

## NOTE

# Why Pyrite Is Unstable on the Surface of Venus

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The observed sulfur vapor abundance near Venus' surface is lower than the amount needed for pyrite to be stable. This conclusion is reached using either the observed  $S_3$  abundance or the  $S_2$  abundance calculated from the observations of  $S_3$ . Furthermore, the atmosphere is too oxidizing for pyrite to be stable. Pyrite is unstable at Venus' modal radius of 6051.4 km (1992. P. G. Ford and G. H. Pettengill, *J. Geophys. Res.* 97, 13,103–13,114) where  $T = 740$  K and  $P = 95.6$  bar (1986. A. Seiff, J. T. Schofield, A. J. Kliore, F. W. Taylor, S. S. Limaye, H. E. Revercomb, L. A. Sromovsky, V. I. Kerzhanovich, V. I. Moroz, and M. Ya. Marov, In *The Venus International Reference Atmosphere* (A. J. Kliore, V. I. Moroz, and G. M. Keating, Eds.), pp. 3–58. Pergamon Press, Oxford). Pyrite is also unstable at 6056 km ( $T = 705$  K,  $P = 71.2$  bar), which is at 4.6 km altitude in the low radar emissivity region (Pettengill *et al.* 1996). Any pyrite on Venus' surface should decompose rapidly to iron oxides and sulfur vapor, as experimentally demonstrated by Fegley *et al.* (1995. B. Fegley Jr., K. Ladders, A. H. Treiman, and G. Klingelhöfer. *Icarus* 115, 159–180). © 1997 Academic Press

**Introduction.** In the early 1980s the Venus sulfur cycle was proposed to explain spacecraft and Earth-based observations of the sulfuric acid clouds, sulfur-bearing gases in the lower atmosphere, and sulfur-bearing phases on Venus' surface (Von Zahn *et al.* 1983, Prinn 1985). Pyrite ( $FeS_2$ ) decomposition to iron oxides and sulfur vapor is an important part of the sulfur cycle, but the reactions involved and the corresponding reaction rates were unknown when the cycle was first proposed.

Fegley *et al.* (1995a) studied pyrite decomposition in  $CO_2$  and  $CO_2$  gas mixtures because of its importance for the Venus sulfur cycle. The measured pyrite decomposition rates in a  $CO_2$ – $CO$ – $SO_2$  gas mixture are equivalent to lifetimes of  $1225 \pm 238$  days/cm at the top of Maxwell Montes ( $\sim 660$  K) and  $233 \pm 133$  days/cm in the plains ( $\sim 740$  K). However, Wood and Brett (1997) claim that the gas mixtures we used are irrelevant to Venus. This criticism is incorrect and our conclusion that pyrite decomposes rapidly on Venus' surface remains robust.

Here, I first show that  $S_2$  is present in our pyrite decomposition experiments. I then show that the measured  $S_2$  pressures in our experiments are in good agreement with literature data for the  $S_2$  vapor pressure over pyrite + pyrrhotite. This is important because the measured  $S_2$  pressures in our experiments are higher than the calculated  $S_2$  pressures at the surface of Venus, and pyrite decomposition occurs in our experiments.

Thus, the experimental pyrite decomposition rates are relevant to Venus where the  $S_2$  pressure is lower than in the experiments of Fegley *et al.* (1995a). I then consider *in situ* observations of Venus' lower atmosphere and use the *observed*  $S_3$  partial pressure and thermodynamic data from the literature to calculate the  $S_2$  pressure in Venus' lower atmosphere. Finally, I show that (1) both the *observed*  $S_3$  pressure and the calculated  $S_2$  pressure in Venus' near-surface atmosphere are lower than the amount needed for pyrite stability, and (2) that Venus' atmosphere is too oxidizing for pyrite to be stable.

**Gas chemistry in the laboratory experiments.** Fegley *et al.* (1995a) studied pyrite decomposition in  $CO_2$  and  $CO_2$  gas mixtures containing 96.3–100%  $CO_2$ , 0–1.9%  $CO$ , and 0–1.8%  $SO_2$ . This was done because the  $CO_2$  abundance is 96.5%, the  $CO$  abundance is 17 parts per million by volume (ppmv), and the  $SO_2$  abundance is 25 ppmv below 12 km altitude in Venus' atmosphere (Bertaux *et al.* 1996, Zolotov 1996). Thus, the laboratory mixtures spanned the observed  $CO_2$ ,  $CO$ , and  $SO_2$  abundances near Venus' surface.

