enough that we can only see a line in our figure. We have plotted an orange “Venus box” based on the calculated values of $S_2$ on Venus; meanwhile the black line corresponds to the tellurium abundance. The abundance of $S_2$ has been calculated to be between 0.02 ppmv and 0.23 ppmv (Moroz, 1980; San’ko, 1980; Zolotov, 2018). The 0.02 ppmv was calculated using the measured $S_3$ abundance (Moroz, 1980; San’ko, 1980), while the 0.23 ppmv was calculated by using the minimal Gibbs free energy in a closed H-C-O-N-S system (Zolotov, 1996). To calculate $f_{\text{Te}_2}$ on Venus we assumed a scenario where all the tellurium in 50 km of a basaltic crust has been outgassed. The 50 km depth is the upper limit of the mean thickness of
Figure 5: The stability of Bi$_2$Te$_3$, Bi$_2$S$_3$, and Bi$_2$Te$_2$S as a function of tellurium and sulfur fugacity at a) 380°C b) 460°C based on Afifi et al., (1988). The orange box represents Venus conditions. Estimated f$_{Te_2}$ on Venus is represented by the dashed line. The Bi$_2$Te$_2$S stability phase is a small area between Bi$_2$Te$_3$ and Bi$_2$S$_3$. In the highlands our dashed line is closer to Bi$_2$Te$_3$ and Bi$_2$Te$_2$S; a slight shift in f$_{S_2}$ will result in their stability. However, thermodynamic values for Bi$_2$Te$_2$S were calculated, and experimentally obtained values are needed to accurately calculate its stability field (see text for details).
the crust which was calculated from gravity data (Grimm and Hess, 1997). We used the abundance for tellurium in a terrestrial oceanic crust, 0.003 ppm, which was the same value used by Schaefer and Fegley, (2004) in their calculation involving atmospheric tellurium on Venus. In the highland temperature condition the dashed line corresponds to \( \log(f_{Te2}) = -5.40 \) and in the lowland temperature condition it is -5.35. A more recent calculation completed by James et al., (2013) stated that the crust is no thicker than 25 km. If this is the case then the \( \log f_{Te2} \) would be -5.7. Since the true tellurium abundance is unknown, we chose to extend the box to the upper and lower y-axis limits.

Figure 5 demonstrates the importance of constraining \( f_{S2} \) and \( f_{Te2} \) to determine the stability of Bi\(_2\)Te\(_3\), Bi\(_2\)S\(_3\), and Bi\(_2\)Te\(_2\)S on Venus. Based on the figures, Bi\(_2\)S\(_3\) is the only mineral that should be stable, however a slight decrease in \( f_{S2} \) or a slight increase in \( f_{Te2} \) in the highlands is enough for Bi\(_2\)Te\(_3\) and Bi\(_2\)Te\(_2\)S to be stable. In the lowland the shift for both would need to be greater, with a shift of \( \log(f_{S2}) \) to less than -6.1 and \( \log(f_{Te2}) \) to greater than -4.9. However, since the thermodynamic values we used for Bi\(_2\)Te\(_2\)S were calculated, they may not be accurate, and values obtained via experiments are needed to precisely calculate its stability field. For example, a larger stability field for Bi\(_2\)Te\(_2\)S would cause the fields of Bi\(_2\)S\(_3\) and Bi\(_2\)Te\(_3\) in our figures to shift, which may alter our conclusions.

5.4 Deposition onto the Highlands

Several studies have examined methods in which a high dielectric material can be deposited on the mountains of Venus. Brackett et al. (1995) used a vapor transport model to calculate the approximate length of time for volatile minerals to be transported from the hotter lowlands to the cooler highlands.

One of the minerals that was part of Brackett et al. (1995)’s study was Bi\(_2\)S\(_3\). Based on their findings Bi\(_2\)S\(_3\) has between moderate to low volatility. Moderate volatility indicates the ability
to move to ~3.5 km in elevation in ~100 kyr. Meanwhile low volatility indicates that it will take well over 8 Myr to move to the same elevation. No other bismuth and tellurium bearing minerals were included in this study. Tellurium is highly volatile and new research completed on terrestrial volcanism has found large quantities of tellurium in volcanic plumes (Milazzo, 2017). It is also often transported away from these plumes as a gas (Milazzo, 2017). When Te\textsubscript{2} is plotted with Brackett et al. (1995)’s data it is found to be highly volatile revealing that it can move to ~3.5 km in altitude in 80 years (Fig 6). Meanwhile bismuth is closer to Brackett et al. (1995)’s calculated value for moderate volatility. The data indicates that they are able to be transported in relatively short time scales and supports the theory that if they were released by volcanoes on Venus, they would be rapidly transported to the highlands. Thermodynamic values for other bismuth and tellurium bearing gases will need to be experimentally obtained in order to calculate their locations on Figure 6.

Lindberg tube oven experiments completed in Port et al. (2016) observed the volatility of tellurium visually based on the formation of tellurium needle crystals in Bi\textsubscript{2}S\textsubscript{3}/3Te and Bi/Te/S experiments at 425°C and 460°C. The samples were placed in the tube at the center of the oven which correlated to either 425°C or 460°C depending on the experiment. The tube was filled with 10 psi of CO\textsubscript{2} and the experiments lasted for 24 hours. Tellurium needle crystals were formed ~8 cm from the center which correlates to 410 ± 10°C in temperature. The tellurium crystals are only found on the far side of the crucible, opposite of the CO\textsubscript{2} cylinder, thus implying the movement of tellurium as a result of the gas flow. The longest needles found were 1.4 cm in length. Since tellurium is a liquid at Venus lowland temperature, it is likely that the tellurium is vaporizing and then transported to a cooler region where it is deposited before forming crystals. The temperature of crystal formation is approximately the conditions found at 5.5-8 km above the average planetary radius, much higher than the start of the critical altitude on all the mountains on Venus. Though
the altitude is different, these results strongly supports that tellurium is highly volatile and can be transported very quickly at Venus temperatures.

The preferential formation of Bi$_2$Te$_2$S indicates that it will form if bismuth, tellurium, and sulfur are present. Unfortunately, at this time we cannot determine its volatility due to insufficient data. Additionally, its dielectric constant, as well as many other minerals, has yet to be measured. Nevertheless Bi$_2$Te$_2$S is a semiconductor (Wang et al., 2018) like Bi$_2$S$_3$ (Benattou et al., 2017; Lukaszewicz et al., 1999; Yang et al., 2013) and Bi$_2$Te$_3$ (Han et al., 2017; Kim et al., 2013; Nassary et al., 2009), and both have high dielectric constants (Bi$_2$S$_3$: $\varepsilon_\infty = 108$ at 720 K and 30 GHz (Lukaszewicz et al., 1999); Bi$_2$Te$_3$: $\varepsilon_\infty = 80$ at unstated temperature and frequency (Nassary et al., 2009)), thus making it likely that Bi$_2$Te$_2$S also has a high dielectric constant.

Figure 6: Using a vapor transport model Brackett et al. (1995) determined the transportation of 0.01 to >10 μm/yr of moderate to highly volatile phases from the lowlands (740 K) to the highlands (660 K). The y-axis is the ratio of the vapor pressure at the lowland to the vapor pressure at the highland (in bars) and the x-axis is the vapor pressure at the lowland (in bars). We plotted the values obtained from their model runs and the available data from minerals and elements pertaining to this paper to determine their volatility. The combined data can be used to estimate the migration timescale of these mineral/elements from the lowlands to the highlands. Te$_2$ was found to have high volatility, meanwhile Bi$_2$S$_3$, and bismuth have moderate volatility. See text for details.
6.0 Conclusion

The results of our experiments confirm that in the presence of bismuth, tellurium, and sulfur a multitude of minerals such as BiTe, Bi$_2$S$_3$, and Bi$_2$Te$_3$ can form under simulated Venus conditions. Lowland condition facilitates the formation of a larger collection of minerals compared to experiments completed in the highland condition. Among our results, tetradymite (Bi$_2$Te$_2$S) was the most preferential and was found in every experiment. Our results indicate that COS influences the stability of Bi$_2$S$_3$ in the Bi$_2$S$_3$/Bi$_2$Te$_3$ mixture, however further work is needed to ascertain the exact chemical reaction. Overall sulfur loss was common, and so S$_2$, a gas found on Venus, might affect the formation and stability of sulfur bearing minerals such as Bi$_2$S$_3$ or Bi$_2$Te$_2$S.

Since bismuth, tellurium, and sulfur are frequently outgassed on Earth and can be found near fumaroles, we can conclude that a similar situation probably exists on Venus. Nevertheless, in our experiments all the minerals that formed in the highlands are also stable in the lowlands. This stability suggests that they can be present all across Venus and so could not explain the radar brightness of the highlands. However, based on the volatility of our elements and minerals they could be removed and transported from the lowlands into the highlands, thus addressing this conundrum. Some of the formed minerals have unknown dielectric constants, but those that are known have high dielectric constants, and could explain the high radar reflective signal. Though the abundance of bismuth, tellurium, and sulfur in the near surface environment of Venus has not been measured, their presence on Earth, volatility, and ability to form high dielectric minerals in the highlands implies that they are likely on Venus and could contribute to the radar reflective signal.

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8.0 References


Chapter 3

An Experimental Investigation into the Impact of Venusian Temperatures, Pressures, and Gases on Lead and Lead Minerals

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Key Points

- PbS formed when Pb and PbO were exposed to CO\textsubscript{2}/SO\textsubscript{2} and CO\textsubscript{2}/COS at the Venus highland condition (380°C/45 bar)
- Lead carbonates formed when Pb and PbO were exposed to CO\textsubscript{2}, CO\textsubscript{2}/SO\textsubscript{2} and CO\textsubscript{2}/COS at the Venus highland condition
- Sulfates and sulfides formed when Pb and PbO were exposed to CO\textsubscript{2}/SO\textsubscript{2} at the highland condition as a result of sulfur disproportionation

1.0 Abstract

In the investigation into the source of the radar reflective signal lead minerals, particularly PbS, have been a prime candidate due to their dielectric constant and volatility. However, their formation and stability under Venus conditions have not been experimentally investigated. Our objective was to study the effects of CO\textsubscript{2}, CO\textsubscript{2}/SO\textsubscript{2}, and CO\textsubscript{2}/COS on Pb, PbS, PbSO\textsubscript{4}, and PbO under Venus temperatures (380-460°C) and pressures (45-95 bar). Samples were exposed to these conditions for ≥ 24 hours and then analyzed using X-Ray Diffraction and X-ray Photoelectron Spectroscopy. This investigation revealed that PbS can form in the highland condition when Pb and PbO are exposed to CO\textsubscript{2}/SO\textsubscript{2} and CO\textsubscript{2}/COS. Experiments with CO\textsubscript{2}/SO\textsubscript{2} and CO\textsubscript{2}/COS were not completed in the lowland environment so the formation of PbS at these conditions was not determined. The formation of lead carbonates was evident in the highland condition but is more prevalent when PbO is present. Sulfate was detected when Pb and PbO
were exposed to CO\textsubscript{2}/SO\textsubscript{2}. This project is the first comprehensive study on the effects of the venusian environment on lead minerals.

2.0 Plain Language Summary

Several of Venus’ mountain ranges are very reflective when observed in radar, however the cause has long been unidentified. Lead minerals, particularly galena (PbS), have been prime candidates because of their high dielectric constants which could explain the signal. However, researchers have yet to experimentally study how these minerals interact with the atmosphere of Venus and if they are stable. Thus, the goal was to study the stability of various lead and lead minerals under Venus temperatures (380-460°C), pressures (45-95 bar), and gases on Venus: CO\textsubscript{2} by itself or mixed with SO\textsubscript{2} or COS. Our samples were tested for 24 h and consisted of pure lead and common lead minerals: galena, anglesite (PbSO\textsubscript{4}), and lead oxide (PbO). Our results show that galena formed when lead and lead oxide were tested in the cooler conditions found on the mountains (380°C/45 bar) in CO\textsubscript{2}/SO\textsubscript{2} and in CO\textsubscript{2}/COS. We also discovered that lead and lead oxide formed lead carbonates in the highland condition in all tested gases. Lead sulfate was found when lead and lead oxide were tested in CO\textsubscript{2}/SO\textsubscript{2} at 380°C/45 bar. A small percent of anglesite was produced in our galena sample, but the percentage after a 24 h and a 75 h experiment were the same. Our experiments can be used to better understand surface-atmosphere interactions on Venus and give useful insight into the source of the radar reflective signal.

3.0 Introduction

There is an unexpectedly high radar reflective signal in the highlands of Venus. This peculiar phenomenon was first observed by Earth based telescopes, such as Arecibo (λ=12.6 cm), before it was detected by orbiters such as Pioneer Venus (λ=17 cm), and Magellan (λ=12.6 cm) (Arvidson et al., 1991; Campbell et al., 1976; Ford & Pettengill, 1983; Garvin et al., 1985). The change in reflectivity from the lowlands of Venus to its highlands is so drastic that the difference between the two is approximately 0.9 (Pettengill et al., 1996). The radar bright signal
manifests at different altitudes depending on the mountain range and can begin at an altitude as low as 2.5 km or as high as 4.75 km (Arvidson et al., 1994; Klose et al., 1992). Researchers have since used experiments and equilibrium chemistry calculations to explain this phenomenon.

It has been hypothesized that the strange radar bright signal could originate from a mineral (or minerals) with a high dielectric constant (Brackett et al., 1995; Klose et al., 1992; Kohler et al., 2012; Pettengill et al., 1991, 1996; Schaefer and Fegley, 2004). Several minerals and elements have been suggested as the source including pyrite (FeS\(_2\)), tellurium (Te), bismuthinite (Bi\(_2\)S\(_3\)), coloradoite (HgTe), and chlorapatite (Ca\(_5\)(PO\(_4\))\(_3\)Cl), among many others (Brackett et al., 1995; Gilmore et al., 2017; Klose et al., 1992; Kohler et al., 2013; Pettengill et al., 1982, 1996; Schaefer & Fegley, 2004; Treiman et al., 2016). However, without direct analysis of the material from Venus, researchers can only hypothesize on its composition through experiments and thermodynamic modeling. This has resulted in numerous debates on the source, such as the debate on pyrite stability which some argue that Venus is much too oxidizing for its presence (Fegley et al., 1992, 1995; Hong & Fegley, 1997; Radoman-Shaw, 2019; von Zahn et al., 1983), while others state that Venus conditions are conducive for its stability (Klose et al., 1992; Wood and Brett, 1997). Other recent Venus simulation experiments have shown that pyrite may form and may be stable, which implies that it may exist on Venus (Berger et al., 2019; Kohler et al., 2015).

Tellurium was proposed by Pettengill (1996) due to its high conductivity, however chemical equilibrium calculations under Venus conditions found that tellurium condenses at 46.6 km in altitude (Schaefer and Fegley, 2004), well above the altitude at which the reflectivity signal is observed on Venus. Furthermore, experiments completed by Kohler (2015) exhibits that it is unstable and readily oxidizes into TeO\(_2\).

Bismuthinite is a promising mineral; Schaefer and Fegley (2004)’s computations revealed that bismuthinite will condense at the altitude where the reflectivity changes (~1.6-2.6 km).
However, Venus simulation experiments have revealed that it is stable at both the lowland and highland conditions on Venus (Kohler, 2015).

Experiments completed on the stability of coloradoite have found that it demonstrates better stability in the highland over the lowland conditions, but further experiments for longer periods of time and incorporating more Venus gases are needed to confirm its stability in the highlands (Kohler, 2015).

The radar reflectivity pattern varies based on the highland region, e.g. in some regions the increase in reflectivity is more abrupt than in others, and some locations exhibit a sudden decrease in reflectivity at even higher elevation. This indicates that there may be more than one source to explain the radar anomaly (Brossier et al., 2019; Gilmore et al., 2017; Treiman et al., 2016). Ferroelectric minerals, such as chlorapatite, could explain the increase in radar reflectivity and the abrupt decrease at higher altitudes seen on some regions such as Ovda Regio (Shepard et al., 1994; Treiman et al., 2016), nevertheless experiments on chlorapatite formation at Venus conditions have not been completed at this time. The ongoing debate on the source of the radar anomaly emphasizes the need for further experiments on the formation and stability of minerals under Venus conditions.

The stability of lead and lead minerals under Venus conditions have not been studied experimentally and warranted further investigation for several reasons. First, several lead-bearing minerals have a high dielectric constant (Young and Frederikse et al., 1973), and can be released via eruption plumes and fumaroles (Chugaev et al., 2007; Toutain et al., 1990). Venus was once volcanically active, this implies that these processes were once common, and may still be present today (Shalygin et al., 2015). Presently, there is no evidence of lead on Venus; it was determined that the upper limit of Pb at Vega 2’s landing site was <0.3 mass % (Surkov et al., 1986). Unfortunately, no other lander has been able to accurately measure the abundance of lead. Since lead is an abundant mineral on Earth (~12.5-17 ppm in the continental crust and ~0.8 ppm in the
oceanic crust (Mclennan et al., 2001; Schaefer and Fegley, 2004; Wedepohl, 1995)), it raises the possibility of its presence on Venus.

