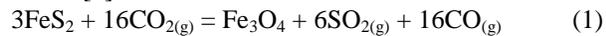


**Stability of Pyrite under Venusian Surface Conditions.** S. T. Port<sup>1</sup>, E. Kohler<sup>1,2</sup>, P.I. Craig<sup>3</sup>, and V. Chevrier<sup>1</sup>.  
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**Introduction:** The existence of pyrite (FeS<sub>2</sub>) on the surface of Venus has been theorized since the 1980s when sulfur was revealed to be an important component of the Venusian atmosphere [1, 2]. Utilizing data obtained from the Venera and Pioneer missions, combined with Earth-based observations, scientists have attempted to determine a geochemical sulfur cycle to explain the replenishment of atmospheric sulfur [3-5]. Past chemical equilibrium calculations illustrate that pyrite, pyrrhotite (Fe<sub>7</sub>S<sub>8</sub>), or anhydrite (CaSO<sub>4</sub>) is the most likely sulfur bearing mineral found on the surface [4-5]. However, based on the temperature range on Venus, CaSO<sub>4</sub> is not expected to greatly affect the concentration of sulfur in the atmosphere and pyrrhotite is thought to be unstable [5]. Pyrite is sensitive to temperature and may form and decompose at different locations on Venus, thereby releasing and absorbing gaseous sulfur from the atmosphere [3]. For instance, pyrite is expected to form at low temperatures and oxidize to magnetite (Fe<sub>3</sub>O<sub>4</sub>) at high temperatures. This process can be observed in the pyrite-magnetite buffer [3]:



Pyrite may also explain the high radar reflectivity regions found on the Venusian highlands due to pyrite's high electrical conductivity [4, 6-9].

However, thermodynamic modeling and experimentation demonstrates that pyrite would decompose into iron oxides, such as magnetite or hematite, and sulfur vapor at all Venusian conditions [10]. This is due to the predicted low sulfur vapor on the surface and because the atmosphere is expected to be quite oxidative. It was measured that pyrite in a CO<sub>2</sub>-CO-SO<sub>2</sub> environment would decompose as rapidly as 1225±238 days/cm on Maxwell Montes [10].

This work intends to investigate the stability of pyrite under Venusian conditions, specifically to determine the effect of SO<sub>2</sub> on pyrite.

**Methods:** Two sets of experiments were completed in order to assess the stability of pyrite on Venus: the Lindberg tube oven experiments and the Venus simulation chamber experiments. The Lindberg tube oven experiments were conducted at the University of Arkansas in Fayetteville. In these experiments 1 gram of powdered pyrite was heated to either 380°C or 460°C under either a 100% CO<sub>2</sub> atmosphere or a simulated Venus atmosphere, which consists of 95.6% CO<sub>2</sub>, 3.5% N<sub>2</sub>, and 150 ppm of SO<sub>2</sub>. The temperature values used in the experiments represent the conditions found

on the highlands (11 km) and lowlands (0 km) of Venus, respectively.

Powdered pyrite was also studied in the Venus simulation chamber at the National Aeronautics and Space Administration Goddard Space Flight Center to observe the effects of pressure on pyrite. Similarly to the oven experiments, 1 gram of pyrite was measured and inserted into the chamber at either Venusian surface or Venusian highland temperatures and pressures (460°C & 95bar, and 380°C & 55bar, respectively). The experiments were conducted in either a 100% CO<sub>2</sub> atmosphere or the Venus simulated atmosphere. Each experiment ran for 18 hours then the samples were removed and weighed. The samples were analyzed using X-Ray Diffraction (XRD) to determine any changes in the composition or phase of the sample.

**Results:** In the Lindberg oven and CO<sub>2</sub> atmosphere experiments, there was partial oxidation of pyrite into hematite (Fe<sub>2</sub>O<sub>3</sub>) at 380°C, with complete oxidation at 460°C. However, in the Venusian atmospheric composition, pyrite was completely stable at 380°C and decomposed into pyrrhotite and sulfur at 460°C.

In the Venus chamber experiments in a CO<sub>2</sub> environment, pyrite was mostly stable (90%) at 380°C, however some magnetite was created (10%). In the 460°C environment the pyrite was less stable (65%) and pyrrhotite (35%) formed. In the Venusian atmosphere at 380°C, 85% of the sample was still pyrite, but solid sulfur was present as well. At 460°C, the entire sample identified as pyrite indicating stability. A summary of results are found in Table 1a&b.

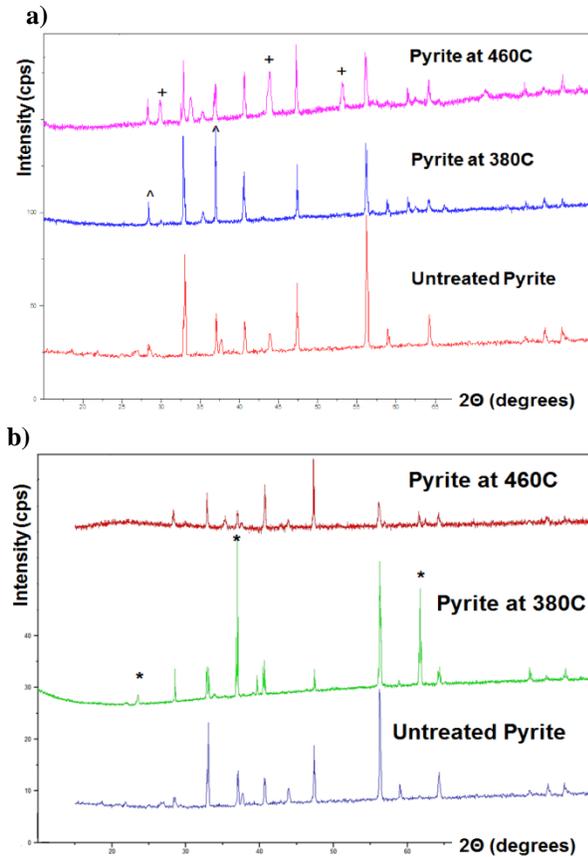
**Table 1a&b:** An overall summary of the experiments and the results are given here. Table 1a displays the conditions and results of the oven experiments and Table 1b displays the conditions and results of the chamber experiments.