Fegley *et al.* (1995a) reported condensation of elemental sulfur in the water-cooled gas outlet fitting at the top of their furnace and suggested that sulfur vapor was present in their gas mixtures. Hong *et al.* (1996) verified this suggestion by using the transpiration method (Merton and Bell 1967) to measure the  $S_2$  pressure over decomposing pyrite in  $CO_2$  and  $CO_2$  gas mixtures. The transpiration method is described in the Appendix. The  $S_2$  pressures measured by Hong *et al.* (1996) as a function of temperature are plotted in Fig. 1 and are tabulated in the Appendix. Literature data for the  $S_2$  vapor pressure over coexisting pyrite+pyrrhotite are also plotted in Fig. 1.

Hong *et al.*'s (1996) data confirm that  $S_2$  is present in the experimental gas mixtures used to study pyrite decomposition. Figure 1 shows that Hong *et al.*'s  $S_2$  pressures are in good agreement with literature data for the  $S_2$  vapor pressure over coexisting pyrite+pyrrhotite. Hong *et al.* (1996) also observed pyrite decomposition in their experiments and found the same pyrite decomposition rate as reported by Fegley *et al.* (1995a).

Wood and Brett (1997) assert that Fegley *et al.* (1995a) included  $SO_2$  in some experiments to control the  $S_2$  pressure. This statement is incorrect and Fegley *et al.* (1995a) do not claim control of the  $S_2$  pressure by  $SO_2$ . Instead, as stated several times in their paper, Fegley *et al.* (1995a) were interested in reproducing the  $SO_2$  molecular number density at the surface of Venus. I have published a series of abstracts and papers arguing that  $CO$ – $CO_2$  and  $CO$ – $CO_2$ – $SO_2$  gas mixtures do not equilibrate in the laboratory at Venus surface temperatures (Fegley *et al.* 1994, 1995a,b, Fegley and Ladders 1995). However, this work is not discussed by Wood and Brett (1997) who instead imply that Fegley *et al.* (1995a) expected gas phase equilibrium in their furnace experiments. In fact this is not the case, and on p. 172 of their paper Fegley *et al.* (1995a) discuss evidence

that furnace gas mixtures probably do not equilibrate at Venus surface temperatures. I return later to the question of gas phase equilibrium between CO, CO<sub>2</sub>, and SO<sub>2</sub> on Venus, which we have already considered elsewhere (Fegley and Lodders 1995, Fegley *et al.* 1997a,b).

*Sulfur vapor abundance near the surface of Venus.* I now discuss observations of sulfur vapor near the surface of Venus. Spectrophotometers on Venera 11-14 measured the absorption of blue sunlight by sulfur vapor in Venus' lower atmosphere (Von Zahn *et al.* 1983, Krasnopolsky 1987). The observed absorption is dominantly due to S<sub>3</sub>, possibly with some contribution from S<sub>4</sub>. As noted by Von Zahn *et al.* (1983) S<sub>3</sub> is a better absorber than S<sub>4</sub> in the 450–550 nm wavelength range of the Venera spectrophotometers. In addition the equilibrium S<sub>3</sub>/S<sub>4</sub> ratio is >1000 below 15 km on Venus (San'ko 1980, Zolotov 1985). The observed S<sub>3</sub> mixing ratios vary from  $1.5 \times 10^{-11}$  at 3 km to  $4 \times 10^{-11}$  at 15 km in the Venera 11/12 data (Von Zahn *et al.* 1983, Zolotov 1996). S<sub>3</sub> mixing ratios of  $2.7 \times 10^{-11}$  and  $8 \times 10^{-11}$  at 5–25 km were observed by Venera 13 and 14 (Krasnopolsky 1987).