The possibility of lead on Venus was first discussed by Khodakovsky (1982), and later by Fegley et al. (1992), then by Brackett et al. (1995), and Schaefer and Fegley (2004). Khodakovsky (1982) calculated that Pb, PbCl₂, PbCl, and PbO should be volatilized on Venus and that PbS (galena) may be stable at the surface. Fegley et al. (1992) considered the possibility of PbCO₃ (cerussite) on Venus due to its relatively high dielectric constant (~20 at 100-1000 MHz). They calculated its stability via two equations:

\[
\text{CO}_2 + \text{PbSiO}_3 = \text{PbCO}_3 + \text{SiO}_2 \quad [1]
\]
\[
\text{PbSO}_4 + \text{CO} = \text{PbCO}_3 + \text{SO}_2 \quad [2]
\]

but determined that it was unstable across the entire surface. Brackett et al. (1995) studied the migration of lead minerals (PbS, PbF₂, PbCl₂) from the lowlands to the highlands over time. They found that PbS in particular is moderately volatile and can move from the surface to 3.5 km in elevation in 100,000 years. Schaefer and Fegley (2004) were motivated by Brackett et al. (1995)’s theory and studied the condensation of lead minerals onto the highlands through equilibria calculations. Schaefer and Fegley (2004) discovered that PbS condenses near the critical altitude (the altitude where the reflectivity changes) if the Pb abundance is similar to that found in basaltic meteorites (eucrites), ~86 ppb. PbS has a high dielectric constant (205 at 1 MHz (Olhoef, 1979) and between 165-235 in the infrared (Young & Frederikse, 1973)); high enough to explain the source (Pettengill et al., 1992; 1997). Both factors make it a good candidate for the source of the radar reflective signal.

While lead minerals have been postulated to exist on Venus, studies on their possible formation and stability in Venusian conditions are scarce. Further, no experiments have been designed or conducted in this area. This study aimed to remedy this issue by testing lead and various lead minerals at two different Venus temperatures/pressures in various carbon, oxygen, and sulfur gases. These experiments will inform us on the numerous interactions that could occur
due to the different gases present on Venus. For example, these minerals may act as a small sink for these gases and studying their stability could give insight into the complexity of the gas cycles on Venus. It will also illuminate the effects that pressure and temperature may play on these interactions. Lastly, given that PbS has a high dielectric constant, monitoring its formation and/or stability will inform us on its prospect of being the source of the high radar reflective signal in the highlands.

4.0 Methods

To complete this study powdered lead (99%; CAS:7439-92-1) and anglesite (PbSO₄) (reagent grade; CAS:7446-14-2) were purchased from Alfa Aesar. Galena (PbS) (CAS:470178-590) was purchased from Ward’s as large cubic chunks. Lead oxide (PbO) (99%; CAS:1317-36-8) was purchased from Acros Organics and is <10 microns in diameter. All other samples were sieved to 125 μm to ensure a similar surface area. PbS was the only mineral that required to be ground first in a ring mill before sieving. The galena was mined from Colorado and Mexico.

Lead powder was selected to directly observe the reactions that can occur between lead and the various carbon, oxygen, and sulfur gases on Venus. PbS and PbSO₄ are one of the most common lead minerals on Earth, and PbS has been postulated as a possible source of the radar reflective signal found on the highlands. PbSO₄ is formed from the oxidation of PbS, and since many of our PbS samples contained trace amounts of PbSO₄, by testing it directly we can reduce any error and better understand our PbS results. As a result of preliminary lead data, PbO was added to the list to better explain our results and interactions that are occurring in the simulated Venus environment.

One gram of each of the samples were tested in one of two different environmental conditions and one of three different gases. The two different environmental conditions represent the conditions found at the average planetary radius (460°C/95 bar) and the conditions found 11 km in elevation from the planetary radius (380°C/45 bar). The conditions were chosen to assess the effect of temperature and pressure on the minerals. Additionally, our selection will also inform
us on their stability in the cooler highlands where the radar anomaly is located. The three different gas combinations consist of 99.999% CO$_2$, 100 ppm SO$_2$ in CO$_2$, and 100 ppm COS in CO$_2$. The purity of the 99.999% CO$_2$ cylinders were measured by AirGas and were tested for O$_2$+Ar+CO (<1.0 ppm), THC (<1.0 ppm), H$_2$O (<3.0 ppm), and N$_2$ (<5.0 ppm). The CO$_2$ cylinders used for the mixed gas was 99.99% pure and was tested for H$_2$O (<10 ppm), hydrocarbons (<10 ppm), N$_2$ (<70 ppm), and O$_2$ (<20 ppm). The COS was 97% pure and was tested for CS$_2$ (<300 ppm), CO$_2$ (<1.7 ppm), N$_2$ (<0.2 ppm), and H$_2$S (<0.8 ppm). The SO$_2$ was 99.98% pure. The 100 ppm was chosen because it is the lowest limit as set by the gas cylinder manufacturer. The special anti-corrosive regulators that were used for the mixed gases do not allow for a high enough output pressure to reach the pressure found in the lowlands, therefore the mixed gases were only used in highland condition experiments.

The experiments were completed in the Cassiopeia Chamber (available at the University of Arkansas W.M. Keck Laboratory for Space and Planetary Simulations), a 500 mL stainless steel 316 vessel purchased from Parr Instruments which can simulate the temperatures and pressures on Venus. The vessel contains an internal thermowell where the thermocouple resides, and the chamber is heated from the exterior via a heating sleeve. The temperature is controlled by a temperature-pressure controller (purchased from Parr Instruments) which is connected to a computer and records the temperature every second. The pressure is measured by an interior pressure gauge and the data is also monitored by the temperature-pressure controller and recorded every second. The chamber is sealed with a graphite gasket.

The samples were placed in a 10 mL porcelain crucible purchased from VWR with a height of 26 mm and a diameter of 31 mm. To begin the experiment, one gram of the sample was placed in the chamber and sealed before all the gas was evacuated using a vacuum pump (0.035 bar). The sample was then flush with one of the three gases at 60 psi for several minutes before it was filled to the desired initial pressure. The heating sleeve around the chamber was then set to the final temperature; since the gas is assumed to behave as an ideal gas the increase in temperature
results in an increase in pressure as dictated by Gay-Lussac's law. The average initial
temperature was 22.5°C and initial pressure as indicated by the controller was -13 psi (0.035 bar
according to the vacuum pump). The average final temperature for the highland condition
experiments was 380.64°C and lowland was 460.0°C, with an average standard deviation of 1°C.
The average pressure over the course of the experiments for the highland condition was 42.84
bar and the lowland was 98.71 bar, with a standard deviation of 4.5 bar.

Each experiment lasted 24 hours before the chamber was vented hot and then placed in
vacuum (0.035 bar). The interior of the chamber was then flushed with 60 psi of N₂ for several
minutes before it was sealed and filled to 20 bar of N₂. The sample was then cooled to room
temperature before removal. This process took around 5 hours. Several samples were tested for
longer periods of time. These included a 100 hr Pb highland CO₂ experiment, a 100 hr PbO
highland CO₂ experiment, a 75 hr PbS lowland CO₂ experiment, and a 100 hr PbSO₄ highland
CO₂/COS experiment. After removal, the samples were analyzed at ambient conditions using X-
Ray Diffraction with a PANalytical's Materials Research Diffractometer (MRD) to determine any
mineralogical changes. We used a CuKα source and the 2theta scan range was between 15-85
degrees, the voltage was 45 kV, and the counting time was 0.8 sec. X’Pert Highscore was used
to determine the phases present within the sample and it was also used to calculate the
abundances of each phase. In some instances, the samples were also analyzed using X-ray
Photoelectron Spectroscopy (XPS) with the VersaProbe from Physical Electronics (PHI) in N₂ gas
to observe any changes to their chemical composition. The X-ray source is a monochromated k-
alpha ray from Al at 1486 eV. We use a pass energy of 117.4 eV for surveys and 58.7 eV or below
for high resolution scans. The samples were exposed to a 2kV/2μA Ar+ beam for 30 seconds to
1 minute prior to analysis in order to remove atmospheric contamination. XPS can analyze the
upper few nanometers of a sample meanwhile XRD determines the bulk composition. The NIST
XPS database, as well as numerous sources of literature, were used to characterize the peaks in
our XPS data.
5.0 Results

Lead oxidizes easily, and according to XRD analysis the lead we purchased for these experiments oxidized over the course of our project from 10% litharge (PbO) at the start, to 25% litharge/massicot (PbO) by the last set of experiments. Due to this result we incorporated PbO powder from VWR into this research project to determine if any of our results were due to lead, or due to the 10-25% PbO found in the lead sample. The PbO we purchased was a mixture of massicot (91%) and litharge (9%). PbS also oxidizes quickly, however we purchased multiple blocks so when the product of oxidized PbS, PbSO$_4$, was detected by the XRD, we ground a new sample of PbS. Using XRD analysis our purchased PbSO$_4$ was found to be 100% pure.

3.1 Experiments Completed in 99.999% CO$_2$

Figure 1: PbO a) before and b) after it was heated to the highland conditions (380°C/45 bar) in CO$_2$. The white arrows indicate the color change in the sample. After the experiment the interior became yellow while the exterior remained orange.

All results for experiments completed in CO$_2$ are displayed in Table 1. When lead was heated to the lowland condition smelted lead beads of varying diameters were visible above the lead “powder”. This “powder” appeared unchanged, but upon closer examination was observed to be fused together. However, when pressed between our fingers it was malleable enough to break the sample apart. The lead beads were fused to the “powder” and a metal rod was needed to pry them apart. Lead tested in CO$_2$ at lowland and highland conditions had near identical
results; both samples contained a combination of Pb and PbO (litharge and massicot). Pb was also exposed in the highland conditions for 100 hours and had the same products as when heated for 24 hours. When tested in the lowlands the sample contained more PbO by ~10%. Our Pb sample in highland condition (24 hr) was also analyzed with the XPS which detected peaks of O1s, C1s, and Pb4f indicating the presence of lead, lead oxide, carbonate, and a compound with a C-C bond.

The heating of PbO in the lowland condition resulted in more litharge than massicott. Most notably the sample underwent a change in color, from orange to orange in the exterior and yellow in the interior (Fig. 1). The color change marks a change in the crystal structure. When it was heated to the highland condition the sample contained litharge and massicot, as well as a lead oxide.

![XRD results of PbO tested in CO₂ in the lowlands (top spectra) and highlands (middle spectra) as compared to the control (bottom spectra). X marks Pb₃O₂CO₃ peaks, L is for litharge, and M is for massicot. Pb₃O₂CO₃ were not detected in the sample displayed here.](image)

Figure 2: XRD results of PbO tested in CO₂ in the lowlands (top spectra) and highlands (middle spectra) as compared to the control (bottom spectra). X marks Pb₃O₂CO₃ peaks, L is for litharge, and M is for massicot. Pb₃O₂CO₃ were not detected in the sample displayed here.
carbonate, either shannonite (Pb$_2$OCO$_3$) or Pb$_3$O$_2$CO$_3$ (Fig. 2). When PbO was heated in the highland condition for 100 hours litharge, massicot, and Pb$_3$O$_2$CO$_3$ were present.

The abundance of PbSO$_4$ increased when the PbS was exposed to Venus conditions. Most of the experiments resulted in an increase of 13-30%, with no correlation with temperature and gas. We also tested PbS for 75 hours in the lowland condition for verification on its stability and only a 10% increase in PbSO$_4$ was observed.

PbSO$_4$ was observed to be unaffected by Venusian temperature and pressure and remained stable in all experiments. When it was examined using the XPS evidence for PbSO$_4$, C-C, and C-O was found.

Table 1: XRD results for all experiments completed in CO$_2$. The (L) stands for litharge (tetragonal) and the (M) stands for massicot (orthorhombic).

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<th>Temperature/Pressure</th>
<th>Length of time (hr)</th>
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<td>460°C/95 bar</td>
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5.2 Experiments Completed in CO$_2$/SO$_2$ and CO$_2$/COS

XRD analysis of Pb tested in CO$_2$/SO$_2$ revealed lead, litharge, massicot, and PbOPbSO$_4$. Meanwhile XPS confirmed a lead oxide and a sulfate, but also revealed a sulfide, a C-O bond, and a C-C bond. When Pb was heated in CO$_2$/COS the collected data by XRD uncovered the presence of lead, litharge, massicot and PbS. The XPS verified a lead oxide and a sulfide, but also detected a C-C bond and a carbonate. All results are summarized in Table 2 and 3.

![Image of PbO before and after heating in CO$_2$/SO$_2$ and CO$_2$/COS mixtures]

Figure 3: PbO a) before and after it was heated to the highland conditions (380°C/45 bar) in b-c) CO$_2$/COS and in d) CO$_2$/SO$_2$. The arrows indicate the change in color to the sample. The top of the sample became grey, the interior became yellow, and the exterior along the bottom of the porcelain bowl remained orange. c) displays the formation of a silver residue that was present after our sample was heated in CO$_2$/COS.

PbO was observed to undergo a color change when heated in both the CO$_2$/SO$_2$ and the CO$_2$/COS mixtures. The samples all exhibited a grey upper layer while the interior of the samples displayed a similar pattern to when PbO was heated in pure CO$_2$. Specifically, the samples were yellow on the inside and were orange along the bottom of the sample (Fig. 3). XRD analysis of
PbO tested in CO$_2$/SO$_2$ and in CO$_2$/COS indicated the same composition; both samples contained litharge, massicot, PbS, and Pb$_3$O$_2$CO$_3$. Unfortunately, due to the absence of the reference intensity ratio (RIR) we could not determine if the two experiments resulted in different abundances. These samples were also analyzed with the XPS which uncovered a carbonate, C-C bonds, a sulfide, and a lead oxide in both samples. Sulfate was found in the sample tested in CO$_2$/SO$_2$, and C-O and a sulfite was found in the sample tested in CO$_2$/COS. These results can be observed in Table 2 and 3.

Both the CO$_2$/SO$_2$ and the CO$_2$/COS mixed gases had no apparent effect on PbS. Similar to the experiments completed in pure CO$_2$, PbSO$_4$ was found in the PbS sample, however the change in abundance is the same as when it was heated in pure CO$_2$.

When the PbSO$_4$ sample was heated in both mixed gases, the color of the sample darkened from a white powder to a light grey. Experiments completed in the CO$_2$/COS resulted in a darker grey than when tested in the CO$_2$/SO$_2$. XRD results detected no change in the mineralogy of the sample and XPS detected the presence of PbSO$_4$, compounds with C-O and C-C bonds, and an unknown peak. PbSO$_4$ was also heated in CO$_2$/COS for 100 hours and the sample darkened once again, but the XRD only detected the presence of PbSO$_4$. 
Figure 4: XPS results (O1s and C1s) for Pb when it was heated in the highland conditions in a) CO2/COS and b) CO2/SO2. In a) evidence for a lead oxide, carbonate, and C-C bond are present. In b) evidence for a C-C bond, a C-O bond, and a lead oxide are observed.
Figure 4 (continued)
Figure 5: XPS results (O1s and C1s) for PbO when it was heated in the highland conditions in a) CO2/COS and b) CO2/SO2. In a) evidence for a lead oxide, carbonate, C-O bond, and C-C bond are present. In b) evidence for a C-C bond, carbonate, and a lead oxide are observed.
Figure 5 (continued)
Table 2: XPS peaks for Pb, PbO, and PbSO$_4$ heated to the highland condition (380°C/45 bar) in the three tested gas mixtures.

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<th>C1s (eV)</th>
<th>Pb4f (eV)</th>
<th>S2s (eV)</th>
<th>S2p (eV)</th>
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Table 3: XRD and XPS results for Pb, PbO, and PbSO$_4$ heated to the highland condition (380°C/45 bar) in the three tested gas mixtures.

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<td>PbSO₄</td>
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<td>sulfate</td>
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6.0 Discussion

6.1 Experiments Completed in 99.999% CO₂

6.1.1 PbS

After exposing PbS to Venus conditions a larger concentration of PbSO₄ was detected in the sample. Since our cylinder of gas has been rated to have < 1 ppm of O₂, the likely culprit is CO₂. The ΔG of a direct reaction between PbS and CO₂ to produce PbSO₄ was calculated, however a suitable carbon compound byproduct to produce a negative ΔG could not be ascertained. For example, the ΔG for a reaction producing CO and a reaction producing C were calculated, but both resulted in a positive ΔG (the former: ΔG=312.9±11.6 kJ/mol; the latter:
ΔG=72.5^{±1.6}_{-1.1} \text{ kJ/mol; data found in supplementary materials). Thus it is uncertain if this reaction is a multi-step process, or if the supercritical nature of the gases affects the thermodynamic values to make these reactions more favorable.}

**6.1.2 Pb**

Analysis of our XRD data revealed that lead is oxidized in both the lowland and highland conditions, but only enough to increase PbO by a few percent. The greatest increase in abundance, 10%, occurred after it was tested in the lowland experiment. Litharge and massicot were present in both the highland and lowland condition experiments. According to literature, massicot is the high temperature and pressure version of PbO (Risold et al., 1998; White, 1961), and the transformation temperature between litharge and massicot is found between 763-873 K at ambient pressure (Risold et al., 1998). Our maximum temperature is 733 K thus it is likely that pressure plays a part in decreasing the conversion temperature. The formation of PbO is likely a result of an interaction between Pb(l) and CO_2, however similar to the issue in the previous section, a reasonable carbon byproduct cannot be verified, thus we cannot confirm the chemical reaction taking place in the chamber.

Analysis completed by the XPS confirmed the existence of a carbonate in the sample. The O1s peak located at 531.27 eV is a good marker for PbO as well as PbCO_3 (Buckley and Woods, 1984; Laajalehto et al., 1993; Zingg and Hercules, 1978). Additional strong evidence for the presence of PbCO_3 appears in the C1s peak located at 288.85 eV (Buckley and Woods, 1984; Laajalehto et al., 1993). The XPS analyzes the upper few nanometers of a sample, and since it was not detected by XRD, the carbonate present in our sample is likely sparse. The formation of PbCO_3 is likely from the interaction between CO_2 and PbO, which aligns with our PbO results (to be discussed in more detail in the following section) and the results of Laajalehto et al. (1993) and Kim et al. (1994). Thus we believe that any appearance of carbonate in this experiment results from either the PbO contamination at the start of the experiments or the PbO that formed during
the experiment, or both. This hypothesis would also explain the low abundance of carbonate in the sample.

