

THE RATE OF CHEMICAL WEATHERING OF PYRITE ON THE SURFACE OF VENUS, B. Fegley, Jr.^{1,2} and K. Lodders¹, (1) Department of Earth & Planetary Sciences and (2) McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130-4899 USA.

Introduction. This abstract reports results of an experimental study of the chemical weathering of pyrite (FeS_2) under Venus-like conditions. This work, which extends the earlier study by Fegley and Treiman [1,2], is part of a long range research program to experimentally measure the rates of thermochemical gas-solid reactions important in the atmospheric-lithospheric sulfur cycle on Venus. The objectives of this research are (1) to measure the kinetics of thermochemical gas-solid reactions responsible for both the production (e.g., anhydrite formation [3]) and destruction (e.g., pyrrhotite oxidation [4]) of sulfur-bearing minerals on the surface of Venus and (2) to incorporate these and other constraints into holistic models of the chemical interactions between the atmosphere and surface of Venus.

Experimental. Experiments were done with single crystal cubes of natural pyrite (Navajun, Logroño, Spain) that were cut and polished into slices of known weight and surface area. The slices were isothermally heated at atmospheric pressure in 99.99% CO_2 (Coleman Instrument Grade) at either 412°C (685 K) or 465°C (738 K) for time periods up to 10 days. These two isotherms correspond to temperatures at about 6 km and 0 km altitude, respectively, on Venus. The reaction rate was determined by measuring the weight loss of the reacted slices after removal from the furnace. The reaction products were characterized by X-ray diffraction, scanning electron microscopy, and energy dispersive spectroscopy on the SEM.

Results. X-ray diffraction data show the presence of unreacted pyrite and pyrrhotite in all samples. When examined in the SEM, the samples reacted at 465°C showed the growth of hexagonal platelets of an Fe sulfide phase, which is probably pyrrhotite, on the surface. These platelets became more abundant as samples were heated for longer times. The XRD peaks due to pyrrhotite also became stronger as samples were heated for longer times. Red coatings on the samples reacted at 412°C indicated the presence of hematite, and the XRD data confirmed minor amounts of hematite in these samples.

The weight loss data along the 412°C and 465°C isotherms are plotted versus time (t) in hours in Figures 1 & 2. The reaction progress is defined as $\alpha^{1/3}$ where α is the fraction of unreacted pyrite remaining in the sample. The data show a linear dependence of $\alpha^{1/3}$ with time which indicates contracting volume kinetics [5]. The unweighted linear least squares fits to the data are: $\alpha^{1/3} = 1.0004 - 6.352 \times 10^{-4}t$ at 412°C and $\alpha^{1/3} = 0.997 - 1.874 \times 10^{-3}t$ at 465°C . The slope of each linear fit is the reaction rate constant for pyrite decomposition to pyrrhotite at that temperature.

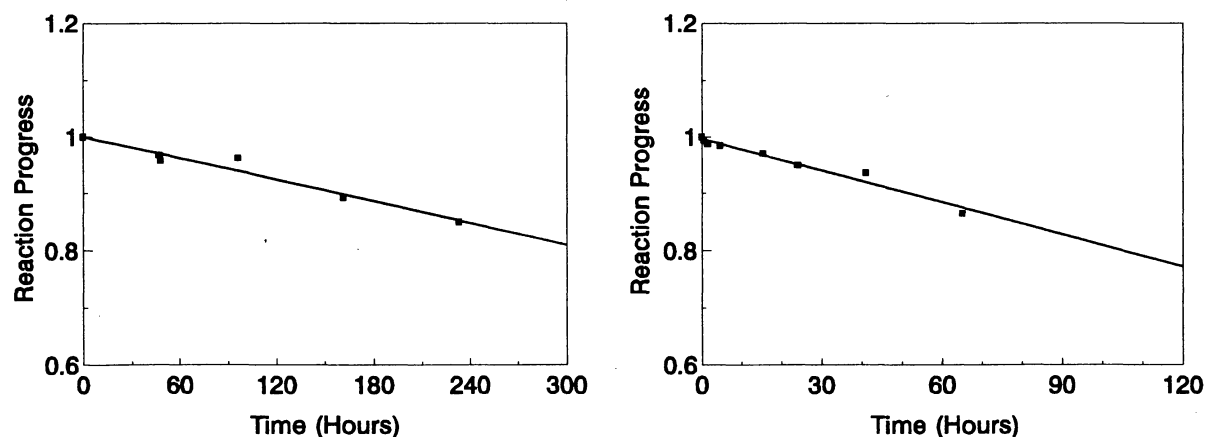


Figure 1 (left), Kinetic data at 412°C , and Figure 2 (right), kinetic data at 465°C . The reaction progress is defined by $\alpha^{1/3}$, where α is the fraction of unreacted pyrite left in the samples.