*Pyrite decomposition on Venus (740 K).* Sulfur vapor is composed of different allotropes (S, S<sub>2</sub>, S<sub>3</sub>, S<sub>4</sub>, S<sub>5</sub>, S<sub>6</sub>, S<sub>7</sub>, S<sub>8</sub>) but S<sub>2</sub> is the dominant gas in sulfur vapor at Venus surface conditions. Only S<sub>3</sub> was measured on Venus because S<sub>2</sub> does not absorb light in the wavelength range of the Venera spectrophotometers. However, the S<sub>2</sub> and S<sub>3</sub> abundances are coupled via the reaction



Unlike CO–CO<sub>2</sub>–SO<sub>2</sub> mixtures, the allotropes in sulfur vapor equilibrate with one another at Venus surface temperatures on laboratory time scales (Braune *et al.* 1951). As discussed below, sulfur vapor allotropes also equilibrate with each other near the surface of Venus (San'ko 1980, Zolotov 1985). Thus, I can use the *observed* S<sub>3</sub> abundances to calculate the S<sub>2</sub> abundance on Venus.

The temperature dependent equilibrium constant from Gurvich *et al.* (1989–1994) for equation (1) is

$$\log_{10}K_1 = 6.789 - 4981.6/T \quad (2)$$

and the S<sub>2</sub> pressure in equilibrium with the S<sub>3</sub> pressure is given by

$$\log_{10}P_{S_2} = (1/3)\log_{10}K_1 + (2/3)\log_{10}P_{S_3}. \quad (3)$$

Using Eqs. (2) and (3) and the observed S<sub>3</sub> mixing ratios of (1.5–8)  $\times 10^{-11}$ , I calculate that the S<sub>2</sub> mixing ratio in Venus' atmosphere at 740 K and 95.6 bar (modal radius of 6051.4 km) is  $X_{S_2} = (1.4\text{--}4.2) \times 10^{-8}$ , in good agreement with values of  $X_{S_2} = 2 \times 10^{-8}$  and  $X_{S_2} = 1.3 \times 10^{-8}$  calculated by San'ko (1980) and Zolotov (1985), respectively, from the observed S<sub>3</sub> mixing ratios. Their calculations only considered the S<sub>3</sub> data from Venera 11/12 and did not take into account the higher S<sub>3</sub> mixing ratios of up to  $8 \times 10^{-11}$  later reported by Venera 13 and 14 (Krasnopolsky 1987). Therefore, my upper limit for the calculated S<sub>2</sub> mixing ratio is larger than their values. San'ko (1980) and Zolotov (1985) also showed that their equilibrium modeling reproduced the vertical profile of the absorption measurements by Venera 11/12 below 12–14 km in Venus' atmosphere. The match between theory and observations indicates that sulfur vapor allotropes are in equilibrium with one another in Venus' near-surface atmosphere (San'ko 1980, Zolotov 1985).

At 740 K, my calculated S<sub>2</sub> pressures  $P_{S_2} = X_{S_2} \times (95.6 \text{ bar})$  are  $(1.3\text{--}4.1) \times 10^{-6}$  bar. For comparison, at 740 K San'ko (1980) and Zolotov (1985) calculated S<sub>2</sub> pressures  $P_{S_2}$  of  $1.9 \times 10^{-6}$  bar and  $1.2 \times 10^{-6}$  bar, respectively. All of these values are lower than the S<sub>2</sub> pressure of  $\sim 7 \times 10^{-6}$  bar over coexisting pyrite and pyrrhotite at 740 K (Barker and Parks 1986; see also Fig. 1). The calculated S<sub>2</sub> pressures on Venus are also

lower than the S<sub>2</sub> pressure at 740 K in our pyrite decomposition experiments (Fig. 1). This comparison shows that the calculated S<sub>2</sub> pressures on Venus are lower than the S<sub>2</sub> pressure needed to prevent pyrite decomposition to pyrrhotite (Fe<sub>1-x</sub>S).

Wood and Brett (1997) present different S<sub>2</sub> pressures on Venus because they do not consider the spacecraft observations of sulfur vapor near the surface of Venus, and instead calculate S<sub>2</sub> pressures assuming chemical equilibria between CO, CO<sub>2</sub>, SO<sub>2</sub>, and OCS. However, as discussed earlier, Wood and Brett (1997) calculate that CO–CO<sub>2</sub>–SO<sub>2</sub> mixtures do not equilibrate in a laboratory furnace, a conclusion already reached by Fegley *et al.* (1995b, 1997a). Thus, we have to ask if C–O–S gases equilibrate on Venus.