The XPS also detected a peak located at 285.52 eV, a strong indicator for the presence of a compound with a C-C bond (Bachman and Vasile, 1989; Titantah and Lamoen, 2006). As mentioned previously, the experiments completed in the chamber often resulted in a thin, dark, soot-like powder coating the inner walls of the chamber. Though direct analysis of the composition has not been completed due to its low abundance, it may be graphite, which aligns with the XPS result. Experiments on various materials completed in the Venus chamber located at NASA Glenn has also confirmed the existence of adventitious carbon via XPS (Lukco et al., 2018). A word of caution, all samples exposed to Earth’s atmosphere, even for short periods of time, can result in adventitious carbon, which peaks at 284.7 eV ± 1 or more; a result of hydrocarbon contamination (Laajalehto et al., 1993; Van der Heide, 2012). In this case we argue that contamination may play a role in our peak, but since the experiments were completed in CO₂, and we formed a black powder during the experiments, this peak may also be due to graphite.

The only unknown peak in this XPS spectra is the C1s peak at 283.43 eV. Typically, this peak represents a metal carbide, and has been seen in various carbides such as WC (Luthin & Linsmeier, 2000), W₂C (Luthin & Linsmeier, 2000), Ni₃C (Wiltner & Linsmeier, 2004), and Fe₃C (Wiltner & Linsmeier, 2004). We could only uncover two papers that stated that the peak located at ~283 eV is related to graphite (López et al., 2003; Titantah & Lamoen, 2006). We remain skeptical of the existence of a lead carbide since such a compound has yet to be confirmed. Furthermore, if it is a lead carbide it is not understood why this peak is only present in this and one other lead experiment, and not in the other lead and PbO samples completed in the mixed gases. The peak was also found in the PbSO₄ control sample, and thus in that case is not an indicator of a lead carbide.

6.1.3 PbO
The heating of PbO in the lowland condition resulted in a drastic decrease in massicot, from 91% to 23%. As mentioned previously, litharge is the low temperature and pressure version of PbO, therefore our results indicate that the conversion to litharge occurs due to the cooling of the chamber to room temperature. The continued existence of massicot is because the reaction rate from massicot to litharge is slow, and massicot has been found to exist for several days at 300 K (Risold et al., 1998).

When PbO was tested in the highland conditions the sample was a mixture of litharge and massicot and at least one oxy-carbonate (shannonite (Pb2OCO3), and/or Pb3O2CO3 (Fig. 2)). The oxy-carbonate minerals have been identified as products of the thermal decomposition of PbCO3 (Criado et al., 1987; Peretti, 1957; San Andres et al., 2008; Yamaguchi et al., 1980; Živković, 1979). Though several of those experiments were completed in varying pressures of CO2, none of them investigated pressures as high as in this project (Ball and Casson, 1983; Criado et al., 1987; Yamaguchi et al., 1980). Nonetheless our results are in good agreement with previous studies with only minor differences on the stability regimes of these minerals.

Due to the temperature sensitive nature of carbonates (Criado et al., 1987; Grisafe and White, 1964; Yamaguchi et al., 1980) there was some uncertainty on if the formation of these minerals were due to a reaction between CO2 and PbO, or perhaps from the creation of PbCO3 upon heating of the chamber before thermally decomposing once we reached our desired temperature/pressure and the experiment officially started. To confirm our results we completed an experiment that involved heating PbO to the highland condition and immediately concluding the experiment once it reached the desired temperature and pressure. We discovered that the sample did not produce any carbonates. This verified that the three minerals mentioned in the previous paragraph forms in the simulated highland condition. None of these minerals were observed in the lowland experiments which implies that they are only stable at cooler temperature/pressure. Based on our experiments and our ΔG calculation (supplementary...
materials) we hypothesize that the formation of Pb$_2$OCO$_3$ results from a direct interaction between PbO and CO$_2$:

$$[3] \ 2\text{PbO} + \text{CO}_2 = \text{Pb}_2\text{OCO}_3$$

Due to the absence of thermodynamic data on Pb$_3$O$_2$CO$_3$ we cannot confirm its formation mechanism, but it likely is a direct reaction between PbO and CO$_2$ via:

$$[4] \ 3\text{PbO} + \text{CO}_2 = \text{Pb}_3\text{O}_2\text{CO}_3$$

Our results attained from the Pb and PbO experiments indicate that the formation of PbO is first required before the formation of carbonates. Without the initial oxygen bonded to lead, the CO$_2$ cannot attach to create carbonates.

6.1.4 PbSO$_4$

PbSO$_4$ was examined with the XRD and XPS both before and after it was exposed to the highland condition in CO$_2$. The XRD spectra taken from before and after the experiments were identical. However, the XPS detected subtle changes in the C1s, S2p and O1s peaks. Both spectra (before and after) have two C1s peaks, the first of these two peaks have very similar binding energies, 283.5 eV (before) and 283.6 eV (after). The second C1s peaks are separated by only 1.62 eV, where the PbSO$_4$ heated in CO$_2$ had the higher binding energy. The second peak in the control is due to a C-C bond, however the second peak in the heated sample could be either due to a C-C or a C-O bond; the peak is located between these two binding energies making it difficult to ascertain its exact origin (Halim et al., 2016; Laajalehto et al., 1993; Qin and Gao, 1990). Of particular interest is a new O1s peak that is only present after a highland experiment and is located at 532.4 eV. This binding energy is close to the literature value for PbSO$_4$: 531.7 eV (Zingg and Hercules, 1978), 531.8 eV (O’Malley, 2010), and 532 eV (van der Heide, 2012). However, we did not observe this peak in our control spectra. This peak signifies the formation of some compound as a result of the experiment and may be related to a C-O bond, or perhaps some other oxygen bearing compound. The disappearance of the S2p peak (160.38
eV) that was present in the sample before the experiment was also observed, however it is unclear what this signifies for the sample.

6.2 Experiments Completed in CO$_2$/SO$_2$ and CO$_2$/COS

6.2.1 Pb

When Pb was heated in CO$_2$/COS the XRD detected 57.4% Pb, 36.7% PbO (an increase of 11.4% from the control) and 5.9% PbS. The XPS results are in good agreement with the data collected by the XRD. The O1s peak located at 529.5 eV is a strong indicator for PbO (Buckley & Woods, 1984), meanwhile the 531.27 eV peak is a good marker for PbO and PbCO$_3$ (Buckley and Woods, 1984; Laajalehto et al., 1993; Zingg and Hercules, 1978) (Fig. 4a). A C1s peak located at 288.85 eV was also detected signifying the presence of a carbonate (Buckley and Woods, 1984; Laajalehto et al., 1993) (Fig. 4a). Strong evidence for sulfide is observed via the S2s peak located at 224 eV and the S2p peak at 160.5 eV. The Pb4f peak located at 137.67 eV indicates both PbS and PbO and the peak at 142.53 eV also signifies the existence of PbS. We also observed a C1s peak located at 284.81 eV evidencing adventitious carbon. The XPS spectra also detected a C1s peak at 283.25 eV, similar to the 283.43 eV peak found in Pb heated CO$_2$. As mentioned previously, we are skeptical of the existence of a carbide and believe that this peak is also due to carbon.

XRD revealed the existence of PbO (litharge:16%; massicot:6%) as well as PbOPbSO$_4$ (32%) mixed into the Pb (46%) when Pb was heated in CO$_2$/SO$_2$. The data collected by the XPS displayed similar results. The existence of a sulfate was supported by the Pb4f peak at 139.74 eV, S2s peak at 232.5 eV, and S2p peak at 168.26 eV. Literature review has indicated that these peaks represent PbSO$_4$, however since XRD detected PbOPbSO$_4$ and not PbSO$_4$, these peaks are likely due to the former as opposed to the latter, though a small amount of PbSO$_4$ in the sample cannot be ruled out. There was also an unknown O1s peak at 532.7 eV, close to where PbSO$_4$ is known to peak, 532 eV (Van der Heide, 2012), but in this case may be attributed to PbOPbSO$_4$ (Fig. 4b). Evidence of sulfide was seen from the Pb4f peak at 142.98 eV and the S2p
peak at 161.5 eV, however a S2s peak at 224 eV was not observed. As mentioned previously, the 284.62 eV peak is likely graphite, however a new peak at 286.18 eV was also observed (Fig. 4b). This peak is typical of a C-O bond and could indicate CO or CO2 adsorption on the surface (Halim et al., 2016; Laajalehto et al., 1993; Qin and Gao, 1990). Other researchers have stated that it could be related to graphite (Bachman and Vasile, 1989). Since our experiments were completed in CO2 either option is plausible.

6.2.2 PbO

XRD analysis of PbO completed in CO2/COS indicate PbO, PbS, and Pb3O2CO3. Evidence of PbO can be seen by the O1s peak at 528.51 eV (Fig. 5a). Meanwhile the C1s peak at 289.08 eV indicates the presence of a carbonate (Fig. 5a) and evidence for sulfide is observed by both Pb4f peaks (138.39 eV and 143.25 eV) and the S2s peak at 223 eV and the S2p peak at 161 eV. The formation of PbS also explains the dark grey compound that formed at the top of the sample. It is currently unknown if all the PbS was only present at the top of the sample, or if PbS formed throughout the sample with a greater abundance found near the surface of the sample. We also have evidence of graphite (C-C bond at 284.83 eV), and more C-O adsorption (286.39 eV). Unlike in previous spectra, we also obtained a S2s peaks at 231 eV and a S2p peak at 166.8 eV; both these peaks could indicate the presence of sulfite (Cant et al., 2015; Choi et al., 2014; Zingg and Hercules, 1978). No evidence of PbSO3 was found via XRD, but some sulfite adsorbed to the surface of our samples cannot be ruled out. A formation mechanism will be discussed in the next section.

XRD analysis of PbO in CO2/CO2 revealed the same minerals as when it was tested in CO2/COS. Our XPS results confirm the presence of a carbonate (C1s=288.89 eV, O1s=531.08 eV) as well as sulfide (Pb4f=137.75 eV, Pb4f=142.61 eV, S2p=160.5 eV) and PbO (O1s=529.02 eV, O1s=531.08 eV) (Fig. 5b). This sample also developed a dark grey compound towards the top of the sample which could be explained by the presence of PbS. However unlike in the XRD we have some evidence of a sulfate via the S2s peak at 232 eV and the S2p peak at 167.75 eV.
6.2.3 Comparison Between the Mixed Gas Results

Our results for the Pb and PbO experiments completed in the mixed gases (CO₂/COS and CO₂/SO₂) share many similarities. Overall evidence of PbS, PbO, and carbon was found in all samples. Sulfate was only present in CO₂/SO₂ experiments, evidence of a C-O compound was found in two unrelated experiments, carbonate was found in all but one experiment, and sulfite was only found in one experiment.

The detection of carbon, carbonates, and a C-O molecule in our Pb and PbO samples attests to Pb/PbO's interaction with CO₂. Both samples also interact with COS, which is evident by the formation of sulfur minerals, however the exact reaction, and the fate of the final carbon and oxygen from COS cannot be determined at this time. When Pb and PbO were exposed to CO₂/COS, PbS formed with the addition of a sulfite in the latter scenario, thus we can hypothesize that a carbon compound, such as CO, is released. We see evidence of a C-O bond in several of our results, however the source of this bond, whether from CO₂ or some other compound, cannot be concluded from our results.

Both COS and SO₂ are observed to interact with Pb and PbO to form sulfur minerals. All analyzed samples had produced enough PbS to be detected by XRD except for Pb in the CO₂/SO₂ sample whose major sulfur bearing mineral was PbOPbSO₄ and only had enough PbS to be detected with the XPS. PbS can form directly from the interaction between Pb/PbO and COS and release CO or CO₂:

[8] PbO+COS=PbS+CO₂

[9] Pb(l)+COS=PbS+CO

The exposure of both the Pb sample and the PbO sample to CO₂/SO₂ resulted in the formation of a sulfide and sulfate. The evidence for a sulfate was only found in Pb and PbO samples exposed to CO₂/SO₂; it was not present when exposed to CO₂/COS. When analyzed via XRD the Pb sample was found to have PbOPbSO₄ and the XPS confirmed the presence of some sulfate. Thus, the reaction likely proceeds as follows:
[10] $7\text{Pb} + 5\text{SO}_2 = 3\text{PbS} + 2(\text{PbOPbSO}_4)$

This reaction is an example of sulfur disproportionation; a process known to occur in reactions involving $\text{SO}_2$ (Kubas, 1994; Mavrogenes & Blundy, 2017). Here, $\text{SO}_2$ is both oxidized and reduced, forming both $\text{PbS}$ and $\text{PbOPbSO}_4$. Sulfur disproportionation was also observed in experiments simulating surface-atmosphere interactions on Io (Burnett et al., 1997). In their experiments $\text{SO}_2$ was reacted with silicate glasses at 850°C; the result was both oxidized and reduced sulfur in the form of $\text{Na}_2\text{SO}_4$ and $\text{Cu}_2\text{S}$.

However, there is one issue with this equation, which is, as stated previously, $\text{PbS}$ was not detected by the XRD, but the XPS identified a sulfide. Therefore, if this is the reaction pathway the cause behind the larger abundance of $\text{PbOPbSO}_4$ in the sample compared to $\text{PbS}$ is uncertain.

Another possible reaction that could be occurring during this ($\text{Pb in CO}_2/\text{SO}_2$) experiment is:

[11] $3\text{Pb} + \text{SO}_2 = \text{PbS} + 2\text{PbO}$

A similar reaction involving copper instead of lead was observed by Burnett et al (1997). However, based on our experimental results we cannot conclude with certainty that this reaction is occurring simultaneously with other Pb/$\text{SO}_2$ reactions.

In the case of PbO (in $\text{CO}_2/\text{SO}_2$) the XRD did not reveal any sulfates, however evidence for its presence was detected by the XPS. We cannot conclude based on the XPS data if this sulfate is $\text{PbOPbSO}_4$ or some other sulfate compound such as $\text{PbSO}_4$. The absence of sulfate in the XRD results indicate that the sulfate concentration is very low and, based on the XPS results, perhaps it only formed on the upper few nanometers of the mineral grains. PbO likely interacts with $\text{SO}_2$ to form PbS and $\text{PbOPbSO}_4$ via:

[12] $7\text{PbO} + 4\text{SO}_2 = \text{PbS} + 3(\text{PbOPbSO}_4)$

If instead $\text{PbSO}_4$ formed, it could be a result of the following reaction:

[13] $4\text{PbO} + 4\text{SO}_2 = \text{PbS} + 3\text{PbSO}_4$
In this scenario we have an opposite situation than the Pb in CO$_2$/SO$_2$ experiments, namely we have clear evidence for PbS via the XRD, but sulfate was only detected by the XPS.

According to Energy-dispersive X-ray Spectroscopy (EDX), PbS was a byproduct when lead oxide (PbO) based platinum (Pt) die-attach paste was exposed to Venus lowland conditions (460°C/94 bar) for 10 days inside the Venus Simulation Chamber (GEER) located at NASA Glenn (Lukco et al., 2018). Based on experiments completed by Vanasse et al. (2001), Lukco et al. (2018) concluded that PbO may have reacted with the 2 ppm H$_2$S present during the experiments to produce PbS. However, their experimental atmosphere also includes 51 ppm of COS and 180 ppm of SO$_2$, thus it is also possible that either or both gases contributed to the formation of PbS.

Sulfite was only found in one sample (PbO in CO$_2$/COS) and only detected with the XPS. Its formation could have been a direct interaction between PbO and COS to produce PbSO$_3$, in which case another lead mineral and a carbon byproduct in the form of either CO or graphite must have formed to balance the reaction. An interaction between PbO, COS, and CO$_2$ may have also triggered its formation. In either scenario the cause for the low abundance of PbSO$_3$ is not explained. Unfortunately, thermodynamic values of PbSO$_3$ are not readily available which hinders our ability to calculate which reaction would be the most favorable.

When PbSO$_4$ was analyzed with the XPS evidence for carbon and a molecule with a C-O bond were found, neither of which were observed in the original, untreated sample. This strongly suggests that both compounds resulted from reactions occurring during the experiments in the chamber and not from contamination as a result of exposure to Earth’s atmosphere. Another unidentified O1s peak found around ~532 eV was only present after the experiments in all tested gas mixtures, and may be due to a C-O or some oxygen related compound. After PbSO$_4$ was heated in CO$_2$/SO$_2$ a peak located at 168.88 eV appeared, however whether this is related to the 167.7 eV peak found in the original sample, or if it indicates the formation of a new compound cannot be confirmed at this time. The cause for the darkening of the sample after it was heated in the mixed gases is inconclusive.
PbS was not examined with the XPS, but given our Pb, PbO, and PbSO\(_4\) results it would be unsurprising to find evidence of a sulfate as well as carbon and C-O adsorbed to the surface.

### 6.3 Implications for Venus

Our understanding of geochemical interactions is limited by our knowledge of the near surface environment on Venus. Above all, our ignorance on the abundance of CO and O\(_2\) restricts our ability to accurately characterize the stability of the tested minerals on Venus. Several data points have been collected on the CO abundance, but at different altitudes and by different methods. The abundance of CO at 36 km was determined via IR to be 23 ± 5 ppm (Pollack et al., 1993). The Pioneer Venus’s probe used a GC to detect 20 ± 3 ppm at 22 km (Hoffman et al., 1980). Meanwhile the Venera 11/12 gas chromatographs detected 17 ± 1 ppm at 12 km (Gel’man et al. 1979; Marov et al. 1989). Assuming that PbS reacts with CO\(_2\) to produce PbSO\(_4\) and CO, between 0.5\(^{+0.0}_{-0.1}\)ppm and 2.4\(^{+0.2}_{-0.3}\) ppm (highland and lowland) of CO is necessary for the equation to reach equilibrium. If Pb(l) reacts with CO\(_2\) to produce PbO and CO, between 1.2±0.1 and 4.3±0.2 ppm (highland and lowland) of CO is necessary for equilibrium. The abundances were calculated using ΔG and the van’t Hoff equation to extrapolate to Venus temperatures (Venus International Reference Atmosphere; Seiff et al., 1986) and CO\(_2\) abundance (supplementary materials). However, as mentioned earlier these two reactions have an overall positive ΔG and may not accurately characterize the reactions that can occur on Venus. Solely based on these equations we would expect PbS and PbO to be more stable than PbSO\(_4\) and Pb(l), respectively, on Venus.