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Interpretation. The weight loss data were analyzed assuming that pyrite decomposed solely to pyrrhotite. This assumption is supported by the XRD data on the reacted samples, by the phase diagram for the Fe-S system [6], and by studies of pyrite decomposition to pyrrhotite in a dynamic vacuum [7], in flowing Ar [8], and in flowing CO₂ [2,9,10]. Not all prior workers presented kinetic data; however, contracting volume kinetics were also found by [7]. The presence of minor hematite in the samples reacted at 412° C is unexpected because the fO₂ for CO₂ self dissociation is well within the magnetite stability field at this temperature. Minor magnetite would be expected instead if the pyrrhotite reacted with the CO₂ [4]. The hematite coatings are not due to reaction with air during quenching because the coatings are absent from all samples reacted at higher temperatures and because samples were not removed from the furnace atmosphere until they cooled to ≤100° C at the top of the furnace. We suggest that hematite was formed by reaction of pyrrhotite with the trace oxygen impurity in the CO₂. The oxygen impurity in Coleman Instrument grade CO₂ is specified as ≤ 20 ppmv O₂, and is plausibly high enough to make the CO₂ oxidizing enough for hematite to form.

Application to Venus. Ten years ago, pyrite was proposed as a source of reduced sulfur gases (COS, H₂S, S_x) at the surface of Venus [11]. Thermochemical equilibrium calculations predict that the amount of COS produced by pyrite oxidation by CO₂ is temperature (and hence altitude dependent) and ranges from several tens of ppmv to several ppmv in the 0-12 km altitude range [2,12]. Recent analysis of IR spectroscopic data for the 30-45 km region of the atmosphere of Venus suggests that COS abundances increase with decreasing altitude in the Venusian atmosphere [13] and supports the proposal that iron sulfides on the surface of Venus are a net source of reduced sulfur gases. The COS abundances retrieved from the spectroscopic data also agree with the predictions of [2] and [12] once an arithmetic error in the calculations of [12] for the equilibrium $2\text{CO} + \text{S}_2 = 2\text{COS}$ was corrected.

However, neither the mechanism nor the kinetics of the weathering reaction(s) are constrained by thermochemical equilibrium calculations. Now that some observational evidence suggests a COS source on the surface of Venus, the rate of COS production is of interest. The present work, coupled with the prior studies of [1,2,4] provides information on the kinetics and mechanism of pyrite chemical weathering on the surface of Venus. The experimental results suggest that pyrite chemical weathering is a two step process with the first step involving the formation of pyrrhotite and the second step involving the oxidation of pyrrhotite to magnetite and reduced sulfur gases. The kinetic data shown in Figs. 1 & 2 show that the first step of this process is very rapid. For example, the kinetic data predict a pyrite lifetime of about 22 days at 465° C (738 K) and about 65 days at 412° C (685 K) on the surface of Venus. The second step, pyrrhotite oxidation, is not as rapid as shown by [4]. However, the fundamental result from the present work, and prior work by [1,2,4] is that sulfide chemical weathering on the surface of Venus is a relatively rapid process on a geological timescale.

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References. [1] B. Fegley & A.H. Treiman 1990 *Bull. Amer. Astron. Soc.* 22, 1055; [2] B. Fegley & A.H. Treiman 1992 in AGU Monograph No. 66, pp. 7-71; [3] B. Fegley & R.G. Prinn 1989 *Nature* 337, 55-58; [4] A.H. Treiman & B. Fegley 1991 *Lunar Planet. Sci.* XXII, pp.1409-1410; [5] W.E. Brown et al 1980 in *Comprehensive Chemical Kinetics* vol. 22, pp. 41-113; [6] G. Kullerud & H.S. Yoder 1959 *Econ. Geol.* 54, 533-572; [7] G. Pannetier & L. Davignon 1964 *Bull. Soc. Chim. Fr.*, pp.1513-1517; [8] A.W. Coats & N.F.H. Bright 1966 *Can. J. Chem.* 44, 1191-1195; [9] G.M. Schwab & J. Philinis 1947 *J. Amer. Chem. Soc.* 69, 2588-2596; [10] F.C. Thompson & N. Tilling 1924 *J. Soc. Chem. Ind.* 43, T37-T46; [11] U. Von Zahn et al 1983 in *Venus*, pp.299-430; [12] B. Fegley et al 1992 *Proc. 22nd LPSC*, pp. 3-20; [13] J.B. Pollack et al 1992 *Bull. Amer. Astron. Soc.* 24, 996.