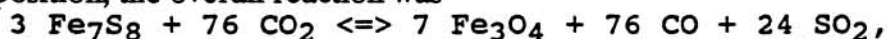


VENUS: THE CHEMICAL WEATHERING OF PYRRHOTITE, Fe_{1-x}S .

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Sulfide minerals are predicted to be important in the sulfur geochemical cycle on Venus [1,2,3], and pyrite (FeS_2) has been suggested as the cause of high radar reflectivity in some regions [4-6]. A related abstract describes experiments on the chemical weathering of pyrite at Venus surface conditions [7]. However, the primary iron sulfide mineral in basaltic rocks on Earth should be pyrrhotite, Fe_{1-x}S , because pyrite decomposes to pyrrhotite + sulfurous liquid above 743°C [8]. The rate of pyrrhotite weathering in a model Venus atmosphere, 1 bar CO_2 , has been experimentally measured from $524\text{--}787^\circ\text{C}$. Preliminary results indicate that pyrrhotite weathers to magnetite, and the amount of pyrrhotite consumed is proportional to $\text{time}^{1/4}$. If these results can be extrapolated to conditions of the Venus surface, mm-sized pyrrhotite grains there will be consumed rapidly, but massive pyrrhotite can persist for millions of years.

EXPERIMENTS: Experiments were done on massive pyrrhotite (Sterling MA) cut into blocks of measured weight and surface area. The blocks were reacted isothermally at temperatures from $524\text{--}787^\circ\text{C}$ in 1 bar 99.95% CO_2 gas for set durations, and then cooled in the same gas to reduce interaction with air. After reaction, the blocks were coated with rinds of magnetite. The progress of reaction, in atoms-S consumed per cm^2 surface area, was determined from weight loss of the block after reaction. For a typical pyrrhotite composition, the overall reaction was



assuming SO_2 was the sulfur gas species; measurement of reaction progress is independent of the sulfur gas species produced. No iron sulfate nor hematite formed during reaction. The observed rate of reaction ($\text{atoms-S cm}^{-2}\text{sec}^{-1}$) varies with the duration of the experiment. The progress of reaction can be divided into two stages (Fig. 1): first, a period of minimal weight change; and then a period of weight loss (reaction progress) linear in $\text{time}^{1/4}$. Only the first stage was observed at the lowest experimental temperature.

INTERPRETATION: The first stage of reaction (minimal weight change) may represent growth of a surface layer of magnetite, fed by diffusion of Fe out of pyrrhotite [9]. Thereafter, reaction progress is linear in $\text{time}^{1/4}$ (Fig. 1); The proportionality or rate constants (slopes on Fig. 1) fit an Arrhenius dependence (Fig. 2) with an activation energy of -18 kJ/mol .

Growth of a reaction layer by simple diffusion should give reaction progress linear in $\text{time}^{1/2}$, the parabolic growth law [10], not in $\text{time}^{1/4}$. One possible explanation for the observed rate law is that creation of O from CO_2 at the magnetite-gas interface is coupled to oxidation of S diffusing from the magnetite-pyrrhotite interface.

IMPLICATIONS FOR VENUS: Assuming that our preliminary rate data are relevant to Venus, we can consider their implications for pyrrhotite on the Venus surface. Assuming that the pyrrhotite surface is saturated with CO_2 at 1 bar, we extrapolated our results to Venus surface temperatures using the regression of Figure 2. If the mechanism does follow an Arrhenius relationship to Venus surface temperatures, the rate constant for pyrrhotite weathering would be approximately $1.85 \times 10^{19} \text{ atom-S-cm}^{-2}\text{sec}^{-1/4}$ (Fig. 2) at the global mean surface T (740K). In this case, a flat slab of pyrrhotite would be weathered 0.4 mm in a year, 4.0 mm in 10^4 years, 4.0 cm in 10^8 years, etc. Pyrrhotite grains in basalts are typically mm-sized or smaller, and could be expected to weather completely within centuries. However, decimeter or meter-sized masses of pyrrhotite, such as occur on Earth in magmatic sulfide and other ore deposits, would not be consumed within millions of years.