Both PbS and Pb are susceptible to oxidation by O\(_2\) on Earth, and a similar scenario must be considered in the situation of Venus. Calculations on the O\(_2\) fugacity have placed it between 10\(^{-21.7}\) to 10\(^{-20}\) bar in the lowlands to around 10\(^{-25}\) bar at 12 km in altitude (Fegley, et al., 1997). If Pb(l) is oxidized via:
And PbS is oxidized via:

[15] PbS + 2O$_2$ = PbSO$_4$

Our calculations indicate that between fO$_2$ = 10$^{-20}$ to 10$^{-25}$ bar (lowlands to highlands) is needed to balance [14] and 10$^{-20}$ to 10$^{-24}$ bar (lowlands to highlands) is needed to balance [15]. Thus Pb(l) and PbS are more likely to form, however the uncertainty of the fO$_2$ implies that the reactions can proceed in either direction, or perhaps are in equilibrium.

Pb (l) and PbO was found to interact with both CO$_2$/COS and CO$_2$/SO$_2$ in the highland condition. However there is one caveat, the abundance of COS used in our experiments, 100 ppm, is greater than the measured abundance on Venus, 4.4 ± 1 ppm at 33 km (Pollack et al., 1993), thus our results may be influenced by the large abundance of COS. However, our tested SO$_2$ abundance is below what has been measured on Venus, 130 ± 50 ppm (Bézard et al., 1993; Marcq et al., 2008), thus assuming SO$_2$ does not plummet below this concentration, our results are reasonable and can be directly compared to Venus.

Our results, and SO$_2$ experimental data collected by others (Burnett et al., 1997; Kubas, 1994; Mavrogenes & Blundy, 2017), indicate that an interaction between SO$_2$ and lead can lead to sulfur disproportionation. On Earth, SO$_2$ (S$^{IV}$) is one of the most abundant sulfur gases released from volcanism (Delmelle et al., 2018; Edmonds & Mather, 2017; Mavrogenes & Blundy, 2017), however sulfur is more generally found at the surface as S$^{II}$ and S$^{VI}$ species which are present in sulfides and sulfates (Mavrogenes & Blundy, 2017). Therefore, if SO$_2$ is present, sulfur disproportionation to form sulfides and sulfates may be a favorable reaction process. Venus’ large SO$_2$ abundance has been hypothesized to be a result of volcanism (Esposito, 1984) and numerical models and experimental results strongly suggests this scenario (Bullock & Grinspoon, 2001; Fegley & Prinn, 1989). Thus we argue that sulfur disproportionation can exist on Venus in the presence of lead, depending on the abundance of SO$_2$ and the surface composition, can be involved in buffering atmospheric SO$_2$.
Our results highlight the complicated relationship between carbon, oxygen, sulfur, and lead. All detected minerals have the potential to form on the highlands of Venus and CO$_2$, SO$_2$, and COS all seem to be equally reactive to lead and lead minerals.

Conversely, in the lowland condition we did not observe the formation of carbonates. This highlights the temperature sensitive nature of carbonates and thus are not likely to be found in these conditions. Since we were unable to simulate lowland conditions with the mixed gases, we couldn’t determine if PbS can form in these hotter conditions. Based on our PbS experiments completed in the lowland condition in pure CO$_2$, we can conclude that it is not temperature sensitive, and if present it is overall stable, with a possibility of minor oxidation to PbSO$_4$.

Surficial C-C and C-O was frequent in all our results, suggesting a similar situation may arise on Venus. The source behind the formation of the C-C bonds in our experiments is not well understood, but likely originates from CO$_2$. The C-O bonds are likely a result of CO and CO$_2$, perhaps COS, and their presence on the outer layers of the sample presumably facilitates the formation of carbonates on Venus.

If PbO, PbCO$_3$, and PbSO$_4$ are present in the highlands they would not contribute to the radar reflective signal due to their low dielectric constants. The dielectric constant needed to explain the source is believed to be greater than 50, with Maxwell Montes having a dielectric constant of perhaps 100 (Pettengill et al., 1992; 1997). In comparison, PbO has a dielectric constant of 12.4 at 1 MHz and 25.9 at 2 MHz (Olhoef, 1979; Young and Frederikse, 1973), PbCO$_3$ is measured to be around 23 at 50 Hz and 18.6 at $10^8$ Hz (Parkhomenko, 1967; Young and Frederikse, 1973), and PbSO$_4$ is around 14.3 at 1 MHz (Olhoef, 1979; Young and Frederikse, 1973). PbS, on the other hand, has been measured to have a very high dielectric constant of around 205 at 1 MHz (Olhoef, 1979).

Though minor oxidation of PbS to PbSO$_4$ did occur, PbS cannot be ruled out as the source of the radar reflective signal for several reasons. Due to the small increase in PbSO$_4$, but the overall stability over long periods of time, it suggests that the oxidation of PbS to PbSO$_4$ only
continued until equilibrium was reached. Moreover, the exact abundance of O₂ and CO on Venus is still uncertain and may not be consistent, which will affect the stability of PbS. Furthermore, based on models of the atmosphere there is debate on if the upper atmosphere is in equilibrium (Krasnopolsky and Pollack, 1994; Krasnopolsky, 2007; Zolotov, 1996) which implies that the calculations and detected values may not be correct leaving a great deal of room for error. Lastly, based on our experiments we do observe that PbS can form from interactions between Pb/PbO and sulfur gases that are known to exist on Venus.

7.0 Summary

The reactivity of lead with oxygen, sulfur, and carbon were well documented in this project. PbS formed in the highland condition when exposed to CO₂/SO₂ and to CO₂/COS. In terms of stability, when PbS was tested in the chamber at all conditions it was found to be generally stable, with some minor oxidation to PbSO₄. PbSO₄ on the other hand, did not experience any changes except for minor darkening when heated by itself in the mixed gases. Some oxidation of Pb to PbO may also be possible on Venus, and our experiments revealed that if PbO is present then carbonates are much more likely to form, particularly in the highland condition.

If lead is readily available on Venus, then PbS is expected to form and could contribute to the radar reflective signal. Lead carbonates, though not a source of the signal due to its low dielectric constant, appears to coexist with PbS in the highlands, and should also be present on Venus. Other lead mineral that formed, such as PbO and PbSO₄, have low dielectric constants and though may exist on Venus, would not explain the radar anomaly.

Our results highlight the interactions that can occur between lead and various venusian gases, however it is not apparent how accurately our results can be compared to the environment on Venus. Without fully understanding the atmospheric composition, and the gas profile from the highlands to the lowlands, there will be some ambiguity on the reactions that can occur. Nevertheless, the results collected from this investigation provide a comprehensive study on lead minerals that may arise on Venus.
8.0 Acknowledgments

This work was funded by the NASA Solar System Workings grant #NNX15AL57G. The authors greatly appreciate the use of the Arkansas Nano & Bio Materials Characterization Facility at the University of Arkansas which houses the MRD and Versaprobe used in this study. We would like to thank our lab manager Walter Graupner for all his continued help in the lab. We would also like to thank Ellen Czapinski for her assistance in preparing this paper. Lastly, we would like to express our gratitude to the reviewers for their invaluable insight and commentary on this paper. Our data will be available on the PI's account on Research Gate.

9.0 References


### Table 10.0 Supplementary Materials

Table of $\Delta G^\circ$ and $\Delta H^\circ$ of various compounds collected for, and related to, the paper ($T=25^\circ C$).

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<td>-393.522 *</td>
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<tr>
<td></td>
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<td>-394.359 ‡</td>
<td>-393.509 ‡</td>
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<tr>
<td>$CO$ (g)</td>
<td>-137.163 *</td>
<td>-110.527 *</td>
</tr>
<tr>
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<td>-137.16 #</td>
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<td></td>
<td>-137.1 †</td>
<td>-110.5 †</td>
</tr>
<tr>
<td></td>
<td>-137.152 ‡</td>
<td>-110.525 ‡</td>
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<td>$COS$ (g)</td>
<td>-165.601 *</td>
<td>-138.407 *</td>
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<tr>
<td></td>
<td>-166.9 #</td>
<td>-142.0 #</td>
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<td>$SO_2$ (g)</td>
<td>-300.125 *</td>
<td>-296.842 *</td>
</tr>
<tr>
<td></td>
<td>-300.1 †</td>
<td>-296.8 †</td>
</tr>
<tr>
<td></td>
<td>-300.13 #</td>
<td>-296.81 #</td>
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<tr>
<td></td>
<td>-299.825 ‡</td>
<td>-296.813 ‡</td>
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<td>$SO_3$ (g)</td>
<td>-371.02 #</td>
<td>-395.7 #</td>
</tr>
<tr>
<td></td>
<td>-371 †</td>
<td>-395.7 †</td>
</tr>
<tr>
<td>$S_2$ (g)</td>
<td>79.687 *</td>
<td>128.6 *</td>
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<td>79.329 ‡</td>
<td>128.365 ‡</td>
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<td>$Pb$ (l)</td>
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<td>4.283 *</td>
</tr>
<tr>
<td>$PbS$ (cr)</td>
<td>-96.685 *</td>
<td>-98.324 *</td>
</tr>
<tr>
<td></td>
<td>-98.7 #</td>
<td>-100.4 #</td>
</tr>
<tr>
<td></td>
<td>-96.8 †</td>
<td>-100.3 †</td>
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<td></td>
<td>-95.8136 ‡</td>
<td>-100.416 ‡</td>
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<tr>
<td>$PbSO_4$ (cr)</td>
<td>-813.1 †</td>
<td>-920 †</td>
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<td>-813.453 ‡</td>
<td>-919.434 ‡</td>
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<td>$PbOPbSO_4$ (cr)</td>
<td>-1032.19 ‡</td>
<td>-1181.98 ‡</td>
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<td>$PbO$ (red; litharge)</td>
<td>-188.9 †</td>
<td>-219.0 †</td>
</tr>
<tr>
<td></td>
<td>-189.283 *</td>
<td>-219.409 *</td>
</tr>
<tr>
<td></td>
<td>-188.9 #</td>
<td>-219.0 #</td>
</tr>
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<td></td>
<td>-189.117 ‡</td>
<td>-219.116 ‡</td>
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<td>$PbO$ (yellow; massicot)</td>
<td>-187.9 †</td>
<td>-217.3 †</td>
</tr>
<tr>
<td></td>
<td>-188.28 ◊</td>
<td>-216.606 ◊</td>
</tr>
<tr>
<td></td>
<td>-188.647 *</td>
<td>-218.062 *</td>
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<td>$PbO_2$ (cr)</td>
<td>-215.397 *</td>
<td>-274.47 *</td>
</tr>
<tr>
<td></td>
<td>-217.3 #</td>
<td>-277.4 #</td>
</tr>
<tr>
<td></td>
<td>-218.3 †</td>
<td>-277.4 †</td>
</tr>
<tr>
<td></td>
<td>-215.853 ‡</td>
<td>-277.023 ‡</td>
</tr>
<tr>
<td>$Pb_3O_4$ (cr)</td>
<td>-601.2 #</td>
<td>-718.4 #</td>
</tr>
<tr>
<td></td>
<td>-601.6 †</td>
<td>-718.7 †</td>
</tr>
<tr>
<td></td>
<td>-601.45 ◊</td>
<td>-718.393 ◊</td>
</tr>
<tr>
<td>$PbCO_3$ (cr)</td>
<td>-625.5 #</td>
<td>-699.2 #</td>
</tr>
<tr>
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<td>-627.182 ◊</td>
<td>-699.565 ◊</td>
</tr>
<tr>
<td>$Pb_2OOCO_3$ (cr)</td>
<td>-818.892 ◊</td>
<td>-920.48 ◊</td>
</tr>
</tbody>
</table>

* Chase et al., 1986
† Robie and Hemingway, 1995
# Dean, 1999
◊ Faure, 1998
To calculate the ΔG and ΔH we used the following equations:

\[ \Sigma n_i G_{f}^{\circ}(\text{products}) - \Sigma n_i G_{f}^{\circ}(\text{reactants}) = \Delta G^{\circ}_R \]

\[ \Sigma n_i H_{f}^{\circ}(\text{products}) - \Sigma n_i H_{f}^{\circ}(\text{reactants}) = \Delta H^{\circ}_R \]

Assuming equilibrium (ΔG_R = 0) we can then calculate ln(K) via:

\[ \Delta G^{\circ}_R = -RT \ln(K) \]

The van’t Hoff equation was used to extrapolate to conditions found on Venus:

\[ \ln(K_T) - \ln(K_{T^\circ}) = -\frac{\Delta H^{\circ}_R}{R} \left( \frac{1}{T} - \frac{1}{T^\circ} \right) \]

Venus conditions were obtained from Seiff et al. (1986)

Table listing all ΔG and ΔH data for equations presented in the paper (T=25°C).

<table>
<thead>
<tr>
<th>Equation</th>
<th>ΔG (kJ·mol⁻¹)</th>
<th>ΔH (kJ·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2PbO+CO₂=2PbOCO₃</td>
<td>-46.41 ±0.3 -0.5</td>
<td>-88.71 ±0.3 -0.6</td>
</tr>
<tr>
<td>3PbO+CO₂=Pb₃O₂CO₃*</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PbO+COS=PbS+CO₂</td>
<td>-136.08 ±0.4 -0.8</td>
<td>-133.54 ±0.9 -1.0</td>
</tr>
<tr>
<td>Pb(l)+COS=PbS+CO</td>
<td>-70.11 ±0.6 -1.1</td>
<td>-73.60 ±0.7</td>
</tr>
<tr>
<td>7Pb+5SO₂=3PbS+2(PbOPbSO₄)</td>
<td>-870.07 ±2.5 -4.7</td>
<td>-1207.94 ±3.1 -3.0</td>
</tr>
<tr>
<td>3Pb+SO₂=PbS+2PbO</td>
<td>-181.71 ±1.3 -2.1</td>
<td>-253.66 ±1.3 -1.6</td>
</tr>
<tr>
<td>7PbO+4SO₂=PbS+3(PbOPbSO₄)</td>
<td>-675.47 ±3.2 -1.2</td>
<td>-936.78 ±4.0 -4.2</td>
</tr>
<tr>
<td>4PbO+4SO₂=PbS+3PbSO₄</td>
<td>-583.55 ±0.7 -0.4</td>
<td>-801.96 ±1.0 -1.2</td>
</tr>
<tr>
<td>PbS+4CO₂=PbSO₄+4CO</td>
<td>312.91 ±1.1 -1.6</td>
<td>311.33 ±1.0</td>
</tr>
<tr>
<td>PbS+2CO₂=PbSO₄+2CO</td>
<td>72.49 ±1.1 -1.6</td>
<td>-33.34 ±0.8</td>
</tr>
<tr>
<td>Pb(l)+CO₂=PbO+CO</td>
<td>65.97 ±0.2</td>
<td>59.58 ±0.1 -0.3</td>
</tr>
<tr>
<td>2Pb(l)+O₂=2PbO</td>
<td>-378.57 ±0.3 -0.5</td>
<td>-447.38 ±0.3 -0.6</td>
</tr>
<tr>
<td>PbS+2O₂=PbSO₄</td>
<td>-716.42 ±1.1 -1.7</td>
<td>-821.68 ±1.0</td>
</tr>
</tbody>
</table>

*the reaction cannot be calculated due to the absence of available thermodynamic data of a compound
Chapter 4

Stability of Pyrrhotite under Experimentally Simulated Venus Conditions

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University of Arkansas, Center for Space and Planetary Sciences, Fayetteville, AR, 72701, United States
saraport@email.uark.edu

Abstract

The stability of pyrrhotite (Fe$_{1-x}$S; Fe$_7$S$_8$) was tested under simulated Venus conditions in 2 different temperature/pressure regimes and 3 different gas mixtures. The two regimes correlate to the average conditions in the lowlands (460°C/92 bar) and the conditions found at the top of Maxwell Montes, 11 km above the planetary radius (380°C/42 bar). The three gas mixtures consisted of 99.999% CO$_2$, 100 ppm SO$_2$ in CO$_2$, and 100 ppm of COS in CO$_2$. All experiments lasted between 24 to 96 hours. Analysis using X-ray Diffraction (XRD) and Laser Induced Breakdown Spectroscopy (LIBS) revealed that pyrrhotite was stable at all tested temperature/pressures and gases. Our results are discussed in the context of other research completed on pyrrhotite stability on Venus. Our results further expand on our knowledge of the chemical reactions that may take place on Venus and highlights the need for in situ measurements of the near surface geology and atmosphere.

Key Words

Venus; Pyrrhotite; Mineralogy; Experiments

1.0 Introduction

Pyrrhotite (Fe$_{1-x}$S) is a sulfide mineral that is commonly present in basaltic rocks on Earth (Becker 2009; Treiman and Fegley 1991), therefore the detection of a basaltic surface by the Venera and Vega probes (Fegley et al. 1997a; Treiman 2007) provides evidence for its existence.
on Venus. Additionally, Venus has an abundance of sulfur in its atmosphere in such forms as SO$_2$, H$_2$S, S$_x$, COS, etc, which is expected to interact with the surface to produce sulfur bearing minerals (Zolotov 2018). Pyrrhotite may also hold clues to the source of the radar anomaly present on several of the highlands on Venus; it was experimentally determined to have a high dielectric constant, >81, (Parkhomenko 1967; Rosenholtz and Smith 1936) and was stated to have a high electrical conductivity by Pettengill et al. (1988). A pyrrhotite-pentlandite assemblage has also been proposed to be the cause of the radar reflectivity seen around impact craters on Venus (Burns and Straub 1993).

