

**THE STABILITY OF PYRRHOTITE AT VENUSIAN CONDITIONS.** S. T. Port<sup>1</sup>, A. C. Briscoe, and V. Chevrier, University of Arkansas, Fayetteville, AR, 72701; <sup>1</sup>(saraport@email.uark.edu)

**Introduction:** Pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) is a common sulfide mineral on Earth whose stability on Venus was first examined in connection to pyrite [1-3].

Pyrrhotite has a high dielectric constant [5-6], and could be a possible source of the radar reflective signal found in the mountaintops on Venus. A pyrrhotite-pentlandite assemblage has also been suggested to explain some of the radar bright region found in the lowlands near impact craters [7]. In addition, it has been proposed to be a source of COS [1,3], a common gas on Venus with around  $4.4 \pm 1$  ppmv at 33 km in altitude [4].

Calculations completed by [3] have stated that the stability of pyrrhotite depends on the oxidizing conditions found on the surface of Venus, and that if pyrrhotite is stable, it would only be found in the lowland conditions. In addition, experimental research has found that pyrrhotite is unstable and will oxidize slowly over millions of years [8]. However, the oxidization state of Venus is not known, and it has been argued that the experiments did not accurately represent Venus since it was an open system [9]. Thus there is still some ambiguity on the stability of pyrrhotite on Venus and if it can be a source of the radar reflective signal.

**Methods:** The stability of one gram of ground pyrrhotite was tested inside a chamber at Venusian temperatures and pressures. The chamber was placed in vacuum before it was filled with one of three different gases: 100%  $\text{CO}_2$ , 100ppm of  $\text{SO}_2$  in  $\text{CO}_2$ , or 100ppm of COS in  $\text{CO}_2$ . In experiments completed in pure  $\text{CO}_2$  the sample was heated to either  $460^\circ\text{C}/95$  bar or  $380^\circ\text{C}/45$  bar. These are the average conditions found at the planetary radius and 11 km above it, respectively. Experiments completed in the mixed gases were only heated to  $380^\circ\text{C}/45$  bar. Pyrrhotite tested in  $\text{CO}_2$  was tested for 24, 72, and 96 hours while experiments completed in the mixed gases have only been tested for 24 and 48 hours at this time.

After the completion of the experiment the gas within the chamber was removed and replaced with  $\text{N}_2$ , and the sample was allowed to cool to room temperature. Afterwards the sample was removed and analyzed using an XRD to observe any compositional or structural changes to the sample.

**Results:** The original sample is a mixture of hexagonal and monoclinic pyrrhotite. When the sample was heated in the lowland condition ( $460^\circ\text{C}/95$  bar) in  $\text{CO}_2$  for 24 hours the sample was either a mixture of hexagonal and monoclinic pyrrhotite or pure hexagonal pyrrhotite. When pyrrhotite was exposed to  $\text{CO}_2$  for 72 hours it was also a mixture of hexagonal and monoclinic pyrrhotite. In the 96 hour experiment the sample

contained 90% pyrrhotite and 10% magnetite ( $\text{Fe}_3\text{O}_4$ ). The XRD spectra for these set of experiments can be seen in Figure 1.

Results collected from all the experiments completed in the highland condition ( $380^\circ\text{C}/45$  bar) are displayed in Table 1. When pyrrhotite was heated in  $\text{CO}_2$  at highland condition for 24 and 72 hours the samples were a mixture of hexagonal and monoclinic pyrrhotite.

The pyrrhotite heated in the highland condition in  $\text{CO}_2/\text{SO}_2$  was all hexagonal pyrrhotite after 24 hour, and it was a mixture of hexagonal and monoclinic when it was tested for 48 hours. The same results were obtained when pyrrhotite was heated in the highland condition in  $\text{CO}_2/\text{COS}$ .

$\text{CO}_2$		$\text{CO}_2/\text{SO}_2$		$\text{CO}_2/\text{COS}$	
24 hr	72 hr	24 hr	48 hr	24 hr	48 hr
FeS (H)	FeS (H)	FeS (H)	FeS (H)	FeS (H)	FeS (H)
$\text{Fe}_7\text{S}_8$ (M)	$\text{Fe}_7\text{S}_8$ (M)	$\text{Fe}_7\text{S}_8$ (H)	$\text{Fe}_7\text{S}_8$ (M)	$\text{Fe}_7\text{S}_8$ (H)	$\text{Fe}_7\text{S}_8$ (M)

Table 1: Summary of all of the results from experiments completed in the highland condition ( $380^\circ\text{C}/45$  bar). H=hexagonal; M=monoclinic