We have already considered the question of C–O–S gas equilibrium on Venus (Fegley and Lodders 1995, Fegley *et al.* 1997b). We compared chemical lifetimes ( $t_{\text{chem}}$ ) for elementary reactions to the mixing time ( $t_{\text{mix}}$ ) for convectively moving atmospheric gas upward to cooler levels where chemistry is kinetically inhibited. This is a standard method used to model kinetics of thermochemical reactions in planetary atmospheres (Prinn and Barshay 1977, Fegley and Prinn 1985).

The  $t_{\text{chem}}$  values are calculated from literature kinetic data. In fact, our kinetic calculations for CO–CO<sub>2</sub>–SO<sub>2</sub> were done using the same kinetic data as used by Wood and Brett (1997) to calculate gas kinetics in laboratory furnaces (Bauer *et al.* 1971 data for reaction (4) below, which we took from the compilation of Mallard *et al.* 1994). The atmospheric mixing time  $t_{\text{mix}}$  is calculated from  $H^2/K_{\text{eddy}}$  where  $H$ , the pressure scale height, is  $\sim 16$  km at 740 K, and  $K_{\text{eddy}}$ , the vertical eddy diffusion coefficient, is  $10^4\text{--}10^6 \text{ cm}^2 \text{ sec}^{-1}$  near Venus' surface. At higher temperatures (lower elevations),  $t_{\text{chem}} < t_{\text{mix}}$  and gas phase thermochemical equilibrium is maintained. Conversely, at lower temperatures (higher elevations), reactions proceed slower,  $t_{\text{chem}} > t_{\text{mix}}$ , and gas phase thermochemical equilibrium is not maintained. In between these two regions is a critical altitude where  $t_{\text{chem}} = t_{\text{mix}}$ . This quench level is different for each elementary reaction. Once atmospheric gas rises to the quench level, reactions with sufficiently large activation energies are quenched by further vertical transport over an altitude increment which is small compared to  $H$ , the pressure scale height.

We found that gas phase chemical equilibrium is reached only, if at all, in the lowest levels of Venus' atmosphere at altitudes below 6052.7 km radius (i.e., temperatures above 730 K). Disequilibrium prevails for reactions involving C–O–S gases at higher elevations in the low radar emissivity region (Fegley *et al.* 1997a,b). Specifically, we found that the elementary reaction



is the fastest way to equilibrate CO, CO<sub>2</sub>, and SO<sub>2</sub> on Venus (Fegley *et al.* 1997b). However, even this reaction is quenched at  $748 \pm 13$  K on Venus. The 748 K quench temperature is for slow atmospheric mixing ( $K_{\text{eddy}} = 10^4 \text{ cm}^2 \text{ sec}^{-1}$ ) and is higher if atmospheric mixing is faster. Our results predict that reactions between C–O–S gases are quenched at  $\sim 748$  K on Venus, 1 km below the modal radius of 6051.4 km. Magellan radar altimetry shows that only  $\sim 1.5\%$  of the surface of Venus is at or below 748 K. Essentially no atmospheric gas on Venus is at this high temperature.

In contrast, Wood and Brett (1997) simply assume gas phase equilibrium at 740 K and at lower temperatures (higher elevations) in the low radar emissivity region where Wood claims pyrite is stable. Wood and Brett's (1997) gas phase equilibrium calculations for S<sub>2</sub>(g) on Venus using C–O–S gases are not applicable for discussing pyrite stability because they do not prove that equilibrium between C–O–S gases is attained faster than atmospheric mixing transports gas upward to cooler altitudes on Venus. Even mixing upward from the modal radius to a few km elevation is sufficient to quench C–O–S gas phase chemistry (Zolotov 1996, Fegley *et al.* 1997b).