Past experiments have disclosed that pyrrhotite is unstable at Venus conditions. Experiments completed by Treiman and Fegley (1991) revealed that pyrrhotite tested at Venus temperatures and ambient pressures in CO$_2$ oxidized to magnetite (Fe$_3$O$_4$). However, there are several caveats; the first is their tested temperatures were at least 80°C hotter than on Venus which was then extrapolated to ascertain its stability on Venus. They also used a cylinder of 99.95% CO$_2$. Straub (1993) stated that their cylinder of 99.95% CO$_2$ contained ~30 ppm of O$_2$ contamination and asserted that the oxidation of pyrrhotite was caused by O$_2$ and not CO$_2$. Although it is unknown if the cylinder acquired by Treiman and Fegley (1991) also contained a significant amount of O$_2$ it is worth taking into consideration.

Experiments completed to resolve the question of pyrite (FeS$_2$) stability on Venus uncovered that it thermally decomposes to pyrrhotite via the release of S$_2$ (Fegley et al. 1995). Their study stated that over time pyrrhotite will decompose to become more iron rich and will also react with CO$_2$ to produce magnetite, which then further oxidizes to hematite (Fe$_2$O$_3$). Fegley et al. (1995) tested their CO$_2$ cylinder and determined that their cylinder contained <1 ppm of O$_2$. Their experimental procedure was scrutinized by Wood and Brett (1997) who highlighted that equilibrium cannot be reached because the experiments were completed in an open system; any outgassed S$_2$ could not back react with the sample and thus stabilize pyrite.
Later experiments to ascertain the stability of pyrite were completed by Hong and Fegley (1997). In their experiments, which were tested in various gas mixtures and temperatures relevant to Venus, they observed its decomposition into pyrrhotite, but no oxidation was detected (except for when it was tested in >100 ppm of O$_2$). Though pyrrhotite stability is not explicitly stated, their results attest to the relative stability of pyrrhotite at Venus conditions. A summary of major experiments exposing pyrite and pyrrhotite to Venus conditions can be found in Table 1.

The stability of pyrrhotite has also been explored through thermodynamic calculations. Based on the low abundance of COS on Venus, only $4.4 \pm 1$ ppmv at 33 km in altitude (Pollack et al. 1993), pyrrhotite has been calculated to be unstable (Fegley and Treiman 1992) and could oxidize via (Zolotov 2018):

$$\text{Fe}_7\text{S}_8 + 6 \text{COS(g)} \rightarrow 7 \text{FeS}_2 + 6 \text{CO(g)}$$ \[1\]

However when CO$_2$/CO/COS/SO$_2$ are reacted until equilibrium at lowland temperature and pressure, the abundance of COS is ~28 ppmv, high enough for pyrite/pyrrhotite stability (Zolotov 2018).

Table 1: A summary of major experiments involving the stability of pyrite and pyrrhotite at Venus conditions. “Interior” indicates that the material was only found within the mineral grain and not at the surface

<table>
<thead>
<tr>
<th>Reference</th>
<th>Starting Mineral</th>
<th>Reacting gases</th>
<th>Temperature and Pressure</th>
<th>Length of time</th>
<th>Resulting Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treiman and Fegley (1991)</td>
<td>Pyrrhotite</td>
<td>CO$_2$</td>
<td>797–1060 K, 1 bar</td>
<td>Not stated</td>
<td>Magnetite Pyrrhotite(interior)</td>
</tr>
<tr>
<td>Straub (1993)</td>
<td>Pyrrhotite</td>
<td>NaHCO$_3$ (to produce pure CO$_2$)</td>
<td>748 K, &lt;1 bar</td>
<td>720 h</td>
<td>Pyrrhotite</td>
</tr>
<tr>
<td>Fegley et al. (1995)</td>
<td>Pyrite</td>
<td>CO$_2$, CO$_2$–H$_2$, CO$_2$–CO, CO$_2$–SO$_2$, CO$_2$–SO$_2$, CO$_2$–Ar</td>
<td>662–1285 K, 1 bar</td>
<td>0.08–454 h</td>
<td>Pyrrhotite Magnetite Maghemite Hematite Pyrite (if present, interior)</td>
</tr>
<tr>
<td>Reference</td>
<td>Starting Mineral</td>
<td>Reacting gases</td>
<td>Temperature and Pressure</td>
<td>Length of time</td>
<td>Resulting Mineral</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------</td>
<td>----------------</td>
<td>--------------------------</td>
<td>----------------</td>
<td>-----------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Hong and Fegley (1997)</td>
<td>Pyrite</td>
<td>He N₂ CO₂ CO₂–CO CO₂–SO₂ CO₂–CO–SO₂ CO₂–O₂ H₂S–H₂</td>
<td>665–864 K, 1 bar</td>
<td>0.28–166 h</td>
<td>Pyrrhotite Hematite (only in CO₂–O₂) Pyrite (if present, interior)</td>
</tr>
<tr>
<td>Radoman-Shaw (2019)</td>
<td>Pyrite</td>
<td>CO₂–N₂–SO₂–COS·H₂O·CO₂–H₂S·HCl·HF</td>
<td>743 K, 92 bar</td>
<td>1008 h, 1920 h</td>
<td>Magnetite</td>
</tr>
<tr>
<td></td>
<td>Pyrrhotite</td>
<td>CO₂–N₂–SO₂–COS·H₂O·CO₂–H₂S·HCl·HF</td>
<td>743 K, 92 bar</td>
<td>1008 h, 1920 h</td>
<td>Magnetite Pyrrhotite (interior)</td>
</tr>
<tr>
<td>This paper</td>
<td>Pyrrhotite</td>
<td>CO₂ CO₂–SO₂ CO₂–COS</td>
<td>653 K, 42 bar 773 K, 92 bar</td>
<td>24–96 h</td>
<td>Pyrrhotite</td>
</tr>
</tbody>
</table>

Other models have concluded that pyrite could be stable in the highlands while magnetite could be stable in the lowlands (Klose et al. 1992; Zolotov 1991). Klose et al. (1992) determined the likely fractional oxygen deficiency on Venus by comparing the atmospheric abundance of gases in their model and the abundances measured in the atmosphere. Though similar, the calculated abundance of COS, H₂S, and CO are slightly different than the observed abundances. At slightly more reducing conditions than calculated in their model pyrrhotite could be stable in
the lowlands instead of magnetite, however in this instance there is a large discrepancy between
the measured and modeled atmospheric gas abundances (Klose et al. 1992). The abundance of
H$_2$S can also facilitate the stability of pyrite and pyrrhotite, however current measurements of H$_2$S
indicate that it’s high abundance would result in pyrite stability over pyrrhotite stability (Fegley and
Treiman 1992; Zolotov 2018). Our limited knowledge on the gas abundances near the surface
make it challenging to accurately model the gas-surface equilibrium. In addition it is not well known
if the atmosphere is in equilibrium, but it is theorized that this is likely not the case at higher
elevation (Fegley et al. 1997b; Zolotov 2018).

Our goal was to revisit the question of pyrrhotite stability on Venus using additional
experimental parameters that were not incorporated by past researchers. Our experiments are
completed in a pressurized and sealed chamber to simulate Venusian pressure and to allow the
gases to back react until equilibrium. We also tested the stability of pyrrhotite when exposed to
100 ppm of COS gas. Though this quantity is significantly greater than what was detected on
Venus, it gives us experimental confirmation on its effect, if any, on pyrrhotite. Lastly our
experiments will use a cylinder of 99.999% CO$_2$ which has <1 ppm of O$_2$.

2.0 Methods

Pyrrhotite (Fe$_7$S$_8$) crystals, originally mined in Galax, Virginia, were purchased from
Ward’s Science (CAG: 470104-418). The pyrrhotite was then ground using a ring mill and sieved
to 125 microns. Using X-ray Diffraction (XRD) via a PANalytical’s Materials Research
Diffractometers (MRD) we determined that the pyrrhotite was a mixture of monoclinic and
hexagonal pyrrhotite. SEM/EDX analysis using a FEI XL-30 Environmental Scanning Electron
Microscope revealed an array of various elements; 43.07 at.% of the sample consisted of O, 46.05
at.% consisted of Fe and S, and the remaining 10.88 at.% was a mixture of Mg, Si, Ca, Pb, Cu,
and Zn. About 10-20 at.% of the oxygen found in the sample is believed to be from atmospheric
contamination.
One gram of the sample was placed in a ceramic bowl with a height of 26 mm and a diameter of 31 mm and inserted into the Cassiopeia Chamber (Venus simulation chamber) available in the W.M. Keck Laboratory for Planetary Simulations, University of Arkansas. The 500 mL, stainless steel 316 chamber was purchased from Parr Instruments. The chamber was sealed then placed in vacuum (0.035 bar) then flushed with 99.999% CO$_2$ at 60 psi for several minutes. The chamber was then filled with one of the three different gas mixtures used to simulate the conditions found on Venus. The gases were pure CO$_2$, CO$_2$ with 100 ppm of SO$_2$, and CO$_2$ with 100 ppm of COS. The purity of the 99.999% CO$_2$ cylinders were measured by AirGas and were tested for O$_2$+Ar+CO (<1.0 ppm), THC (<1.0 ppm), H$_2$O (<3.0 ppm), and N$_2$ (<5.0 ppm). The CO$_2$ cylinders used for the mixed gas was 99.99% pure and was tested for H$_2$O (<10 ppm), hydrocarbons (<10 ppm), N$_2$ (<70 ppm), and O$_2$ (<20 ppm). The COS was 97% pure and was tested for CS$_2$ (<300 ppm), CO$_2$ (<1.7 ppm), N$_2$ (<0.2 ppm), and H$_2$S (<0.8 ppm). The SO$_2$ was 99.98% pure. We used 100 ppm of the minor gases because it is the lower limit set by the gas manufacturer. The mixed gases were only used in highland condition experiments because the regulators used were not high output regulators, thus we could not attain the pressures needed to simulate the lowland condition.

The chamber was then heated to one of two different conditions found on Venus to replicate the average conditions found in the lowlands and the conditions found at the top of Maxwell Montes, approximately 11 km above the average planetary radius. To heat, the chamber was fitted with an external heating sleeve that was attached to a temperature/pressure controller. In order to reach the desired final pressure, the chamber was filled to an initial pressure which was calculated using the Ideal Gas Law. The increase in heat via the heating sleeve increased the internal pressure. To monitor the temperature the chamber has an internal thermowell where the thermocouple resides. The chamber also has an interior pressure gauge to monitor the pressure. Both are recorded by the temperature/pressure controller every 30 seconds. The
average initial temperature was 22.6°C ± 1.8°C and the average initial pressure for the lowland was 38.2 bar ± 0.6 bar and the highland was 19.1 bar ± 1.2 bar. During the experiment the average lowland condition was 460.0°C ± 0.7°C and 92.2 bar ± 0.1 bar while the tested highland condition was 380.4°C ± 1.3°C and 42.4 bar ± 0.3 bar. All experiments lasted from 24 to 96 hours and all tested conditions are displayed in Table 2.

Table 2: All tested experimental conditions for pyrrhotite completed during this project

<table>
<thead>
<tr>
<th>Temperature/Pressure</th>
<th>Gas</th>
<th>Length of time (hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>380°C/45 bar</td>
<td>CO₂</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>CO₂/SO₂</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>CO₂/COS</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>96</td>
</tr>
<tr>
<td>460°C/95 bar</td>
<td>CO₂</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>96</td>
</tr>
</tbody>
</table>

At the end of each experiment the chamber was vented while still hot and evacuated (0.035 bar). It was then flushed with N₂ for several minutes, then filled with N₂ (20 bar) and allowed to cool to room temperature which took approximately 5 hours. The sample was then removed and analyzed using the MRD to determine any changes to the sample’s mineralogical composition. The settings on the MRD were 15-85° for 2θ and the voltage/current was 45 kV/40 mA with a counting time of 0.8 seconds. We used a Cu-Kα radiation source. The MRD spectra were examined using X’Pert Highscore and its accompanying spectral library. Some samples were also tested in the Rigaku Miniflex X-Ray Diffraction (XRD) located at the High-Density Electronics Center (HiDEC) at the University of Arkansas. The settings for the XRD were 30 kV/15
mA. The spectra obtained from this instrument was analyzed using “Match!”. Several of the samples were also analyzed for changes in chemistry via Laser Induced Breakdown Spectroscopy (LIBS) using the Chemistry & Camera (ChemCam) located at Los Alamos National Labs. The samples were all shot in an argon atmosphere at Mars pressure. Each sample was shot in three spots and each location has 30 laser shots. Each of the laser shots had ~13 mJ of energy, 5 ns pulse width, and 3 Hz rep rate.

3.0 Results

![Fe₇S₈ in 99.999% CO₂ Atmosphere](image)

**Fig. 1** XRD spectra of pyrrhotite tested in CO₂ for 96 hours. The bottom spectrum is pyrrhotite before an experiment. The middle spectrum displays when it was tested in highland condition, and the topmost spectrum is after it was exposed to the lowland condition. No differences between the spectra was observed
Based on XRD analysis our pyrrhotite samples did not exhibit any changes in composition regardless of the tested temperature/pressure, atmospheric gas, or experimental duration (Fig. 1 & 2). Analysis of the samples using a LIBS did not detect any significant changes in the composition of the samples. Differences in peak intensity for oxygen and sulfur were found with the LIBS, but the differences are minimal and show no pattern in relation to the experimental conditions (Fig. 3). At the end of experiments completed in the lowland condition parts of the interior of the chamber were lightly dusted with a dark powder. EDX analysis of this dark powder revealed that it was a carbon deposit which likely originated from CO₂. The LIBS did not detect any carbon in the samples.

**Fig. 2** XRD spectra of pyrrhotite tested in the highland conditions for 96 hours. The spectra correlated to when it was exposed to CO₂ (bottom), CO₂/COS (middle), and CO₂/SO₂ (top). No differences between the spectra was observed.
Although standard in XRDs, a Cu-Kα radiation source is not the most ideal source when analyzing Fe. Fe is fluorescent at the Cu-Kα wavelength, 1.54 Å, which can result in decreased peak intensity and increased noise. Due to the cost and rarity of other radiation sources, such as Co-Kα, we used Cu-Kα for this project. Nevertheless, during analysis of the XRD pyrrhotite spectra taken by the MRD we did not discern any new peaks signifying the formation of another iron mineral. Spectra obtained by the XRD Rigaku were cleaner than the MRD with more clearly defined, distinguishable peaks, yet we also did not observe any new peaks that could indicate the presence of a different mineral. To further bolster our results, Fegley et al. (1995) and Hong and Fegley (1997) used an XRD Rigaku powder diffractometer with a Cu-Kα source and was able to detect peaks of pyrite, pyrrhotite, magnetite, and hematite in their samples.

Fig. 3 Several of the pyrrhotite samples exposed to different conditions were analyzed with the ChemCam at LANL. Each sample was analyzed 3 times. ChemCam data shows no observable differences in sulfur abundance between the different samples.
In order to confirm that pyrite, magnetite, and hematite were not present in our spectra, our data was compared to XRD spectra obtained from The RRUFF project (rruff.info), a database of XRD spectra. All compared spectra were exposed to the same radiation source, Cu-Kα, for better comparison. The selected pyrite spectra was pyrite that was collected from Mina San Jose de Huanzala, Minero de Huallanca District, Department de Huanuco, Peru, the magnetite spectra was from magnetite collected from 2500' level, Zinc Corporation of America mine #4, Balmat, New York, USA, and the hematite spectra was from hematite collected from near Covered Wells, Papago Indian Reservation, Arizona, USA. Figure 4 compares all three spectra with our pyrrhotite tested in CO₂/COS in the highland condition. Comparison of the spectra reveals no discernable peaks of magnetite, hematite, or pyrite in our pyrrhotite spectra.

**Fig. 4** XRD spectra comparing our spectra with pyrite (FeS₂), magnetite (Fe₃O₄), and hematite (Fe₂O₃) spectra found on rruff.info. Our spectra does not contain any peaks that indicate the presence of these three minerals.
4.0 Discussion

4.1 Previous Work Completed by Others

Experiments completed by Treiman and Fegley (1991) and Fegley et al. (1995) observed the oxidation of pyrrhotite to magnetite via CO$_2$. The experimental length was not recorded in Treiman and Fegley (1991), but the experiments in Fegley et al. (1995) were recorded to have lasted from 5 minutes to 454 h with a median of 58.15 h. Treiman and Fegley (1991) asserted that pyrrhotite oxidized via:

$$3 \text{Fe}_7\text{S}_8 + 76 \text{CO}_2 (g) = 7 \text{Fe}_3\text{O}_4 + 76 \text{CO} (g) + 24 \text{SO}_2 (g) \ [2]$$

Meanwhile Fegley et al. (1995) stated that pyrrhotite likely oxidized via:

$$3 \text{Fe}_7\text{S}_8 + 28 \text{CO}_2 (g) = 7 \text{Fe}_3\text{O}_4 + 12 \text{S}_2 (g) + 28 \text{CO} (g) \ [3]$$

$$\text{Fe}_9\text{S}_{10} + 12 \text{CO}_2 (g) = 3 \text{Fe}_3\text{O}_4 + 5 \text{S}_2 (g) + 12 \text{CO} (g) \ [4]$$

Depending on the Fe/S ratio of the pyrrhotite. Fegley et al. (1995) also observed further oxidation from magnetite to hematite. However when the $\Delta G$ of these equations are calculated they are positive (see Supplementary Materials), which means the reactions are generally unfavorable.

