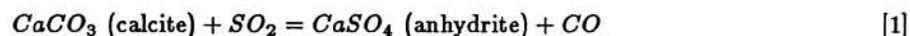


THERMOCHEMICAL KINETICS OF SO_2 REACTIONS WITH
POSSIBLE VENUS CRUSTAL MINERALS: FIRST DATA FOR CALCITE.

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Introduction. 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 important part of a hypothesized cycle of thermochemical and photochemical reactions responsible for the maintenance of the global sulfuric acid cloud cover on Venus (1, 2). However, despite the importance of these thermochemical gas-solid reactions, they are poorly understood because of an absence of relevant kinetic data. The lack of data is unfortunate because a number of recent observations strongly suggest that chemical interactions between sulfur-bearing gases and crustal minerals are kinetically controlled and are not at chemical equilibrium (3-5). For example, the Pioneer Venus and Venera 11 and 12 abundance data reviewed critically by von Zahn *et al.* (3) show that SO_2 dominated over H_2S and OCS above 22 km altitude and had a volume mixing ratio ~ 150 ppm between 22 km and 50 km (the cloud base). Figure 1 illustrates that the observed SO_2 abundance is not in chemical equilibrium with the Venus surface, but is higher than the chemical equilibrium value predicted by Lewis and Kriemendahl (6). Temporal variations in the SO_2 abundance (both below and above the clouds) have been observed (4, 7) and also suggest that the SO_2 abundance is kinetically controlled. Indeed Prinn (1, 2) has emphasized that the sources and sinks of sulfur-bearing gases are not expected to be in balance so that variations in their abundances are expected.

Experimental. The net reaction illustrated in Figure 1,



is predicted to be an important sink for incorporation of SO_2 into Venus crustal minerals (6). Calcite is also predicted to buffer the CO_2 abundance on Venus via the Urey reaction (8). These theoretical considerations plus the availability of high purity $CaCO_3$ in several forms and the exemplary nature of reaction [1] make it ideal for study. Preliminary results of this study have already been presented (9); more recent work and a more detailed discussion is given here.

Reaction [1] was studied experimentally by heating calcite samples in a SO_2 -bearing gas stream for varying time periods. Experiments were done at atmospheric pressure with a $SO_2 - CO_2$ gas mixture nominally containing 1% SO_2 . Standard techniques were used to monitor and control temperature and gas flow. The progress of reaction [1] was followed by weighing samples heated for different time periods and by EDS/SEM examination of the samples after removal.

Results. Analyses by EDS/SEM show that calcite samples heated in $SO_2 - CO_2$ gas streams for periods ranging from hours to days develop sulfur-bearing coatings or layers which are presumably composed of anhydrite, the thermodynamically stable product of reaction [1]. Figures 2 and 3 illustrate representative SEM micrographs of the fracture surfaces of two different calcite samples heated at constant temperature for times differing by a factor of ~ 40 . SEM and EDS/SEM examination of many reacted samples shows that the sulfur-bearing coatings or layers are chemically and morphologically distinct from the underlying calcite. SEM examination also reveals that all exposed calcite surfaces become coated with these layers, which are an advancing reaction interface.

The thickness of the sulfur-bearing layers is a function of the reaction time and can be used to monitor the extent of reaction. Kinetic data so obtained correlate well with kinetic data based on weight gain measurements and geometric surface area determinations. In particular, both techniques indicate that the initial gas-solid reaction rate is faster than the rate subsequent to the development of a sufficiently thick product layer. This behavior is consistent with initial chemical control and later diffusion control of the kinetics.

Discussion. The laboratory rate measurements can be used to estimate the chemical time constant for removal of the observed SO_2 column density on Venus by incorporation into crustal minerals via reaction [1]. This will be described at the meeting. Additional rate measurements for other suggested SO_2 removal reactions and for suggested sulfur gas production reactions (e.g., pyrite weathering) are also feasible using

similar techniques. Such kinetic data have applications in several areas including interpretation of radar reflectivity data from the planned Magellan mission.

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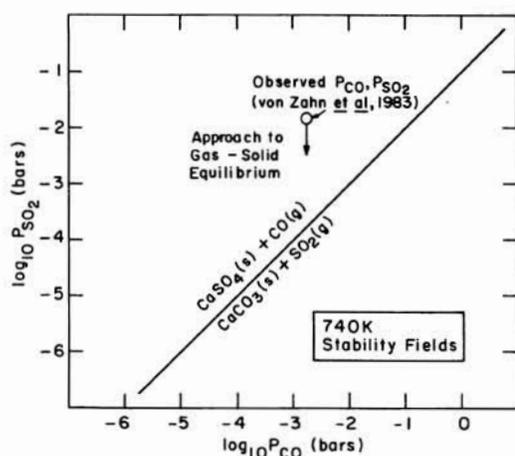


Figure 1. Observed SO_2 abundance on Venus is higher than the predicted chemical equilibrium value.



Figure 2. Fracture surface of a reacted calcite sample. The scale bar is 50 microns.



Figure 3. Fracture surface of a reacted calcite sample heated ~ 40 times longer at the same temperature. The scale bar is 50 microns.