VENUS VOLCANISM: RATE ESTIMATES FROM LABORATORY STUDIES OF SULFUR GAS-SOLID REACTIONS. K. Ehlers, B. Fegley, Jr., and R.G. Prinn, Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MÂ 02139

Thermochemical reactions between sulfur-bearing gases in the atmosphere of Venus and calcium-, iron-, magnesium-, and sulfur-bearing minerals on the surface of Venus are an integral part of a hypothesized cycle of thermochemical and photochemical reactions responsible for the maintenance of the global sulfuric acid cloud cover on Venus (1-3). As schematically illustrated in Figure 1, $\mathrm{SO}_{2}$ is continually removed from the Venus atmosphere by reaction with calcium-bearing minerals on the planet's surface. Maintenance of the global $\mathrm{H}_{2} \mathrm{SO}_{4}$ clouds, which are formed by the ultraviolet-sunlight-powered conversion of $\mathrm{SO}_{2}$ into $\mathrm{H}_{2} \mathrm{SO}_{4}$ cloud particles (4), requires a comparable sulfur source to balance this $\mathrm{SO}_{2}$ sink. The most plausible endogenic source is volcanism, which has occurred on Venus in the past (5), and which may have led to increased $\mathrm{SO}_{2}$ levels above the Venus cloud-tops observed by the Pioneer Venus orbiter ( 6,7 ). The rate of volcanism required to balance $\mathrm{SO}_{2}$ depletion by reactions with calcium-bearing minerals on the Venus surface can therefore be deduced from a knowledge of the relevant gas-solid reaction rates combined with reasonable assumptions about the sulfur content of the erupted material (gas + magma).

We are carrying out a laboratory program to measure the rates of reaction between $\mathrm{SO}_{2}$ and possible crustal minerals on Venus. At present we have studied the reaction $\mathrm{CaCO}_{3}$ (calcite) $+\mathrm{SO}_{2} \rightarrow \mathrm{CaSO}_{4}$ (anhydrite) +CO (see Figure 2). Experimental details and preliminary results have been given by Fegley (8) and Fegley and Prinn (9). We find that the temperature dependence of the reaction is given by the equation $\mathrm{R}=10^{19.64}( \pm 0.28)$ $\exp (-15,248( \pm 2970) / \mathrm{T})$ molecules $\mathrm{cm}^{-2} \mathrm{~s}^{-1}$ and that the reaction rate exhibits no statistically significant variation with either $\mathrm{O}_{2}$ or $\mathrm{CO}_{2}$ partial pressure. If this reaction rate represents the $\mathrm{SO}_{2}$ reaction rate with calcium-bearing minerals on the Venus surface (an assumption which we are currently investigating by studying $\mathrm{SO}_{2}$ reactions with other minerals such as anorthite and diopside) then all $\mathrm{SO}_{2}$ (and thus the clouds) in the Venus atmosphere will disappear in $1.9 \times 10^{6}$ years unless volcanism replenishes the lost $\mathrm{SO}_{2}$. The Venus surface composition at the Venera 13,14, and Vega 2 landing sites implies a volcanism rate of approximately $1 \mathrm{~km}^{3} \mathrm{yr}^{-1}$; a range of $0.4-11 \mathrm{~km}^{3} \mathrm{yr}^{1}$ is implied by assuming S/Si ratios appropriate for ordinary chondrites or for the terrestrial crust (9).

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Figure 1 The cycle of sulfur compounds in the Venusian atmosphere (Prinn 1985). Volcanic eruptions or reactions of $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{CO}_{2}$ with volcanic surface rocks yields $\mathrm{COS}, \mathrm{H}_{2} \mathrm{~S}, \mathrm{~S}_{2}$, and $\mathrm{SO}_{2}$. Various photochemical reactions convert these species to concentrated $\mathrm{H}_{2} \mathrm{SO}_{4}$ or elemental suifur particles in the Venusian clouds. The $\mathrm{H}_{2} \mathrm{SO}_{4}$ evaporates at the cloud base, producing $\mathrm{SO}_{3}$, which can then either recondense or be reduced to $\mathrm{SO}_{2}$. Reactions of $\mathrm{SO}_{2}$ with $\mathrm{Ca}^{2+}$ in rocks provides a sink that must be balanced by the volcanic and surface sources.


Figure 2. Scanning electron micrograph of the fracture surface of a reacted calcite crystal. The scale bar is 50 micrometers long. The horizontal white line on the micrograph shows the position of an X-ray line scan for the element sulfur. The wavy white line shows that sulfur $X$-rays are produced only at the reacted surface where grains of the mineral anhydrite ( $\mathrm{CaSO}_{4}$ ) are formed as a result of the gas-solid reaction.

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