

⁵⁷Fe MÖSSBAUER STUDIES OF THE KINETICS OF PYRITE DECOMPOSITION ON THE SURFACE OF VENUS, G. Klingelhöfer¹, B. Fegley, Jr.^{2,3}, and K. Lodders² (1) Institut für Kernphysik, Technische Hochschule, 64289 Darmstadt, Germany, (2) Dept. of Earth & Planetary Sciences, and (3) McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130-4899 USA.

Introduction. After the Pioneer Venus mission, pyrite was suggested to be present in high radar reflectivity regions at high altitudes on Venus. This led us to determine experimentally whether or not pyrite is stable on the surface of Venus. Fegley and coworkers [1-4] showed that pyrite decomposes to pyrrhotite in CO₂, CO₂-CO, CO₂-SO₂, and in CO₂-CO-SO₂ gas mixtures at temperatures of ~ 660 to 1120 K, which spans the range of surface temperatures (~ 660 to 760 K) on Venus. The experiments were done by isothermally heating cut slices of natural pyrite crystals in controlled gas mixtures at about one atmosphere total pressure for different time periods. The pyrite decomposition rate was determined by measuring the weight losses of the heated samples. Here we present Mössbauer data for samples heated along three isotherms (689±4 K, 742±3 K, and 804±3 K) in CO₂ and in a CO₂-CO-SO₂ gas mixture. The Mössbauer data and the gravimetric data for the amount of pyrite reacted as a function of time give consistent results for the pyrite decomposition kinetics.

Mössbauer Method. Mössbauer spectroscopy (MS) is a nuclear technique, which measures for a Mössbauer isotope the resonance absorption of recoil free emitted gamma quanta. The absorption rate is measured as a function of the energy shift of the Mössbauer quanta, which is obtained by moving the Mössbauer source (or the absorber) with a periodically changing doppler velocity v . Due to electric and magnetic hyperfine interaction (HFI), the nuclear levels are shifted (isomer shift) and/or split and resonance absorption occurs at different velocities. For ⁵⁷Fe two and six resonance lines appear in the Mössbauer spectrum for pure electric quadrupole and magnetic HFI respectively. If both electric quadrupole and magnetic HFI are absent, a single resonance line is observed. The HFI values are characteristic for a particular Fe compound. Therefore MS determines the different Fe bearing phases in the sample as well as their relative intensities, given by the area of the subspectrum, which is proportional to the relative amount of the Fe phase and its Debye Waller factor f [5]. From this the weight percentage of each Fe component can be calculated taking into account the stoichiometric factor S . The elemental abundance of Fe in the sample cannot be determined by MS. We have measured the Mössbauer spectra in transmission geometry at room temperature. A ⁵⁷Co/Rh source was used with an activity of about 70 mCi and a line width of about 0.16 mm/s. The experimental setup consists of a loudspeaker type drive running in constant acceleration mode, and a Si Pin-diode for the detection of the 14.4 keV Mössbauer radiation. The absorber thickness was about 20 mg cm⁻². Typical recording times are 2-4 days for one spectrum. The data have been fitted by a sum of 9 subspectra. This was necessary because the reacted samples contain residual pyrite (1 doublet) which is contaminated by minor amounts of chloritoid (1 doublet), and the reaction products pyrrhotite (3 to 4 sextets), hematite (1 sextet) and magnetite (2 sextets). The iron oxides are not present in all samples. Figure 1 shows the spectra for three samples (R12, R32, R41) heated in pure CO₂ at three different temperatures.

Results. The weight loss and Mössbauer data for the % pyrite in the reacted samples are given in Table 1. There is generally good agreement between the two independent methods. The weight loss data underestimate the small amounts (< 3%) of pyrite left in heavily reacted samples which are predominantly pyrrhotite (e.g., R41-43, R73). The disagreement for R45 is probably due to heterogeneous sampling because the MB work is done on a portion of the entire sample. Fig. 2 shows graphically the good agreement between the two methods. The temperature dependence of the MB rate data along these three isotherms gives an activation energy of 151±17 kJ mole⁻¹, in good agreement with the values of 153±19 kJ mole⁻¹ reported by [3] from weight loss data along five isotherms, and of 142 kJ mole⁻¹ reported by [1] from weight loss data over the 739-1118 K range.

Summary. The Mössbauer results confirm the pyrite decomposition rates and activation energy determined from weight loss measurements. These kinetic data show that pyrite rapidly decomposes on the surface of Venus. Furthermore, this study also demonstrates the potential utility of Mössbauer spectroscopy for chemical analyses of the surface of Venus using a Mössbauer spectrometer which is being developed for the Russian Mars-96 mission [6-7].

References. [1] B. Fegley, Jr. & A.H. Treiman 1992 in AGU Monograph No. 66, pp. 7-71; [2] B. Fegley, Jr. & K. Lodders *Lunar Planet. Sci. XXIV*, pp. 467-468; [3] B. Fegley, Jr. & K. Lodders 1993 *EOS Trans. AGU* **74**, 190; [4] B. Fegley, Jr., K. Lodders, and G. Klingelhöfer 1993 *Bull. Amer. Astron. Soc.* **25**, 1080; [5] W. Meisel, P. Griebach, H.J. Grabke, P. Gütlich 1990 *Hyperfine Interactions* **57**, 2001; [6] G. Klingelhöfer, J. Foh, P. Held, H. Jäger, E. Kankeleit, R. Teucher 1992 *Hyperfine Interactions* **71**, 1449; [7] G. Klingelhöfer et al 1992 *Lunar*

Planet. Sci. **XXIII**, pp. 695-696. **Acknowledgments.** The work at St. Louis was supported by grants from the NASA Planetary Atmospheres and VDAP Programs. We thank D. Kremser and R. Poli for technical assistance.