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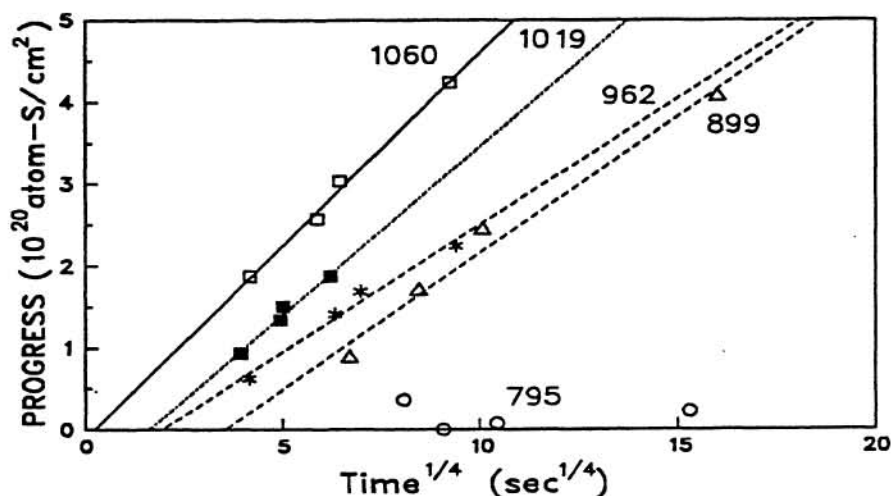


Figure 1. Experimental data, with unweighted linear regressions for each T(K). Data for 795K are not distinct from zero; other data points are uncertain to $\pm 10\%$, mostly from measurement of surface area.

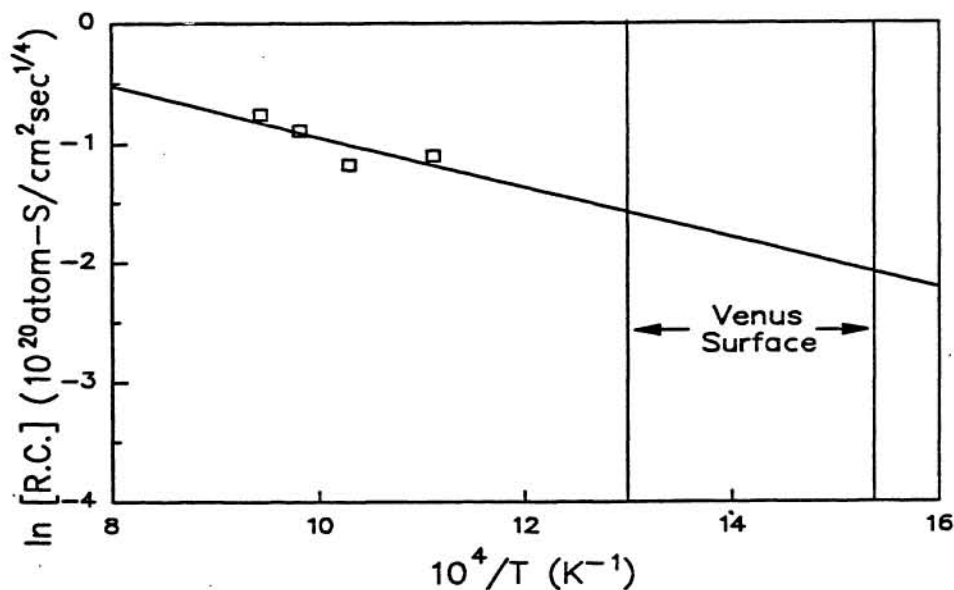


Figure 2. Temperature dependence of rate constants (slopes) from Fig. 1. Linearity here (with unweighted regression fit) suggests that the rate constants follow an Arrhenius relationship.