THE EFFECTS OF VENUSIAN TEMPERATURES, PRESSURES, AND CO_2 ON LEAD MINERALS. S. T. Port[1], A. C. Briscoe, V. F. Chevrier, and A. B. Fitting. University of Arkansas, Fayetteville, AR, 72701; [1](saraport@email.uark.edu)

Introduction: Numerous mountains and mountain ranges on Venus exhibit unusually high radar reflectivity [1-3]. The cause has yet to be determined, but since its discovery researchers have hypothesized various sources for the signal such as surface roughness, chemical weathering, or atmospheric deposition [1-2,4-6]. Here we propose that the latter process is the likely cause of these radar reflective regions.

Galena (PbS) has been put forth as a possible source based on results obtained by computer models [6-7]. However, experiments completed in the past have shown that it is stable in CO_2 at all temperature/pressure conditions on Venus [8]. On Earth, PbS is prone to oxidize and forms anglesite ($PbSO_4$) [9-10]. Depending on the oxidation state of Venus anglesite could be present.

Pb and PbO were also chosen for this study in order to observe if they can react with the gases chosen for our experiments (CO_2, SO_2, COS) to form minerals such as galena or cerussite ($PbCO_3$). Cerussite has a high dielectric constant and could explain the source, and is also borderline stable at the conditions found in the highlands [11-12]. Experiments in SO_2 and COS have not been completed during the writing of this abstract and will be completed in the near future.

Methods: Three different powders were selected for our experiments: Pb, PbO, and $PbSO_4$. One gram of the sample was placed in a Venus simulation chamber and tested at two different temperature/pressure conditions representing two different elevations on Venus. These conditions include the average temperature/pressure around the median planetary radius (460°C/95 bar) and the conditions found near the top of Maxwell Montes (380°C/45 bar), which is approximately 11 km above datum. Each experiment was completed in 99.999% pure CO_2 for 24 hours. After the end of the experiment the sample was cooled to room temperature in pure N_2 before being removed and analyzed via XRD to determine any changes in sample composition or crystal structure.

Results: The results for all the experiments are displayed in Table 1.

XRD analysis revealed that the Pb we purchased for this study has a contamination of PbO, ~25%. The XRD also determined that the PbO that we purchased is a combination of massicot (91%) and litharge (9%); minerals of the same composition, but different crystal structure.

Our XRD results indicate that when Pb was heated in either temperature/pressure condition the results were very similar. In both cases the sample had Pb and PbO. In addition, more PbO was present in the experiment completed in the lowland condition.

When PbO was heated at the lowland condition both massicot and litharge were present, though litharge became much more abundant than massicot. A color change was also observed in the sample. Originally the sample was a uniform color of orange, indicating a mixture of litharge (red) and massicot (yellow), however after the experiment the interior of the sample was yellow, and the exterior was orange. In the highland condition experiment litharge and massicot were present as well as minor amounts of Pb_2O_3 and shannonite (Pb_2OCO_3). In Figure 1 the presence of massicot is highlighted in the untreated PbO, while the small unlabeled peaked are litharge peaks. Meanwhile the presence of litharge is highlighted in the 460°C/95 bar experiment, and the smaller unlabeled peaks are massicot. The 380°C/45 bar spectrum is a combination of all four compounds and the peaks that do not signify either massicot or litharge are either Pb_2O_3 or Pb_2OCO_3.

Anglesite ($PbSO_4$) was found to be unaffected by either temperature/pressure condition.

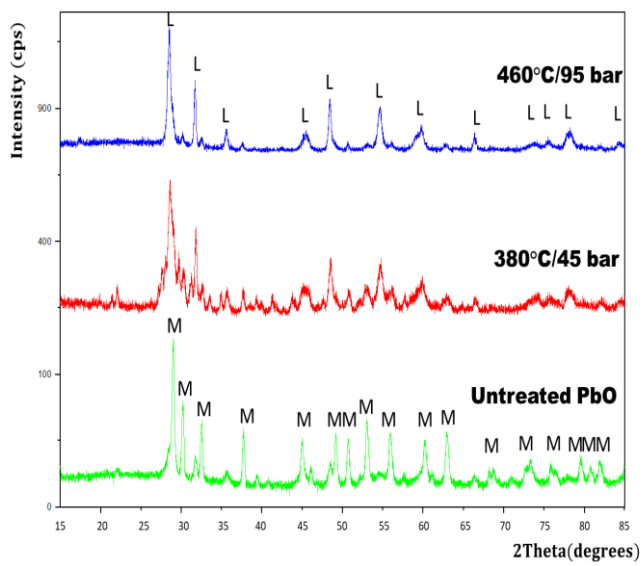

Figure 1: XRD results of PbO. The bottom spectrum is the result for untreated PbO, the middle spectrum is after it was heated to 380°C/45 bar in CO_2, and the top spectrum is after it was heated to 460°C/95 bar in CO_2. M=massicot; L=litharge

Table 1: Summary of all results collected thus far on the stability of lead and lead minerals in CO_2 at two Venus temperature/pressure regimes. M=massicot; L=litharge