Radoman-Shaw (2019) completed experiments on pyrrhotite stability in the Venus chamber (GEER) located at NASA Glenn. His 42- and 80-day experiments used the 9 most abundant gases in Venus’ atmosphere (CO$_2$, COS, SO$_2$, CO, N$_2$, H$_2$O, H$_2$S, HCl, HF), and it was tested only in the lowland condition (470 ± 20°C and 92 ±5 bar). He asserted that pyrrhotite was unstable and oxidized to magnetite, but no further oxidation into hematite was observed. Although he determined via EDS that sulfur is still present in the sample underneath the oxidation signature, he concluded that pyrrhotite is unstable on Venus.
Most thermodynamic models have also shown that at equilibrium pyrrhotite is likely unstable on Venus and will form either magnetite and/or pyrite (Klose et al. 1992; Fegley and Treiman 1992; Zolotov 1991; 2018):

\[
3 \text{Fe}_7\text{S}_8 + 28 \text{CO}_2 (g) \rightarrow 7 \text{Fe}_3\text{O}_4 + 24 \text{COS} (g) + 4 \text{CO} (g) \quad [5]
\]

\[
\text{Fe}_7\text{S}_8 + 4 \text{CO}_2 (g) \rightarrow \text{Fe}_3\text{O}_4 + 4 \text{FeS}_2 + 4 \text{CO} (g) \quad [6]
\]

Or via equation [1]. As mentioned in the introduction, results from thermodynamic equilibria models of the Venus atmosphere indicate that the COS abundance is too low for pyrrhotite stability. However, when \(\text{CO}_2/\text{CO}/\text{COS}/\text{SO}_2\) is modeled and equilibrated to conditions found at the radius, COS is around ~28 ppm. Assuming this abundance holds for highland conditions, pyrite/pyrrhotite could be stable (Zolotov 2018), but at even larger abundances pyrite should form at the expense of pyrrhotite. Radoman-Shaw (2019) did not observe the formation of pyrite even though COS was 51 ppm in his experiments. He also used thermodynamic modeling (FactSage) to compare with his experiments (his models included all 9 gases used in the GEER) and not only concluded that pyrrhotite would be stable under Venus conditions, but also that pyrite would form (magnetite did not form in his models). Thus even though his and Zolotov (2018)’s models suggested that pyrite could form, experimentally Radoman-Shaw (2019) was not able to produce pyrite.

**4.2 Comparison with the Present Work**

The results obtained from this project contradicts two major conclusions about pyrrhotite stability under Venus conditions. First, we did not detect any iron oxides in our samples. Although Fegley et al. (1995) concluded that pyrrhotite oxidizes to magnetite, magnetite was not present in every one of their experiments. There was a greater chance of oxidation if the experiments were completed for longer periods of time, >100 hours, but this was not always the case. Additionally, oxidation became more prevalent when they completed experiments at temperatures greater than
on the surface of Venus, > 525°C. They stated that the cause for the inconsistency was due to overlapping pyrrhotite, magnetite, and hematite formation reactions. They also stated that in lowland condition experiments pyrrhotite oxidation was slower than the pyrite/pyrrhotite conversion, but in the highland condition pyrrhotite oxidation was faster than the pyrite/pyrrhotite conversion. The latter reaction occurred so quickly that pyrite and hematite were present in their samples, but not pyrrhotite. This was not observed in our experiments. Furthermore, when Hong and Fegley experimentally tested pyrite stability in 1997 they observed decomposition to pyrrhotite, but no magnetite, and hematite was only observed in experiments completed in >100 ppm of O₂. Overall these set of experiments were completed for <100 hours, but several were tested for >100 hours and their experiments were all between 392°C to 591°C. The absence of hematite in highland condition experiments could be because they never completed experiments at highland temperatures using the same gases as in Fegley et al. (1995). Nevertheless, they did not form iron oxides even when the experimental conditions were the same as in Fegley et al. (1995). Kohler (2016) observed the decomposition of pyrite into pyrrhotite, but no oxidation into magnetite or hematite when tested in a CO₂/N₂/SO₂ gas mixture. The formation of pyrrhotite was only observed in the experiment simulating lowland temperature (467°C), but ambient pressure (open system experiment). She did not observe decomposition of pyrite to pyrrhotite when it was pressurized to 95 bar (closed system experiment). In order to eliminate the presence of O₂ in the experiment, Straub (1993) tested pyrrhotite stability in a cell under NaHCO₃, which thermally decomposes to CO₂. After 720 hours at 475°C (≤1 bar) (sealed) she had indirect evidence of CO₂ in the cell and found no evidence of oxidation. Hong and Fegley (1997)’s, Straub’s (1993), and Kohler (2016)’s results are more in line with our results, none of us observed the formation of iron oxides. Though their results differ, Fegley et al. (1995), Hong and Fegley (1997), and several of Kohler (2016)’s experiments were completed in an open system; thus any gas produced would leave the system preventing any back reactions.
Radoman-Shaw (2019)’s pyrrhotite experiments were completed in a closed system and yet, contradictory to his models, he detected magnetite on his pyrrhotite samples. The different results between Fegley et al. (1995), Hong and Fegley (1997), Kohler (2016), and Radoman-Shaw (2019) is likely due to differences in the experimental conditions, namely the opened versus sealed, pressurized versus unpressurized set-up, as well as differences in atmospheric composition. Meanwhile the cause for the discrepancy between our results and that of Radoman-Shaw’s could be due to different lengths in experimental time, the gas mixture used in the experiments, or perhaps since he tested the stability of numerous minerals/rocks at the same time, it is related to interactions between them all back reacting and interacting with one another. Moreover, Radoman-Shaw (2019) did not test conditions found in the highlands as we did, and since many of Venus’ gases are not supercritical at these elevations, this might affect mineral stability. CO₂, among many other gases on Venus, are supercritical in the lowlands, and have characteristics of a liquid and a gas (Han and Poliakoff 2012). However, a very limited number of dry supercritical CO₂ experiments have been completed at this time; thus its effects on minerals is currently not well understood. Therefore, our pyrrhotite highland results may be more applicable to conditions found on the highlands of Venus.

In regard to the effect of COS, our pyrrhotite was exposed to 100 ppm of COS, which, according to Zolotov (2018)’s calculations, should result in pyrite stability via equation [1], however we did not witness any evidence of pyrite. The lack of pyrite in our samples after pyrrhotite was tested in CO₂/COS may be a result of our overestimation of COS’s reactivity, or perhaps its interactions are less favorable when compared to other reactions that are occurring in the chamber. It may also be that 96 hours is not long enough to facilitate the formation of pyrite in our experiments. Our CO₂/COS experiments were completed in highland conditions where the gases are not supercritical, but Radoman-Shaw (2019) only tested lowland conditions where they are supercritical. The oxidation of pyrrhotite in Radoman-Shaw (2019)’s experiments may be because
the interactions between the various gases, including supercritical CO$_2$, to produce magnetite were more favorable than an interaction with COS to produce pyrite. However, if this is the case, then equation [6] (which produces pyrite from pyrrhotite + CO$_2$) must be less favorable than other pyrrhotite + CO$_2$ interactions that produce magnetite. Radoman-Shaw (2019) does not discuss the change in COS over the course of his experiments, thus it may also be possible that as the system equilibrates the abundance of COS, and other gases, may change, and even a shift of a few ppm can change the stability field. This may be one of the causes between our divergent results and could even be the cause for the absence of pyrite in our experiments.

The discontinuity between the results obtained from various mentioned thermodynamic models and experimental work highlights our misunderstanding on the most favorable reactions occurring on Venus. This is a result of either the very complicated environment due to the various gases found near the surface of Venus, or our lack of understanding of supercritical fluids, which is likely reflected in current thermodynamic models. Future thermodynamic models incorporating the characteristics of supercritical fluids and their ability to interact with other supercritical fluids and minerals is imperative in order to better model the reactions that could be occurring in the lowlands of Venus.

4.3 Pyrrhotite on Venus

4.3.1 Effect of H$_2$S

Our results indicate that pyrrhotite has good stability over short time scales, however the large abundance of sulfur and oxygen bearing gases on Venus makes it difficult to assess its stability over longer timescales. Below we’ll discuss several gases of importance for pyrrhotite stability on Venus as well as present several equations that can be used to hypothesize on its stability.
Zolotov (2018)'s calculations demonstrated that H\textsubscript{2}S might play an important role in pyrite and thus pyrrhotite stability. He notes that it may form via:

$$\text{FeO (in minerals) + 2H}_2\text{S(g)} = \text{FeS}_2 + \text{H}_2\text{O(g)} + \text{H}_2 (g) \ [7]$$

Therefore, it may be possible that pyrrhotite forms from a similar reaction:

$$7 \text{FeO} + 8 \text{H}_2\text{S (g)} = \text{Fe}_7\text{S}_8 + 7 \text{H}_2\text{O (g)} + \text{H}_2 (g) \ [8]$$

This could be one possible reaction to form pyrrhotite on Venus. When Zolotov (2018) calculated the abundance of H\textsubscript{2}S based on SO\textsubscript{2}/H\textsubscript{2}O/H\textsubscript{2}S equilibrium, it was 2.89 ± 2 ppmv less than the measured abundance. When he plotted pyrite, pyrrhotite, and magnetite stability on a phase diagram of fCO versus fH\textsubscript{2}S, pyrite was calculated to be stable at the measured abundance of H\textsubscript{2}S, and sometimes the calculated value depending on the fCO. The calculated, but not measured, H\textsubscript{2}S abundance lies within or close to the pyrrhotite stability field. Only Radoman-Shaw (2019) has tested the stability of pyrrhotite under H\textsubscript{2}S (2 ppm), and he did not observe any evidence of pyrite formation, whether on pyrrhotite or on any other iron bearing mineral. Currently the exact effect of H\textsubscript{2}S on pyrrhotite at Venus conditions is uncertain and further experiments will need to be completed to assess its reactivity.

4.3.2 Effect of S\textsubscript{2}

S\textsubscript{2} is another important gas constituent in the atmosphere of Venus (Krasnopolsky 2007; 2013; Zolotov 1991; San’ko 1980; Zolotov 1992). The effect of S\textsubscript{2} fugacity on pyrite stability was discussed by Zolotov (1991) and by Wood and Brett (1997), however the effect of S\textsubscript{2} on pyrrhotite at Venus temperatures has never been studied experimentally. This is partly because the S\textsubscript{2} fugacity has never been measured on Venus. The reported abundance of S\textsubscript{2}, 0.02 ppmv, was originally calculated based on the measured values of S\textsubscript{3} (1.5-8e\textsuperscript{-5} ppm) obtained from Venera 11/12/13/14 (Von Zahn et al. 1983; Zolotov 1996; Krasnopolsky 1987; Zolotov 2018).
Fegley (1997) recalculated the abundance of $S_2$ using the abundance of $S_3$ and found that the mixing ratio on Venus is 0.014-0.042 ppm. However, recent atmospheric equilibria models places the abundance around 0.2-0.3 ppm (Fegley et al. 1997b; Krasnopolsky 2007; Zolotov 1996; Fegley 1997). Using Gibbs free energy and the van’t hoff equation and assuming 17 ppm of CO, equation [3] will proceed to the left to form pyrrhotite above ~7 km from the planetary radius. This could have important implications for the source of the radar reflective signal found in the highlands. There may be a modest supply of $S_2$ in the highlands of Venus, however results obtained via equilibria models should be treated with caution because the atmosphere may not be in equilibrium (Fegley et al. 1997b; Zolotov 2018).

4.3.3 Effect of Oxygen

A process jeopardizing the stability of pyrrhotite on Venus is oxidation. Pyrrhotite is reported to be oxidized by a multitude of gases such as CO$_2$, CO, COS, SO$_2$, O$_2$, and H$_2$O (Fegley 1997; Fegley and Treiman 1992; Zolotov 2018). We did not witness any oxidation from CO$_2$, COS, and SO$_2$, however there are many factors that limit our ability to determine pyrrhotite’s stability on Venus. The second major issue is our limited data on the abundance of gases near the surface due to the limited number of landers that were able to take measurements (Johnson and de Oliveira 2019). Gas abundances may vary at different altitudes near the surface and this may affect mineral stability. Subtle changes in gas abundance, as seen in calculations completed by Zolotov (2018), can cause shifts in mineral stability. For example, using the van’t hoff equation and assuming CO is 17 ppm and COS is 4.4 ppm equations [5] and [6] will proceed to the left and form pyrrhotite at elevations of >7 km [5] or at the planetary radius [6] (see Supplementary Materials). However we do not know the abundances of CO and COS near the surface (<15 km) because they have not been measured (Arney et al. 2014; Marcq et al. 2017). Some gases, like COS, appear to increase in abundance at lower altitudes (Pollack et al. 1993; Marcq et al. 2017).
Measurements obtained from future landers on Venus is imperative in order to accurately determine surface-atmosphere interaction.

Pyrite and pyrrhotite are often discussed in similar contexts, however pyrrhotite decomposition has been found to be much slower than pyrite decomposition (Fegley et al. 1995; Radoman-Shaw 2019). Treiman and Fegley (1991) calculated that if meter to decameter sized boulders of pyrrhotite are present on Venus they could exist for millions of years. In Hong and Fegley (1997), except for experiments completed in CO₂/O₂, pyrrhotite was found in experiments tested for up to ~160 hours, even when pyrite was no longer present. Meanwhile in Radoman-Shaw (2019)'s pyrrhotite experiments he stated that even after 80 days sulfur was present in the sample under a layer of oxide.

If pyrrhotite is indeed unstable on Venus, it's important to understand how its oxidation to an iron oxide proceeds. Experiments studying the oxidation rate of pyrrhotite, but under Earth atmosphere and oxygen, disclosed that the oxidation reaction is a multi-step process (Janzen et al. 2000; Jones et al. 1992; Mycroft et al. 1995; Pratt 1994). In each of these experiments pyrrhotite was exposed to oxygen or air for varying lengths of time. During the experiments the pyrrhotite broke into several layers; a ferric oxyhydroxide layer at the surface, followed by an iron poor but sulfur rich layer, followed by unreacted pyrrhotite (Jones et al. 1992; Legrand et al. 2005; Mycroft et al. 1995; Pratt 1994). There are two competing theories on the composition of the iron poor/sulfur rich layer: 1) it is composed of pyrrhotite as well as disulfides and polysulfides 2) it is two separate layers where the layer closest to the surface is FeS₂ + other polysulfide bearing iron species and the second layer is Fe₂S₃+Fe₇S₈ (Jones et al. 1992; Mycroft et al. 1995; Pratt 1994). This pattern is produced by the diffusion of iron to the surface where it becomes a ferric oxyhydroxide, creating a sulfur rich/iron poor layer underneath, followed by an untouched pyrrhotite layer beneath that.
This reaction is not expected to stop, however there are several issues that will slow down the rate of reaction. The first is the thick ferric-oxyhydroxide layer will slow down the rate at which iron diffuses to the surface. The second is that electron transfer from the interior to the surface will be hindered due to this thick layer, a process involved in the formation of ferric-oxyhydroxide. A delay in the reaction rate was observed by Pratt et al. (1994); the thickness of the ferric-oxyhydroxide layer in their pyrrhotite was \(~4\ \text{Å}\) thick after a 6.5-hour experiment and \(~8\ \text{Å}\) thick after 50 hours. Over the same two time periods Pratt et al. (1994) observed that the iron poor/sulfur rich layer increased in thickness from \(20\ \text{Å}\) to \(28\ \text{Å}\). This indicates that the rate of oxidation slows down significantly over time, and though we do not know if this mechanism can be applied to other oxygen-bearing gases such as CO\(_2\), it gives important insight into how these ions interact at the surface-gas boundary. According to experiments completed by Straub (1993) O\(_2\) and not CO\(_2\) is the culprit of oxidation into iron oxides on Venus, which means if enough oxygen is present, this reaction mechanism could be occurring. It is important to note that these experiments were completed in ambient temperature, and an increase in temperature will increase the oxidation rate (Janzen, 1996; Lehmann et al. 2000).

A similar layering on the outer rim of pyrrhotite was not reported by Radoman-Shaw (2019), but he mentioned that oxides did not appear to penetrate the entire sample and that the oxide grew in layers. Thus pyrrhotite may not oxidize as quickly as originally calculated, and may potentially be present within rocks or the subsurface on Venus today. Future landers equipped with drills may be able to observe pyrrhotite within rocks, which can inform us on weathering processes on Venus and can also assist in age dating of the surface.

4.3.4 Crystal Structure

Our experiments were completed with a mixture of monoclinic (magnetic) and hexagonal (nonmagnetic) pyrrhotite. It is unclear if Pratt et al. (1994)’s and Mycroft et al. (1995)’s experiments were completed with monoclinic or hexagonal pyrrhotite. Magnetic pyrrhotite was
experimentally found to be more reactive and oxidized at a quicker rate than nonmagnetic pyrrhotite (Becker 2009; Gerson and Jasieniak 2008; Lehmann et al. 2000). Becker (2009) attributed this to the more abundant vacancies in the monoclinic structure, which facilitates the flow of electrons. Monoclinic pyrrhotite also has more ferric iron as opposed to ferrous, and ferric iron itself is an oxidizing agent that can help facilitate oxidation within the structure (Becker 2009; Pratt et al. 1994; Janzen et al. 1996; 2000). On Venus pyrrhotite will take the form of the high temperature structure, hexagonal. Therefore, it may take more time for pyrrhotite to oxidize on Venus.

4.3.5 Recent Volcanism

There has been new research that supports recent or current volcanic activity on Venus. Reinvestigation of Magellan data has revealed evidence of lava flow as young as several decades old (Bondarenko et al. 2010). Analysis of three possible hot spots on Venus by the VIRTIS (Visible and Infrared Thermal Imaging Spectrometer) on Venus Express (VEX) uncovered NIR emissivity anomalies which has led to the conclusion that the flows in these regions are young, possibly younger than 250,000 years (Smrekar et al. 2010). Lastly, observations of bright spots taken by the VMC (Venus Monitoring Camera) on VEX may be a result of recent volcanic eruptions (Shalygin et al. 2015). Thus even if pyrrhotite is not stable for long periods of time, several hundreds to million years according to Treiman and Fegley (1991)’s calculations, since pyrrhotite is the most common mineral in basalt, pyrrhotite formation may be transpiring at this time.

5.0 Conclusion

In our experiments we found that pyrrhotite was stable for up to at least 96 hours when heated at 2 different temperature/pressure regimes and 3 different gas mixtures relevant to Venus. This implies that pyrrhotite is stable at Venus conditions for at least short timescales. Our results offer a unique comparison to other experiments with special relevance to experimental
length, gas composition, and pressurized versus unpressurized vessels. However, future studies with longer experiments are required to further determine the individual effects that CO$_2$, SO$_2$, H$_2$S, and COS have on pyrrhotite stability.