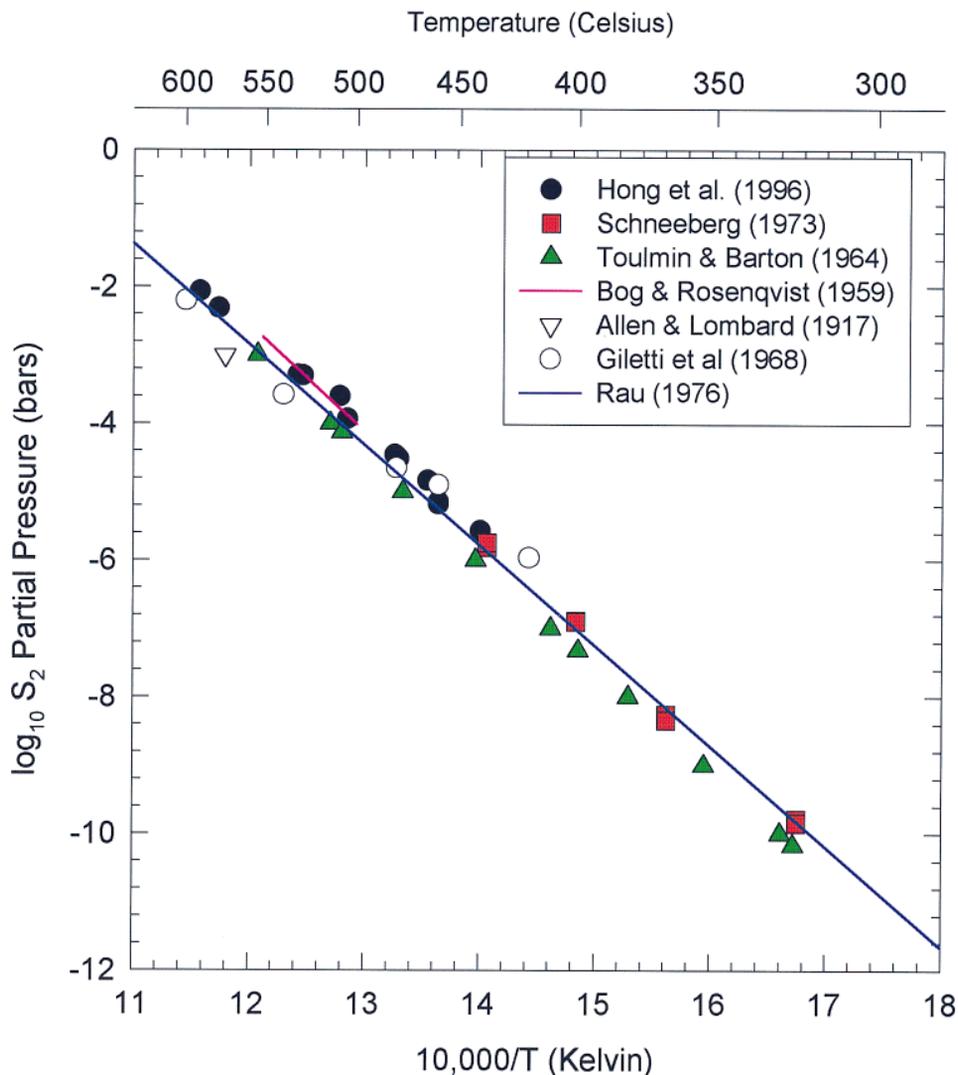
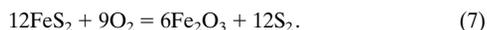
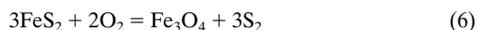


FIG. 1. The measured  $S_2$  pressure as a function of temperature for pyrite decomposition experiments in  $CO_2$  is compared with literature data for the  $S_2$  equilibrium vapor pressure over coexisting pyrite + pyrrhotite. See Barker and Parks (1986) for a similar plot of literature data and for the details of analyzing Rau's (1976) measurements. The plotted data, measured by Hong *et al.* (1996) using the transpiration method, are tabulated in Table A1.

I now want to point out another important factor governing pyrite stability, namely oxygen fugacity. Wood and Brett (1997) do not discuss oxygen fugacity in their calculations. However, depending on the  $O_2$  fugacity and sulfur pressure at Venus' surface (using either the calculated  $S_2$  pressure or the *observed*  $S_3$  pressure), pyrite either decomposes to pyrrhotite or oxidizes to magnetite ( $Fe_3O_4$ ) or hematite ( $Fe_2O_3$ ):