	460°C/95 bar		380°C/45 bar	
Pb	Pb PbO (L) PbO (M)	63% 26% 11%	Pb PbO (L) PbO (M)	71% 15% 14%
PbO	PbO (L) PbO (M)	77% 23%	PbO (L) PbO (M) Pb_2O_3 Pb_2OCO_3	RIR not available
$PbSO_4$	$PbSO_4$	100%	$PbSO_4$	100%

Discussion: Our preliminary results indicate that CO_2 has little to no effect on the sample in both tested conditions. More litharge is present in the lowland experiments, however the change in percent is low and may be attributed to error. Massicot, the high temperature/pressure version of PbO [13-14] was also present in both experiments. At ambient pressure the transition between litharge and massicot on average occurs between 763K and 873K, however a transition at 423K has also been observed [13]. In our Pb experiments both litharge and massicot were observed at the highland conditions and thus the addition of pressure likely decreased the transition temperature. The kinetics required to turn from litharge to massicot is faster than in the other direction [13], which explains the presence of massicot even after the sample was cooled to room temperature.

When PbO was exposed to the lowland condition the sample changed from 91% massicot to 23%. As mentioned in the previous paragraph the transition from massicot to litharge has a very slow reaction rate, therefore this result was unexpected. However, the sample collected from this experiment exhibited a separation of massicot, and perhaps the sample was not very well mixed when analyzed in the XRD. This experiment will need to be repeated to determine the accuracy of this result.

In the highland experiment massicot, litharge, and two previously unseen minerals were detected: Pb_2O_3 and Pb_2OCO_3. Two scenarios could explain the formation of Pb_2OCO_3. Either PbO reacts with CO_2 to produce Pb_2OCO_3, or Pb_2OCO_3 forms via the decomposition of cerussite ($PbCO_3$). Since cerussite is stable at cooler temperatures it may be possible that $PbCO_3$ forms as the chamber heats up and then decomposes once the experiment reaches the desired temperature for the experiment. Not much research has been completed on Pb_2O_3, so the exact formation mechanism is unknown, but it likely also forms from an interaction between PbO and CO_2. It is clear, however, that Pb_2OCO_3 and Pb_2O_3 are unstable at hotter temperatures and thus are unlikely to be found in the lowlands of Venus. Though PbO was present in the Pb experiment, no evidence of Pb_2OCO_3 and Pb_2O_3 was seen in those experiments. This is likely because the Pb samples did not have enough PbO to form a detectable level of Pb_2OCO_3 and Pb_2O_3.

$PbSO_4$ was found to be very stable in all tested conditions. It is doubtful that there will be any change to the sample when it is exposed to SO_2 and COS since both gases will be at very low concentrations. According to our calculations the oxygen fugacity on Venus should be high enough to form $PbSO_4$, however this will depend on other reaction pathways that could occur due to the other gases on Venus. Future experiments of Pb and PbO completed in SO_2 and COS may help to answer this question.

Conclusion: Lead (Pb) did not exhibit any considerable changes at Venusian conditions in CO_2. Anglesite ($PbSO_4$) is very stable at all conditions and so is likely to be stable if present on Venus. Both Pb_2OCO_3 and Pb_2O_3 only formed in the PbO experiment completed in highland conditions, and thus are unlikely to be stable in lowland conditions. Currently the dielectric constant of either mineral is unknown. In addition, it is unclear on if Pb_2OCO_3 is forming from the starting compounds or if it is a decomposition product of $PbCO_3$. Future experiments of Pb and PbO completed in SO_2 and COS will be completed to observe if lead and sulfur minerals, such as PbS, can form.

Acknowledgments: This work was funded by the NASA Solar System Workings grant #NNX15AL57G.

References: [1] Masursky, H. et al., (1980) J. Geophys. Res 85, A13, 8232-8260 [2] Pettengill, G.H., Ford, P.G. and Nozette, S. (1982) Science 217, 640-642. [3] Ford, P. G., and Pettengill, G.H., (1983) Science 220, 4604, 1379-1381. [4] Pettengill, G.H., et al., (1980) J. Geophys. Res. 85, A13, 8261-8270 [5] Klose, K.B., Wood J.A., and Hashimoto, A. (1992) J. Geophys. Res. 97, 16353-16369. [6] Brackett, R.A., et al., (1995) J. Geophys. Res., 100, 1553- 1563. [7] Schaefer, L. and Fegley Jr., B. (2004) Geophys. Res. Letters 21, 469-472. [8] Port, S. T., Briscoe, A. C., and Chevrier, V. F. (2018) International Venus Conference, Abstract # 0019 [9] Hagihara, H. (1952), J. Phys. Chem. 56, 610-615 [10] Ponsot, B., Saloman, J., Walter, Ph. (1998) Nucl. Instr. and Meth. in Phys. Res. B 136, 1074-1079 [11] Young, K.F., and Frederikse, P.R. (1973) J. Phys. Chem. Ref Data 2, 2, 313-409 [12] Yamaguchi, J., et al (1980) Thermochimica Acta 35, 307-313 [13] Risold, D., Nagata, J.J., and Suzuki, R.O. (1998) J. Phase Equilibria, 19, 3, 213-233 [14] White, W.B., Dachille, F., and Roy, R. (1961) J. Am. Ceram. Soc. 44, 4, 170-174