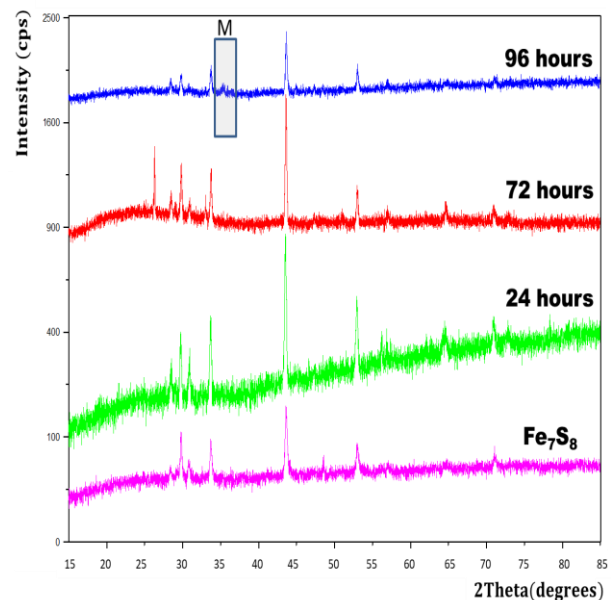


Figure 1: XRD results for pyrrhotite when it was heated in the lowland condition ( $460^\circ\text{C}/95$  bar) in pure  $\text{CO}_2$  for different lengths of time. The bottommost spectrum is the control. The spectra above this is the result for the 24 hour long experiment and above this is the 72 hour long experiment. The topmost spectrum is when it was heated for 96 hours. The box highlights the formation of magnetite in the sample.

**Discussion:** It is important to briefly outline the major differences between hexagonal and monoclinic pyrrhotite before discussing our results. The formation of hexagonal and monoclinic pyrrhotite is correlated to the iron/sulfur ratio and is also temperature sensitive. Hexagonal pyrrhotite forms either when the Fe/S ratio approaches one or the temperature is elevated to  $\sim 250^\circ\text{C}$  or higher [8,10]. Monoclinic pyrrhotite is the low temperature version of pyrrhotite and is stable at a smaller Fe/S ratio. The crystal structure is temperature dependent, thus the sample will convert from monoclinic to hexagonal when heated and will revert upon cooling.

Our original pyrrhotite sample is a mixture of FeS (hexagonal) and 4C (monoclinic) pyrrhotite. At the end of several of our experiments our samples contained 3C (monoclinic) pyrrhotite, a structure that is more stable at slightly higher temperatures than 4C [10]. In these cases when the sample was cooled it was quenched somewhere within the 3C stability field instead of reverting to 4C pyrrhotite at room temperature.

When pyrrhotite was heated in the lowland condition in  $\text{CO}_2$  no drastic changes were observed in the 24 and 72 hour experiments. There was one instance where the sample was pure hexagonal pyrrhotite, but this was not reciprocated in any other experiment. This is likely due to the sample being sufficiently quenched at the end of the experiment. Due to the frequency at which monoclinic pyrrhotite is present in our samples, we can conclude that most of the samples are not quenched quickly enough to prevent its formation.

In the lowland condition  $\text{CO}_2$  experiment completed for 96 hours our sample contained monoclinic pyrrhotite and magnetite, but there was no evidence of hexagonal pyrrhotite. In this case the sulfur is lost from the sample in the form of either  $\text{S}_2$  or COS as seen in equations 1-4:

- (1)  $3\text{Fe}_7\text{S}_8 + 28\text{CO}_2 = 7\text{Fe}_3\text{O}_4 + 12\text{S}_2 + 28\text{CO}$  [8]
- (2)  $3\text{Fe}_{0.875}\text{S} + 3.5\text{CO}_2 = 0.875\text{Fe}_3\text{O}_4 + 3\text{COS} + 0.5\text{CO}$  [2]
- (3)  $6\text{FeS} + 8\text{CO}_2 = 2\text{Fe}_3\text{O}_4 + 3\text{S}_2 + 8\text{CO}$
- (4)  $3\text{FeS} + 4\text{CO}_2 = \text{Fe}_3\text{O}_4 + 3\text{COS} + \text{CO}$  [1]

In highland condition  $\text{CO}_2$  experiments there were no observable changes to the samples regardless of the experimental length. In both mixed gas experiments pure hexagonal pyrrhotite was found in 24 hour and a mixture of hexagonal and monoclinic was found in the 48 hour experiment. Though sulfur is found in these gases, they appear to have no influence on the sample. The abundance of hexagonal pyrrhotite in the 24 hour experiments is likely due to the sample not being quenched rapidly enough rather than any change to the sulfur abundance in the sample. If the latter were the case, we would expect to see a larger abundance of FeS

and perhaps some  $\text{Fe}_9\text{S}_{10}$ , however there is no evidence for either.

**Conclusion:** Based on our preliminary results pyrrhotite is unaffected by temperature, pressure, and gas over short periods of time. The only experiment that resulted in a change to the sample was when it was tested in the lowland condition for 96 hours. Therefore the length of exposure time to Venus conditions appears to play a role in its stability. In this case there is clear evidence that the  $\text{CO}_2$  oxidized the pyrrhotite to form magnetite.

**Future Work:** Our next step is to study the stability of pyrrhotite for 100 hours at both the highland and lowland condition in  $\text{CO}_2$  in order to assess if temperature/pressure influences the oxidation of pyrrhotite to magnetite. We will also test its stability at highland conditions for 100 hours in both mixed gases to observe if sulfur gases can impact the stability of pyrrhotite over longer periods of time.

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