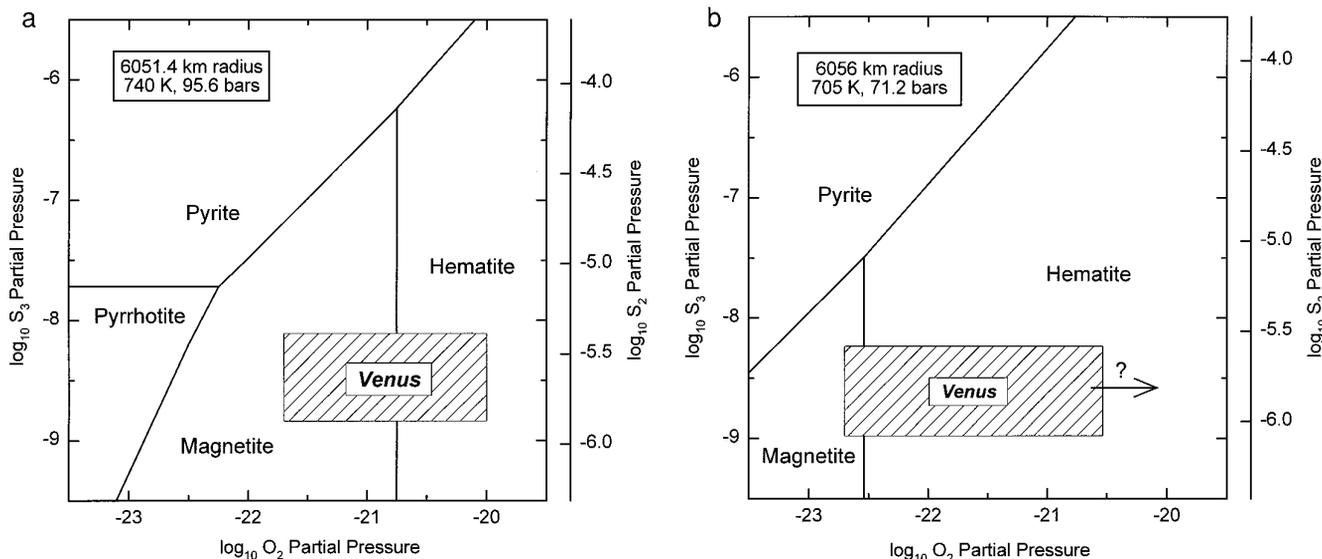


I have written Eq. (5) using  $Fe_7S_8$  (Fe/S atomic ratio = 0.875) as the formula for pyrrhotite because pyrrhotite in equilibrium with pyrite at 740 K has this Fe/S ratio (Stølen and Grønvold 1987). Equations (5)–(7)

could also be written in terms of  $S_3$  because the  $S_3$  and  $S_2$  pressures are coupled via reaction (1). The net thermochemical reactions (5)–(7) occur in the laboratory at Venus surface temperatures and thus are faster than the gas phase chemistry which is quenched on Venus (Fegley *et al.* 1995a).

Next consider pyrite oxidation via reactions (6) and (7). The thermodynamic data for minerals are from Robie and Hemingway (1995) and for gases (including  $S_2$  and  $S_3$ ) are from Gurvich *et al.* (1989–1994). I take  $\log_{10}P_{O_2} = -20.0$  to  $-21.7$  at 740 K on Venus for my calculations of iron oxide and sulfide stability because this range is consistent with gas abundances measured at 0–15 km by Venera and Vega spacecraft, with thermodynamic and kinetic calculations of gas chemistry, with spectral reflectivity measurements indicating the presence of hematite at the Venera 9 and 10 landing sites, and with the CONTRAST experiment at the Venera 13 and 14 landing sites (Pieters *et al.* 1986, Zolotov 1996, Fegley *et al.* 1997b).

Figure 2a plots the regions where pyrite, pyrrhotite, magnetite, and



**FIG. 2.** Two plots showing the regions where hematite, magnetite, pyrite, and pyrrhotite are stable at 740 K in the plains (a) and 705 K in the low emissivity region in the highlands (b). The  $S_3$  and  $O_2$  partial pressures at the surface of Venus are also shown and plotted in the region where iron oxides are stable at both altitudes. The corresponding  $S_2$  pressures calculated from equations (1)–(3) are also shown. Thermodynamic data for solids are from Robie and Hemingway (1995) and thermodynamic data for gases (including  $S_2$  and  $S_3$ ) are from Gurvich *et al.* (1989–1994).