Table 1 Experimental results for samples studied by Mössbauer spectroscopy.

Run No.	Temp. (K)	Duration (Hours)	Wt. % Pyrite		Run No.	Temp (K)	Duration (Hours)	Wt. % Pyrite	
			WL*	MB*				WL*	MB*
8 ^a	740	24	83.4	83.3	43 ^a	806	65	0	0.1
9 ^a	738	65	58.9	59.4	44 ^a	802	5	68.2	67.6
11 ^a	741	41	79.2	79.4	45 ^a	805	16	12.1	1.1
12 ^a	685	96	87.4	91	47 ^a	803	2.5	84.4	79.2
14 ^a	686	161	66.2	62.4	49 ^a	806	8	53	58.2
18 ^a	686	233	55	60.2	61 ^b	690	24.7	93.1	90.5
32 ^a	739	187	33.2	41.3	62 ^b	740	21	80.7	81.4
33 ^a	745	329	34.1	27.8	63 ^b	739	1.1	99	96.8
38 ^a	694	140	82.6	85.7	65 ^b	741	142.8	17.5	10.7
41 ^a	807	97.5	0	0.1	66 ^b	691	211	70.7	82.4
42 ^a	798	43	0	0.5	73 ^{b,c}	745	94	0	2.7

Notes: *WL = weight loss and MB = Mössbauer spectroscopy, ^aRun done in CO₂ (Coleman Instrument Grade, 99.99% pure), ^bRun done in CO₂(97%)-CO(1.5%)-SO₂(1.5%), ^cR73 fell out of the sample holder at an unknown time during the run which lasted for 94 hours.

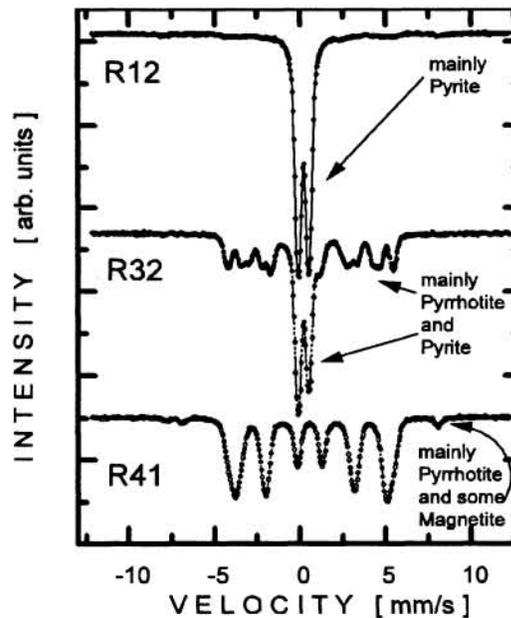
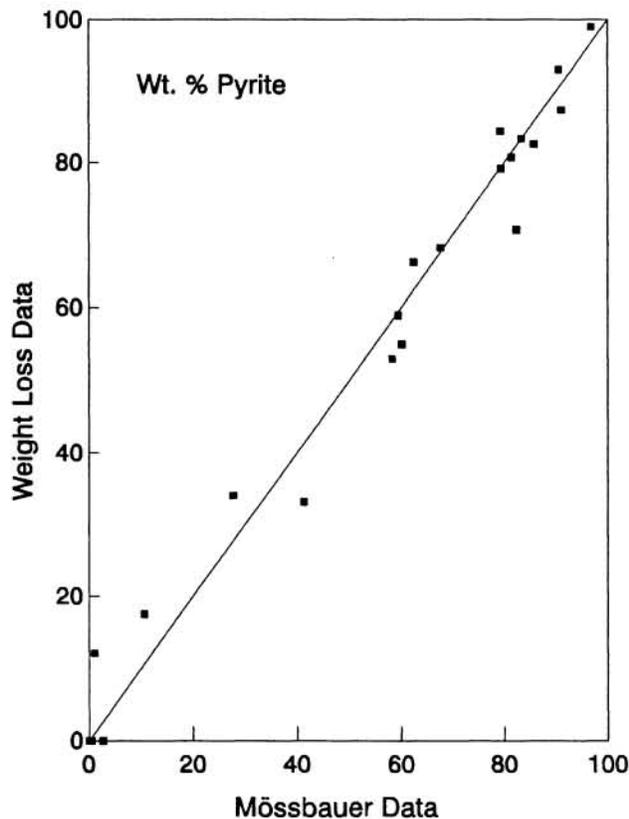


Fig. 1 (above) Mössbauer spectra of samples R12, R32, and R41. The data are normalized to the individual background count rate. Fig. 2 (left) A comparison of weight loss and Mössbauer data for the amount of pyrite left in the reacted samples.