a)

	460°C, 1 bar		380°C, 1 bar	
CO <sub>2</sub> (100%)	Fe <sub>2</sub> O <sub>3</sub>	100%	FeS <sub>2</sub>	88%
			Fe <sub>2</sub> O <sub>3</sub>	12%
CO <sub>2</sub> (95.55%), N <sub>2</sub> (3.5%), SO <sub>2</sub> (150ppm)	Fe <sub>0.875</sub> S <sub>2</sub>	70%	FeS <sub>2</sub>	100%
	S	30%		

b)

	460°C, 95 bar		380°C, 55 bar	
CO <sub>2</sub> (100%)	FeS <sub>2</sub>	65%	FeS <sub>2</sub>	90%
	Fe <sub>0.875</sub> S <sub>2</sub>	35%	Fe <sub>3</sub> O <sub>4</sub>	10%
CO <sub>2</sub> (95.55%), N <sub>2</sub> (3.5%), SO <sub>2</sub> (150ppm)	FeS <sub>2</sub>	100%	FeS <sub>2</sub>	85%
			S	15%



**Figure 1:** a) XRD results of chamber experiments of pyrite in a CO<sub>2</sub> atmosphere. Untreated pyrite is graphed at the bottom, followed by pyrite heated to 380°C (55bar), followed by pyrite heated to 460°C (95bar) b) XRD results of chamber experiments of pyrite in the Venus simulated atmosphere. Untreated pyrite is graphed at the bottom, followed by pyrite heated to 380°C (55bar) followed by pyrite heated to 460°C (95bar). (+) shows peaks of pyrrhotite, (^) shows peaks of magnetite, and (\*) shows peaks of sulfur.

**Discussion:** Similar to the findings in previous thermodynamic models, pyrite was unstable and readily oxidized in a pure CO<sub>2</sub> environment at all pressures, with the exception of the 460°C/95 bar experiment [5, 10]. However, when the samples were placed in a mixed atmospheric environment, pyrite was found to be more stable than expected with no oxidation. The only experiments that demonstrated instability was the 460°C/1 bar and the 380°C/55 bar experiments.

The stability of pyrite in a Venus simulated atmosphere was unexpected. It appears that the SO<sub>2</sub> in the atmosphere prevents the oxidation of pyrite. Additionally, the identification of elemental sulfur in the 380°C and 55 bar experiment was unanticipated. Possible causes are that the sulfur was dissociated from the pyrite, or from the SO<sub>2</sub> in the atmosphere. If the former hypothesis is the case, then an iron byproduct would be

detected. However, the absence of iron as an observable byproduct strongly supports the latter conclusion.

**Conclusion:** Our results show that pyrite is stable under Venusian temperature, pressure, and atmospheric conditions, but only partially stable in a 100% CO<sub>2</sub> atmosphere. Previous experiments did not account for pressure which may in part explain the disparity between our results. The exact source of the solid sulfur has not been determined, but it may originate from the dissociation of SO<sub>2</sub> gas.

**Future Work:** The Center for Space and Planetary Sciences at the University of Arkansas will be obtaining a Venus simulation chamber that can be connected to a gas chromatograph and will feature a sapphire window. With these new accessories, we hope to measure the atmospheric composition during the experiments. An understanding of the change in atmospheric composition will uncover more about the chemical reactions that possibly take place on Venus.

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**References:** [1] Prinn, R. G. (1985) *The Photochemistry of Atmospheres* (J. S. Levine, Ed.), pp. 281–336. Academic Press, New York. [2] Von Zahn et al. (1983) *Venus* pp. 299-430. Univ. of Arizona Press, Tucson. [3] Hashimoto, G. L., and Abe, Y. (2000) *Earth Planets Space*, 52, 197-202. [4] Klose, K.B., Wood J.A., and Hashimoto, A. (1992) *J. Geophys. Res.*, 97, 16353-16369. [5] Fegley Jr., B. and Treiman, A.H. (1992) *AGU, Geophysical Monograph No. 66*, 7-71. [6] Pettengill, G.H., et al. (1982) *Science*, 217, 640-642. [7] Pettengill, G.H., et al. (1988) *J. Geophys. Res.*, 93, 14,881-14,892. [8] Ford, P.G., and Pettengill, G.H. (1983) *Science*, 220, 1379-1381 [9] Wood, J. A. and Brett, R. (1997) *Icarus*, 128, 472-473.4. [10] Fegley Jr., B. (1997) *Icarus*, 128, 474-479.