hematite are stable at 740 K as a function of the  $S_3$  and  $O_2$  pressures. A box indicating the  $S_3$  and  $O_2$  pressures at the surface of Venus is also shown and plots in the region where magnetite and/or hematite are stable. The size of the box reflects the uncertainties in the data. The right hand vertical axis also shows  $S_2$  pressures calculated from Eqs. (1)–(3). The calculated  $S_2$  pressures are larger than the observed  $S_3$  pressures due to the equilibrium constant for reaction (1). However, the calculated  $S_2$  pressures at the surface of Venus are much lower than the  $S_2$  pressure needed for pyrite to be stable. Likewise, the observed  $S_3$  pressure is lower than that required for pyrite to be stable. The uncertainties in the thermodynamic data, in the  $S_3$  observations, and in the  $O_2$  fugacity do not alter the conclusion that pyrite is unstable on the surface of Venus. In contrast, Wood and Brett (1997) conclude that pyrite is stable because they neglect the Venera 11–14 sulfur vapor observations, they do not consider pyrite oxidation to hematite and magnetite, and they assume gas phase equilibrium.

**Pyrite decomposition at higher altitudes on Venus.** Pioneer Venus and Magellan radar data show that the electrical properties of Venus' surface change above a critical altitude of  $\sim 6054$  km (equatorial regions) to  $\sim 6055.5$  km (high northern latitudes) (Pettengill *et al.* 1996). Pyrite has been proposed to explain the low radar emissivity observed at high altitudes, but I show here that pyrite is also unstable in the venusian highlands.

My results are displayed in Fig. 2b, which shows the regions where pyrite, hematite, and magnetite are stable at 705 K (6056 km radius). The pyrrhotite region is off the diagram at the bottom left. Again, the right hand vertical axis shows  $S_2$  pressures calculated from Eqs. (1)–(3), and the box shows the  $S_3$  and  $O_2$  pressures at this altitude in Venus' atmosphere. They do not plot in the pyrite region, but are again in the iron oxide region. The observed  $S_3$  mixing ratios of  $(1.5\text{--}8) \times 10^{-11}$  times the total pressure (71.2 bar) give  $S_3$  pressures of  $(1.1\text{--}5.7) \times 10^{-9}$  bar. The minimum  $O_2$  pressure is the gas phase equilibrium value at this altitude (Zolotov 1996), while the maximum  $O_2$  pressure corresponds to quenching C–O–S gas equilibria at 0–2 km altitude (Zolotov 1996, Fegley and Lodders 1995, Fegley *et al.* 1997a,b).

Zolotov (1996) concluded that reactions between C–O–S gases are probably quenched at 1–2 km altitude on Venus. He also considered the redox state of Venus' atmosphere as a function of altitude and concluded that hematite could be stable in the lowlands and formed at 4.7 km in the highlands. As mentioned earlier, Fegley and Lodders (1995) and Fegley *et al.* (1997a,b) calculated that C–O–S gas equilibria are quenched at 6050.4 km radius (748 K). Thus, atmospheric conditions at 705 K (6056 km radius) are probably more oxidizing than that predicted from complete gas phase equilibrium. The venusian atmosphere contains too little sulfur vapor and is too oxidizing for pyrite to be stable at this altitude, and pyrite should decompose to iron oxides and sulfur vapor.

**Summary.** The discussion above shows that pyrite is unstable on Venus because of two factors: (1) the observed abundance of sulfur vapor is lower than the abundance needed to prevent pyrite decomposition or to allow pyrite to form and (2) atmospheric conditions are too oxidizing for pyrite to be stable. Pyrrhotite is also unstable on Venus. Any iron sulfides in fresh volcanic rock, or that are exposed by landslides, should decompose rapidly to sulfur vapor and iron oxides as shown by the experimental data of Fegley *et al.* (1995a). The higher sulfur vapor abundances observed by the Venera 14 spacecraft could be due to decomposition of recently exposed iron sulfides in that region of Venus. Although higher than the Venera 11–13 measurements, the  $S_3$  abundance observed by Venera 14 is still lower than the amount needed for pyrite to be stable.

The experimental data of Fegley *et al.* (1995a) predict that pyrite should decompose rapidly on Venus' surface. Thus, as already concluded by Fegley *et al.* (1995a), pyrite is probably not responsible for the radar properties of the venusian highlands. Instead, other phases such as ferroelectric minerals (Shepard *et al.* 1994) or a coating of volatile metallic vapors, halides, and sulfides emitted from volcanoes (Brackett *et al.* 1995, Pettengill *et al.* 1996) are more plausible candidates.