Though strong evidence for pyrrhotite instability at lowland conditions was observed by Radoman-Shaw (2019), its fate in the highlands is still uncertain. The different conditions (temperature, pressure, gas abundance, supercritical fluid versus gas) may influence its stability; thus, it may still have a hand in explaining the radar anomaly. Even in the instance that pyrrhotite does decompose on Venus, experiments have shown that this process occurs relatively slowly. This suggests that it may still exist on Venus, particularly in newly cooling lava flows. This has important implications for data obtained from future landers on surface weathering as well as age dating on Venus.

6.0 Acknowledgements

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8.0 References


Table of $\Delta G^\circ$ and $\Delta H^\circ$ of various compounds collected for, and related to, the paper (T=25°C).

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<td></td>
<td>-107.110◊</td>
<td>-105.437◊</td>
</tr>
</tbody>
</table>

* Chase et al., 1986
† Robie and Hemingway, 1995
# Dean, 1999
◊ Faure, 1998
To calculate the ΔG and ΔH we used the following equations:

\[ \Sigma n_i G_i^{\circ}(\text{products}) - \Sigma n_i G_i^{\circ}(\text{reactants}) = \Delta G^\circ_R \]

\[ \Sigma n_i H_i^{\circ}(\text{products}) - \Sigma n_i H_i^{\circ}(\text{reactants}) = \Delta H^\circ_R \]

Assuming equilibrium (\( \Delta G_R = 0 \)) we can then calculate \( \ln(K) \) via:

\[ \Delta G^\circ_R = -RT\ln(K) \]

The van't Hoff equation was used to extrapolate to conditions found on Venus:

\[ \ln(K_T) - \ln(K_{T^\circ}) = \frac{\Delta H^\circ_R}{R} \left( \frac{1}{T} - \frac{1}{T^\circ} \right) \]

Venus conditions were obtained from Seiff et al. (1986)

Table listing all ΔG and ΔH data for equations presented in the paper (T=25°C).

<table>
<thead>
<tr>
<th>Equation</th>
<th>ΔG (kJ·mol(^{-1}))</th>
<th>ΔH (kJ·mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}_7\text{S}_8 + 6 \text{CO}(g) \rightarrow 7 \text{FeS}_2 + 6 \text{CO}(g) )</td>
<td>-29.6 ±2.6 -0.4</td>
<td>-39.7 ±4.2 -0.8</td>
</tr>
<tr>
<td>( \text{Fe}_7\text{S}_8 + 76 \text{CO}_2(g) = 7 \text{Fe}_3\text{O}_4 + 76 \text{CO}(g) + 24 \text{SO}_2(g) )</td>
<td>694.3 ±1.2 -1.1</td>
<td>858.3 ±0.1 -1.1</td>
</tr>
<tr>
<td>( 3 \text{Fe}_7\text{S}_8 + 28 \text{CO}_2(g) = 7 \text{Fe}_3\text{O}_4 + 12 \text{S}_2(g) + 28 \text{CO}(g) )</td>
<td>147.7 ±4.2 -2.6</td>
<td>171.6 ±5.0 -2.8</td>
</tr>
<tr>
<td>( 3 \text{Fe}_7\text{S}_8 + 28 \text{CO}_2(g) \rightarrow 7 \text{Fe}_3\text{O}_4 + 24 \text{COS}(g) + 4 \text{CO}(g) )</td>
<td>236.1 ±10.6 -6.0</td>
<td>232.8 ±9.8 -3.0</td>
</tr>
<tr>
<td>( \text{Fe}_7\text{S}_8 + 4 \text{CO}_2(g) \rightarrow 7 \text{Fe}_3\text{O}_4 + 4 \text{FeS}_2 + 4 \text{CO}(g) )</td>
<td>48.5 ±6.7 -1.7</td>
<td>40.0 ±8.4 -2.3</td>
</tr>
<tr>
<td>( \text{FeO} \text{ (in minerals)} + 2\text{H}_2\text{S}(g) = \text{FeS}_2 + \text{H}_2\text{O}(g) + \text{H}_2(g) )</td>
<td>-73.0 ±2.4 -4.3</td>
<td>-102.7 ±2.4 -4.1</td>
</tr>
<tr>
<td>( 7 \text{FeO} + 8 \text{H}_2\text{S}(g) = \text{Fe}_7\text{S}_8 + 7 \text{H}_2\text{O}(g) + \text{H}_2(g) )</td>
<td>-50.5 ±4.9 -3.3</td>
<td>-56.3 ±5.7 -3.5</td>
</tr>
<tr>
<td>( 7 \text{FeS}_2 + 6 \text{H}_2(g) = \text{Fe}_7\text{S}_8 + 6 \text{H}_2\text{S}(g) )</td>
<td>13.4 ±2.8 -0.5</td>
<td>33.6 ±3.6 -0.0</td>
</tr>
</tbody>
</table>
Chapter 5
The Effect of Surface Temperature on the Critical Altitude and SO$_2$ Abundance on Venus

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1.0 Abstract

The origin of the radar reflective signal found on several mountain ranges on Venus is still under debate. Here we hypothesized that the altitude at which the reflective signal changes is closely tied to an important greenhouse gas present in the atmosphere, SO$_2$. We assumed that the change in reflectivity is due to the pyrite-magnetite buffer, where pyrite (FeS$_2$) is present in the highlands and magnetite (Fe$_3$O$_4$) is in the lowlands. Using 1D models of the atmosphere of Venus we altered the temperature at the surface to observe its effect on 1) the elevation of the critical altitude where the stable phase switches between pyrite and magnetite and 2) the atmospheric SO$_2$ abundance. Our results indicate that the temperature, SO$_2$ concentration, and critical altitude elevation are closely correlated on Venus. An increase in temperature by 3 K is enough to shift the elevation by 30 meters and increase the corresponding SO$_2$ abundance by 28 ppm. The data obtained from this project can be compared to radar data to uncover if a recent change in climate has occurred on Venus.

2.0 Introduction

Although Venus’ atmosphere is dominated by CO$_2$, there is a significant amount of sulfur bearing compounds present in its thick atmosphere. The most abundant of the sulfur species is SO$_2$, with a mixing ratio of 130 ± 40 to 180 ± 70 ppm (Bézard et al., 1993; Pollack et al., 1993). The upper atmosphere exhibits less SO$_2$, with concentrations as low as a few ppb (Vandaele et al., 2017) (Fig. 1). The remainder of the atmospheric sulfur is believed to be bound in COS, along with trace amounts as S$_x$, SO, SO$_3$, and H$_2$S (Krasnopolsky and Pollack, 1994; Marcq et al., 2017;
Oyama et al., 1979; Prinn, 1973; Prinn, 1985; von Zahn et al., 1983). In addition, sulfur is also captured in sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) droplets that make up a majority of the clouds enshrouding the planet (Prinn, 1973; von Zahn et al., 1983; Pollack, 1978).

Such a large quantity of SO\textsubscript{2} elicits the question of if and how does it interact with the surface. Pyrite (FeS\textsubscript{2}), an iron sulfide and a fairly common mineral on Earth, was suggested as a sulfur bearing mineral on Venus (Barsukov et al., 1980; Lewis & Kreimendahl, 1980; von Zahn et al., 1983). Energy minimization models were used to determine the most likely mineral phases on Venus assuming equilibria; these models found that pyrite and magnetite (Fe\textsubscript{3}O\textsubscript{4}) may be present (Klose et al., 1992; Khodakovskky et al., 1978; 1979). Analysis of the SO\textsubscript{2} mixing ratio on Venus was found to be very close to the equilibrium mixing ratio for a pyrite/magnetite reaction, thus the pyrite-magnetite buffer was hypothesized to occur on Venus (Klose et al., 1992; Zolotov, 1991):

\begin{equation}
[2] \text{Fe}_3\text{O}_4 + 6\text{SO}_2 + 16\text{CO} = 3\text{FeS}_2 + 16\text{CO}_2
\end{equation}

Furthermore, pyrite has been postulated to be stable in the cooler highlands, while magnetite would dominate in the lowlands (Hashimoto & Abe, 2000; Klose et al., 1992). This

![Figure 1: The abundance of SO\textsubscript{2} expressed in volume mixing ratio versus altitude collected from past missions and experiments. VEx is not included. The data shows the largest concentration of SO\textsubscript{2} is found in the mid-atmosphere region with lower concentrations found near the upper atmosphere and surface. Figure obtained from Vandaele et al. (2017).](image-url)
hypothesis would also explain the radar reflective surfaces that are seen in the highlands as a result of pyrite’s high dielectric constant (Klose et al., 1992; Pettengill et al., 1982).

A series of experiments and thermodynamic modeling completed in the 1990s claimed that pyrite is unstable at Venus conditions for long periods of time, only surviving on the surface for hundreds to millions of years depending on the grain size (Fegley et al., 1995). They also stated that pyrite releases $S_2$ and decomposes into pyrrhotite, before the pyrrhotite reacts with $CO_2$ to produce magnetite, $CO$, and $S_2$ (Fegley et al., 1995). It has been emphasized that the stability of Venus’ pyrite cannot be discussed based on their experimental results because their experiments used sulfur-free gases (Hashimoto and Abe, 2005). Conversely, Wood and Brett (1997) contended that $S_2$, which was omitted in past research, is important in the sulfur cycle and has the ability to stabilize pyrite. Additionally, recent experiments claim that pyrite is stable under simulated Venus temperature, pressure, and $CO_2$-$SO_2$-$N_2$ abundance, and thus may be stable on Venus (Kohler et al., 2015). Berger et al. (2019) has also produced evidence for the formation of pyrite in their Venus simulation experiments. As a result, pyrite can still be considered a candidate for the radar reflective signal observed in the highlands.

$SO_2$ is also present on Earth, however Venus’ atmosphere contains approximately 100,000 times more $SO_2$ (Taylor, 2010). Due to its volcanic origins on Earth, the source of $SO_2$ on Venus is also expected to be a consequence of volcanism (Bullock & Grinspoon, 2001; Esposito, 1984; von Zahn et al., 1983). Furthermore, some models have suggested that the current concentration of $SO_2$ on Venus is not in equilibrium, therefore a recent, sudden eruption that disrupted the balance must be the origin for such an overabundance of $SO_2$ in the current Venus atmosphere (Fegley and Treiman, 1992; Bullock & Grinspoon, 2001). In order to explain the abundance currently seen on Venus, volcanism must have transpired as recently as 20 million years ago (Bullock and Grinspoon, 2001). Additional evidence was detected by past missions sent to Venus which observed variations in $SO_2$ abundance in the upper atmosphere (Fig 2).
Thermal emissions and bright spots detected by Venus Express even points to possible recent or current volcanic activity at the surface (Shalygin et al., 2015; Smrekar et al., 2010).

A volcanically active period(s) in Venus’ history would have triggered episodes of climate change. Though researchers currently have no proof of climate change on Venus, evidence of a global resurfacing event is present (Bullock & Grinspoon, 2001; Head et al., 1991). Computer modeling of the history of Venus has supported the hypothesis of possible cooling and warming periods over the course of its history due to volcanism (Bullock & Grinspoon, 2001). Due to the temperature sensitive nature of sulfur bearing minerals it is possible that these warming and cooling periods affected the stability of sulfur bearing minerals on the surface. The change in the stability of sulfur minerals will initiate changes in abundance of gaseous sulfur in the atmosphere, and in turn sulfur bearing gases may cause a climate change by disturbing the radiative balance.

3.0 Methods

The purpose of this study is to observe how a change in the surface temperature would alter the height of the critical altitude (the height where the stable phase changes) and the abundance of SO$_2$. The first part of the project was to input elemental abundances into a code...
(program A) that will calculate all possible chemical reactions and run them until the system was in equilibrium. In this model we incorporated the gases and abundances recommended by Krasnopolsky (2007): CO₂, N₂, SO₂, HCl, CO, COS, HF, and NO. The abundances of each of these gases can be seen in Table 1. The abundances for COS and NO are both recommended by Krasnopolsky (2007) based on previous models of the atmosphere. We assumed that the pyrite-magnetite buffer controls the sulfur abundance and thus the only minerals included in this model were pyrite and magnetite. Our atmospheric temperature profile of Venus was taken from the Venus International Reference Atmosphere (VIRA) (Seiff et al., 1986). The critical altitude (the altitude where magnetite turns into pyrite) is calculated to be 3.35 km, which is close to the average critical altitude found on Venus.

Table 1: The gases and corresponding abundances used in our model. Values were taken from Krasnopolsky (2007).

<table>
<thead>
<tr>
<th>CO₂</th>
<th>N₂</th>
<th>SO₂</th>
<th>COS</th>
<th>H₂O</th>
<th>CO</th>
<th>HCl</th>
<th>HF</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.965</td>
<td>0.034</td>
<td>1.3E-4</td>
<td>2.7E-5</td>
<td>3.0E-5</td>
<td>8.0E-6</td>
<td>5.0E-7</td>
<td>5.0E-9</td>
<td>5.5E-9</td>
</tr>
</tbody>
</table>

We then changed the surface temperature (the temperature at the planetary radius) to observe how this affected the critical altitude. To complete this task, we used program A and combined it with an equation used by Hashimoto & Abe (2000):

\[ S_{\text{tot}} = S_{\text{atm}} + S_{\text{max}} \times (H(z_{\text{py}})) \]

\( S_{\text{tot}} \) represents the total abundance of sulfur in the atmosphere and in the surface, \( S_{\text{atm}} \) is the total amount of sulfur found in \( \text{SO}_2 \), \( S_{\text{max}} \) is the maximum abundance of sulfur potentially fixable in the surface as FeS₂, and \( H(z_{\text{py}}) \) is the fraction of the area that is covered in pyrite. A detailed account on the values used in this equation are explained in Hashimoto & Abe (2000), thus only a brief discussion will be presented in this chapter. The value for \( S_{\text{atm}} \) was set to 130 ppm which is the observed sulfur abundance in the current Venus atmosphere. Since we do not know the exact abundance of sulfur on Venus, we utilized abundances that are found on Earth to calculate \( S_{\text{max}} \).
First, we used the S/C ratio in Earth’s crust which is 3.1*10^{-2} (Ronov & Yaroshevskiy, 1967). Assuming that all carbon in Venus’ surface is present in the atmosphere, the total abundance of sulfur in Venus’ surface is 3.1% when all sulfur is SO₂. Since the atmosphere contains only 130 ppm of SO₂, almost all sulfur is fixed in the minerals. Next, in order to determine the amount of sulfur trapped in FeS₂ we needed to incorporate CaSO₄ into our calculations. The reason we included CaSO₄ is because Venera landers revealed a relatively large percent of Ca bearing minerals leading many to speculate the presence of CaSO₄ on the surface (Bullock & Grinspoon, 2001; Lewis & Kreimendahl, 1980; Barsukov et al., 1980). CaSO₄ is not sensitive to Venus temperatures and thus would be stable everywhere on Venus (Fegley & Treiman, 1992). Assuming all Ca is only found in CaSO₄, we determined the ratio of sulfur trapped in FeS₂ to that trapped in CaSO₄ in the highlands using Fe/Ca=0.72 which is the ratio found in Earth’s crust (Ronov & Yaroshevskiy, 1967). We also know that our H(zpy)=0.026 since our critical altitude is located at 3.35 km. Thus, the ratio of the sulfur trapped in FeS₂ to that trapped in CaSO₄ in the Venus surface is 2*0.72*0.026. That is, \( \frac{2*0.72*0.026}{1+2*0.72*0.026} = 3.6\% \) of surface sulfur is trapped in FeS₂.

Since the sulfur fixed in the surface is 3.1% as atmospheric SO₂ concentration, the actual sulfur trapped in FeS₂ is 0.11%. The sulfur trapped in FeS₂ is \( S_{\text{max}}H(z_{py}) \). Our obtained value of \( S_{\text{max}} \) is 4.3 vol. % as atmospheric SO₂ concentration and \( S_{\text{tot}} \), is 0.12 vol %.

We assumed that the temperature profile of Venus lower atmosphere is given by a polytrope:

\[
\frac{P_s}{P} = \left( \frac{T_s}{T} \right)^{\frac{\gamma}{\gamma-1}}
\]

where \( P \) is pressure, \( T \) is temperature, \( \gamma \) is the ratio of the specific heat at constant pressure to the specific heat at constant volume, and the \( s \) subscript are the values at the planetary radius. When the temperature and pressure at the planetary radius are given, we can calculate the
temperature at any pressure. Our tested surface temperature range was between 722 K and 765 K.

We needed to determine the critical altitude and the atmospheric SO$_2$ abundance simultaneously. While the atmospheric SO$_2$ abundance depends on the critical altitude, the critical altitude depends on both the temperature and the atmospheric SO$_2$ abundance. When the surface temperature is increased the critical altitude moves up in elevation ($Z_2$). However, this releases more SO$_2$ which causes the critical altitude to move down in attitude ($Z_3$). This process then decreases the amount of SO$_2$ in the atmosphere which causes the critical altitude to move somewhere between $Z_3$ and $Z_2$ (not pictured). This process continues until equilibrium is reached. To find the equilibrium, we needed to run a calculation until equation [3] and the pyrite/magnetite

Figure 3: The feedback mechanism that occurs when the surface temperature is altered. Any changes in temperature results in a change in the critical altitude and thus the fugacity of SO$_2$. However, a change in the fugacity also alters the height of the critical altitude. This loop continues until it reaches equilibrium.
buffer code (program A) reached the same value, i.e. the new atmospheric abundance of sulfur. This will also give us the new critical altitude.