**Appendix: Transpiration Experiments.** The  $S_2$  pressure in our pyrite decomposition experiments was measured by the transpiration method, which has been used to study gas–solid reactions for about 150 years (Merten and Bell 1967). In transpiration experiments, a carrier gas is

TABLE AI  
S<sub>2</sub> Partial Pressure Measurements in CO<sub>2</sub>

Run No.	Time (hr)	Temp. (C)	Wt. loss (mg)	P(S <sub>2</sub> ) (bars)	log <sub>10</sub> fS <sub>2</sub>
H27	92.0	441	6.388	2.70 × 10 <sup>-06</sup>	-5.57
H28	64.0	465	24.090	1.46 × 10 <sup>-05</sup>	-4.84
H25	20.0	509	129.961	2.52 × 10 <sup>-04</sup>	-3.60
H26	5.1	529	66.217	5.04 × 10 <sup>-04</sup>	-3.30
H36	109.0	460	18.732	6.67 × 10 <sup>-06</sup>	-5.18
H75	161.5	460	29.933	7.20 × 10 <sup>-06</sup>	-5.14
H58	44.0	479	34.923	3.08 × 10 <sup>-05</sup>	-4.51
H53	14.0	480	8.332	2.31 × 10 <sup>-05</sup>	-4.64
H50	22.8	480	19.627	3.34 × 10 <sup>-05</sup>	-4.48
H68	64.0	481	58.062	3.52 × 10 <sup>-05</sup>	-4.45
H63	16.3	505	49.924	1.19 × 10 <sup>-04</sup>	-3.92
H60	3.0	532	39.962	5.17 × 10 <sup>-04</sup>	-3.29
H87	17 min	579	35.774	4.90 × 10 <sup>-03</sup>	-2.31
H86	22 min	591	81.567	8.64 × 10 <sup>-03</sup>	-2.06

passed over a solid at a known flow rate for a known time period. The solid is in the isothermal hot zone of a furnace. In our experiments the solid is pyrite and the carrier gas is CO<sub>2</sub> or a CO<sub>2</sub> gas mixture at ambient atmosphere pressure (~1 bar). The vapor pressure of the solid is determined by either measuring the weight loss of the solid or by measuring the weight of condensed vapor collected at some point downstream from the solid sample. In our experiments the weight loss of the solid is measured. If the composition and molecular weight of the evolved vapor is known (S<sub>2</sub> in this case), the vapor pressure over the solid can be calculated from the equation (Merten and Bell 1967)

$$P_{S_2} = n_{S_2} / (n_{S_2} + n_c) \times P, \quad (\text{A1})$$

where  $P_{S_2}$  is the S<sub>2</sub> vapor pressure over pyrite,  $n_{S_2}$  and  $n_c$  are the number of moles of vapor and carrier gas, and  $P$  is the total pressure (~1 bar). The moles of S<sub>2</sub> are calculated from the weight loss of the solid and the ideal gas law. The moles of carrier gas are calculated from the gas flow rate and duration of the experiment. The gas flow rate of 150 cm<sup>3</sup> min<sup>-1</sup> (STP) was controlled by calibrated electronic mass flow controllers. Hong *et al.* (1996) verified that this flow rate was appropriate for the transpiration experiments and was neither too slow nor too fast (see Merton and Bell 1967). Although several allotropic species (S, S<sub>2</sub>, S<sub>3</sub>, S<sub>4</sub>, S<sub>5</sub>, S<sub>6</sub>, S<sub>7</sub>, S<sub>8</sub>) exist in sulfur vapor, experimental measurements of the density and pressure of sulfur vapor show that S<sub>2</sub> is the dominant species at the temperatures and pressures used in the laboratory and at the surface of Venus. Gurvich *et al.* (1989–1994) summarize the experimental measurements on sulfur vapor and give recommended thermodynamic data for these allotropes in their compilation.

Our calculated S<sub>2</sub> pressures for pyrite decomposition experiments in purified CO<sub>2</sub> are given in Table AI. These data are plotted in Fig. 1 and were presented by Hong *et al.* (1996). The data show that the S<sub>2</sub> pressures in our pyrite decomposition experiments are close to the literature values for the S<sub>2</sub> vapor pressure over coexisting pyrite and pyrrhotite and are larger than the calculated S<sub>2</sub> pressure at the surface of Venus. Finally, Hong *et al.* (1996) used X-ray diffraction and electron microprobe analyses to verify that only pyrite and pyrrhotite were present in their experimental samples.

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