In order to verify that the code was calculating correctly, we originally only incorporated gases to calculate the composition of the atmosphere. All gas abundances, with the exception of CO, were similar to the calculated values as recommended by Krasnopolsky (2007). Although the abundance calculated in our program was low, around 5 ppm at the surface and only decreased with altitude, it is a well-known fact that CO concentration in the Venus lower atmosphere is higher than the equilibrium concentration (Krasnopolsky, 2007). To amend this issue, CO was fixed at 8 ppm in our calculation and our code gave an overall composition very similar to that expected on Venus. A future project will involve rectifying this issue by improving the code to calculate the CO abundance.

4.0 Results

When increasing the surface temperature by 10 K it caused the critical altitude to move up 0.16 km (Fig 4a). A large increase, such as 30 K, caused the altitude to increase by 0.88 km. A drop of 10 K from its current temperature plunged the critical altitude by 0.09 km.

As the surface temperature increased, the abundance of SO$_2$ at the critical altitude increased exponentially due to a strong dependence of chemical equilibrium on temperature (Fig 4b). When the surface temperature was raised by 10 K the abundance at the critical altitude doubled to ~260 ppm. An increase by 30 K increased the abundance by 6.5 times to ~845 ppm. Meanwhile a drop of 10 K resulted in a drop in SO$_2$ abundance of more than half its original value, ~57 ppm.
Figure 4: a) The new critical altitude on Venus based on a different surface temperature b) The new SO$_2$ abundance found at the new critical altitudes based on the new surface temperature. An increase in surface temperature results in a larger change in SO$_2$ abundance and a larger shift in the critical altitude than a decrease in temperature.
5.0 Discussion

In our project we assumed that the SO$_2$ is buffered with the surface and we did not consider other sources of sulfur. However, if SO$_2$ is unstable on Venus then it needs to be replenished. This implies that the atmosphere is not in equilibrium. Then, our results can only be applied to Venus during a geologically quiet period.

Our model demonstrates the sensitivity of SO$_2$ abundance to temperature; an increase in surface temperature resulted in a larger abundance of SO$_2$ and a higher elevation for the critical altitude. A raise in surface temperature caused a larger change in the critical altitude compared to the cooling of the surface. This is a result of the exponential dependence of chemical equilibrium on temperature.

The critical altitude calculated by the model is 3.35 km, however the actual average taken from 11 mountain ranges is 3.58 km. Assuming that the critical altitude is the same across Venus, this indicates that the surface temperature at some point in the past was ~748.5 K, much warmer than what is currently observed on Venus today. Such a decrease in temperature to present conditions can be explained by the formation of more H$_2$SO$_4$ at the expense of SO$_2$. When H$_2$SO$_4$ increases in abundance it increases the planetary albedo, which will compensate the greenhouse effect of SO$_2$. SO$_2$ can also be removed from the atmosphere by interaction with surface minerals (Bullock & Grinspoon, 2001; Fegley, 1997). Thus, if SO$_2$ has not been replenished relatively recently, then it is possible that Venus was once warmer.

If we assume the lowest critical altitude (Z=2.5 km) observed on Venus is where the critical altitude should be, this implies that the surface temperature was once much colder than even the 722 K we incorporated in our calculations (Z$_f$=3.25 km). If Venus ever reached such low temperatures this suggests that some recent climate change caused it to increase to the current level today. The origin of such an increase would have at least in part been a result of volcanic
activity which would involve the addition of some SO$_2$ from the mantle. Though not tested, any input in SO$_2$ abundance would likely facilitate an even larger shift in surface temperature.

In our model the critical altitude is only found at one elevation across Venus, however the critical altitude has been observed to start as low as 2.5 km and as high as 4.75 km in elevation depending on the highland region (Klose et al., 1992). Several theories have been proposed to explain this phenomenon, including different sources of the radar anomaly (Treiman et al., 2016), a heterogenous atmosphere, or temperature differences centered around topography (Klose et al., 1992). Thermodynamic modeling of the atmosphere of Venus evidenced that the atmosphere, particularly in the upper atmosphere may not be in equilibrium (Krasnopolsky and Pollack, 1994; Krasnopolsky, 2007). Our model assumes that the atmosphere is in equilibrium which may explain the discrepancy. However, Klose et al. (1992) reasoned that if pockets of different abundances of gases such SO$_2$ and O$_2$ exists, then it would need to exist for millions of years in order to enable a large enough change in the surface composition to explain the high radar reflective signal. Such a situation would require a mechanism that would allow for its stability. Topography may create temperature differences in the highlands of Venus since it is known to induce local temperature differences on Earth (Kubokawa et al., 2016; Raupach & Finnigan, 1997). However there is currently not enough data on the near surface environment of Venus to determine if such an effect is present. Only several probes survived to collect data on the surface of Venus, and none of them acquired temperature data in the highlands.

A factor that was not considered in this project was the SO$_2$/H$_2$SO$_4$ feedback loop. This loop, which was discussed in Hashimoto and Abe (2000) has been found to influence the surface temperature by counteracting the warming effect of SO$_2$ and stabilizing the surface temperature. However, this correlation only continues up until 740 K. At warmer temperatures, such as the 748.5 K that we propose Venus once was, the loop decouples from the SO$_2$ abundance and no longer regulates the surface temperature. Further studies are required to determine its effect on
our model, however assuming Venus’ surface was much warmer than 740 K its effect may be negligible.

6.0 Conclusion

Surface temperature, critical altitude, and SO$_2$ abundance are all intricately intertwined on Venus. A shift in one condition will trigger a radical shift in all the other components. Using this information, we can deduce the occurrence of recent changes in climate on Venus. However, there were several conditions that were assumed because of a lack of data on Venus. These include the stability of pyrite and the assumption that the critical altitude is the same elevation at all locations.

Experiments and computer models have both argued for and against pyrite stability (Fegley et al., 1995; Klose et al., 1992; Kohler et al., 2015; Wood & Brett, 1997). If pyrite is unstable then the pyrite-magnetite buffer does not hold on Venus and some other buffer likely exists. A future mission to explore Venus’ mineralogy is necessary to resolve this dispute and determine the existence of this buffer.

Furthermore, there is no clear explanation as to why the critical altitude on Venus varies based on the highlands. It’s possible that disparities in temperature and gas composition could exist due to topography. Recent research has also hypothesized that the radar reflective signal arose from multiple sources as a result of differences in surface composition (Treiman et al., 2016).

The absence of data in the near surface environment on Venus severely limits our ability to understand the SO$_2$ cycle and its effect on surface mineralogy. Though the results from this project offers valuable insight into the effects of temperature on the critical altitude, future missions are vital in order to produce models that are more comparable to the processes occurring on Venus.
7.0 Acknowledgements

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8.0 References


Chapter 6

Conclusions

1.0 Summary of Results

Since the discovery of the unusual radar reflective signal found in the highlands of Venus researchers have attempted to explain its source through experiments and computer modeling. In this project we used the former to study this phenomenon by examining the stability of various minerals and elements under Venusian conditions: Bi/Te/S, Bi$_2$S$_3$/3Te, Bi$_2$S$_3$/Bi$_2$Te$_3$, Pb, PbO, PbS, PbSO$_4$, and Fe$_7$S$_8$. We also used computer modeling when we studied the effect of surface temperature on the elevation of the critical assuming that the highland emissivity mineral was composed of FeS$_2$.

In Chapter 2 we investigated the possibility of Bi, Te, and S minerals as the source of the reflectivity signal. We simulated three different temperature/pressure regimes which correlate to conditions found at three different altitudes from the planetary radius on Venus. Our results revealed the formation of numerous Bi-, Te-, and S- bearing minerals in all three conditions, with more minerals forming in the lowland condition. One mineral appeared in every experimental scenario completed in this project: tetradymite (Bi$_2$Te$_2$S). We expect that if Bi, Te, and S are sufficiently abundant on Venus to interact with one another then Bi$_2$Te$_2$S should be present. This mineral has not been discussed in the past because there are no thermodynamic values for it on record and thus it cannot be modeled at Venus conditions. Although minerals such as Bi$_2$S$_3$ and Bi$_2$Te$_3$ have high dielectrics, the dielectric constant of Bi$_2$Te$_2$S is unknown. Experiments to determine its dielectric constant are needed to conclude on its ability to explain the source.

If Bi$_2$Te$_3$ was initially present in the tested mixture, it was also present at the end of the experiments. It did form in several experiments, but only in the lowland condition, implying that it may not form in the highlands on Venus. On the other hand, depending on its volatility it may be able to be transported and condense on the cooler highlands. Bi$_2$S$_3$, another mineral of interest, formed when Bi, and S interacted together, however its ability to form on Venus will depend on
the abundance of sulfur and also tellurium. This is because when Bi$_2$S$_3$ was mixed with Te, Bi$_2$Te$_2$S formed, although there was some Bi$_2$S$_3$ remaining at the end of every experiment. The unreacted Bi$_2$S$_3$ may due to a slow reaction rate, therefore the reaction was not completed by the end of the experiments and longer experiments are needed in the future.

One unusual reaction was the interaction between Bi$_2$S$_3$/Bi$_2$Te$_3$ in the highland conditions under CO$_2$/COS gas; in these experiments Bi$_2$S$_3$ was not present at the end. Further experiments are needed to explain the reaction occurring in this scenario, particularly because other experiments that had Bi$_2$S$_3$ in the initial sample still retained some by the end of the experiments. Many of our samples had sulfur loss, therefore if gaseous sulfur, such as S$_2$, is sufficiently abundant on Venus, then it could stabilize sulfur minerals such as Bi$_2$S$_3$ and Bi$_2$Te$_2$S.

All the minerals that formed in the highland condition experiments also formed in the lowland condition experiments. Therefore, if these minerals are to explain the source there must be a mechanism to explain its presence only in the highlands, such as the volatilization and cold-trapping of these minerals in the highlands. Though there is currently no evidence of Bi, Te, and S minerals on Venus, their presence in volcanic vents and fumaroles on Earth, and their volatility and ability to form minerals with high dielectric constants implies that they could be present on Venus and contribute to the source of the radar anomaly.

In Chapter 3 we discussed the stability of various lead and lead minerals (PbS, PbO, and PbSO$_4$) at the lowland (460°C/95 bar) and highland (380°C/45 bar) conditions exposed to three different gas mixtures incorporating gases on Venus. Of the materials tested, only PbS has a high enough dielectric constant to explain the radar anomaly. In our experiments PbS was found to be moderately stable in all experiments with minor oxidation to PbSO$_4$; however, the 24 h and 75 h experiments resulted in a similar abundance of PbSO$_4$. This could indicate that in the case of the chamber the reaction may have reached equilibrium after some abundance of PbSO$_4$ was formed. It is unclear if PbS would continue to oxidize on Venus or would also stop after a certain amount of PbSO$_4$ was produced. When PbSO$_4$ was exposed to Venus conditions XRD results indicated
that it was stable, however the sample darkened in color after exposure to CO\textsubscript{2}/COS and CO\textsubscript{2}/SO\textsubscript{2} implying some change in crystal structure. Analysis via XPS also did not reveal any correlation with the Venus gases. Therefore, at this time we cannot conclude on the cause for the color change.

PbS was produced when Pb and PbO were exposed to CO\textsubscript{2}/COS and CO\textsubscript{2}/SO\textsubscript{2}. This is the first evidence that PbS can form in the highlands of Venus from an interaction between Pb and sulfur gases. Pb and PbO samples exposed to all gases also formed carbonate in the highland condition. Since Pb had minor contamination of PbO before the experiments, and minor oxidation into PbO during the experiments occurred, it’s likely that the carbonates formed from PbO, and not Pb. Carbonates do not have a sufficiently high dielectric constant to explain the signal, but if Pb is present, carbonates likely exist in the highlands.

Due to its ability to form under simulated Venus conditions and its widespread occurrence on Earth, PbS may exist on the surface of Venus. Combining this data with its high dielectric constant there is reasonable evidence that it could be a source of the radar reflective signal. Our results also verify the reactivity of Pb to various gases, such as CO\textsubscript{2}, SO\textsubscript{2}, and COS, found on Venus. Currently, we do not know the exact abundance of these gases in the highlands as well as their stability over time. Furthermore, we do not know if the atmosphere in the highlands is in equilibrium. Both factors are vital to accurately determine the near surface atmosphere and mineralogy of the highlands.

In Chapter 4 we discussed what occurs when pyrrhotite (Fe\textsubscript{7}S\textsubscript{8}) is exposed to Venus conditions for up to 96 hours at the highland and lowland conditions in three different mixtures of gases. Our XRD and LIBS results show that pyrrhotite is stable for at least up to 96 hours. These results contradict previous experiments completed by other researchers who tested pyrrhotite in a variety of different conditions including experiments completed at ambient pressure, open ovens, various gas mixtures, and exposures longer than 96 hours. Based on the numerous and distinct experimental procedures completed on pyrrhotite, it is difficult to exactly determine what
causes its stability and instability. If pyrrhotite is unstable on Venus, our results show that the decomposition is slow or even kinetically inhibited; thus, any pyrrhotite that may have formed in the past may still be present on Venus today. If pyrrhotite is present within rocks or in the subsurface, understanding on its reaction rate could assist future researchers with determining weathering rates and age dating of the Venus surface.

Experiments on its stability in the highland conditions have only been tested by one other research group, however their chamber was unpressurized and open. Equilibrium models have shown that pyrrhotite stability is greatly influences by the abundances of sulfur gases (COS, H₂S, S₈) on Venus. Therefore, the stability of pyrrhotite on Venus will strongly depend on 1) the composition of the atmosphere 2) Any temporal changes in atmospheric abundance and 3) if the atmosphere in the highlands is in equilibrium. Only a future lander sent to the highlands will be able to address these questions and if pyrrhotite is stable on Venus.

Finally, in Chapter 5 we used computer modeling to observe how much of an impact the surface temperature on Venus has on the SO₂ abundance and altitude where the radar anomaly begins. Assuming that the highland is composed of FeS₂ and lowland is Fe₃O₄, we simulated a climate change on Venus by altering the surface temperature. Our results verified our hypothesis and showed that the surface temperature greatly influences the SO₂ abundance and the height of the critical altitude. When the temperature was raised by ~3 K the critical altitude shifted upwards by ~30 m and the SO₂ abundance at the new critical altitude increased by ~27 ppm. An increase in temperature caused the altitude to increase greatly compared to a decrease in temperature because of the exponential dependence of chemical equilibrium on temperature. Our results showed the important effects that climate change can have on Venus and can be used to hypothesize on recent climate changes that could have occurred on this planet.

1.1 Future Work

None of the tested scenarios formed a high dielectric mineral in the highland and not the lowland condition. The only exception was PbS, but due to instrument limitations we could not
test if it could form in the lowland condition. The majority of the minerals that formed were stable in both the highland and lowland conditions (e.g. tetradymite). Either these minerals are not the source because of their stability in both regimes, or there needs to be a mechanism for these minerals to only be present in the highlands, such as volatilization and further trapping of these minerals in the much cooler highlands. Further experiments investigating the ability of these minerals to be transported from the hotter to the cooler conditions would greatly enhance the strength of candidate minerals. For instance, experiments involving an apparatus that simulates both the lowland and the highland condition; this would facilitate the study of the migration of volatile elements/minerals from the lowland condition to their condensation in the highland condition.

Overall longer experiments incorporating other gases on Venus, such as H$_2$S, H$_2$O, and S$_x$, are needed to observe their effect on the stability of candidate minerals. The effect of sulfur gases in particular merits further investigation because of their ability to react and/or stabilize sulfur minerals. Though many of these minerals appeared to be stable in the 24 to 100 h experiments, experiments for >100 h would give better insight into their reaction rates. Understanding of the reaction rate between each of the Venus gases and the minerals will allow us to determine which reaction proceeds the fastest and will elucidate on which minerals are more likely to form on Venus. In situ analysis within the chamber via Raman or infrared spectroscopy would inform us on which minerals are present while exposed to Venus conditions and would allow for observation of any compositional changes in real time. Additionally, frequent measurements of the gas within the chamber via a Gas Chromatograph would inform us on the reactions taking place and will also assist in calculating reaction rates.

In regard to Chapter 5, a future model that incorporates a very important loop, the SO$_2$/H$_2$SO$_4$ loop, would more accurately simulate conditions found on Venus and improve our conclusions. The SO$_2$/H$_2$SO$_4$ feedback loop is a negative feedback loop, if the surface
temperature decreases, so does the abundance of \( \text{SO}_2 \) which then decreases the production of \( \text{H}_2\text{SO}_4 \). This results in a decreased planetary albedo which then increases the surface temperature. This feedback loop stabilizes Venus’ atmosphere from small changes in solar flux and atmospheric abundance of \( \text{CO}_2 \), but only if the surface temperature does not exceed 740 K (Venus’ surface is approximately 735.3 K). At hotter temperatures the loop is overcome by \( \text{SO}_2 \)’s greenhouse effect which will continue to warm the planet until all of the surficial sulfur is present in the atmosphere. The effects of this cycle are important in better understanding climate changes on Venus over time and must be incorporated in future models.

Unfortunately, the equilibrium model we used for this project did not produce the correct abundance of atmospheric \( \text{CO} \) as seen on Venus. In the future we will need to determine the cause for this discrepancy, and what this could mean for the C and O cycles on Venus. It is possible that the measured value may not be entirely accurate since it was only measured \textit{in situ} near the surface (12 km in altitude) once by Venera 12. The acquisition of the abundance today is important to verify that these models accurately simulate the atmosphere of Venus. Since it is a minor greenhouse gas, understanding its role in the atmosphere of Venus is crucial, and its abundance may affect the elevation of the critical altitude on Venus.

Lastly, many of the minerals studied in this project either do not have measured values for their dielectric constant, or since the dielectric constant is influenced by temperature and observing frequency, the dielectric constant has not been measured at Venus conditions. Therefore, experiments to determine their dielectric constant, as well as study their emissivity at these temperatures is vital in order to compare them with Venus surface data. Since the source of radar anomaly may be different depending on the highland, it is important to compare the emissivity of these minerals to the emissivity of these highlands. Any investigation into both properties is imperative to elucidate on which minerals and elements could be the source of this unusual phenomenon.