Estimation of the rate of volcanism on Venus from reaction rate measurements

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Maintenance of the global H_2SO_4 clouds on Venus requires volcanism to replenish SO_2, which is continually removed from the atmosphere by reaction with calcium minerals on the planet's surface[1-4]. Here we present laboratory rate data for the reaction between SO_2 and calcite ($CaCO_3$) to form anhydrite ($CaSO_4$). If this reaction rate represents the SO_2 reaction rate on Venus, then all SO_2 in the venusian atmosphere (and thus the clouds) will disappear in 1.9 Myr unless volcanism replenishes the lost SO_2. The required volcanism rate, which depends on the sulphur content of the erupted material, is in the range $0.4-11\ km^3$ of magma erupted per year. The Venus surface composition at the Venera 13, 14 and Vega 2 landing sites[5,6] implies a volcanism rate of approximately $1\ km^3\ yr^{-1}$. This geochemically estimated rate can be used to determine if either (or neither) of two discordant geophysically estimated rates ($2\ km^3\ yr^{-1}$ versus $200-300\ km^3\ yr^{-1}$)[7-9] is correct. It also suggests that Venus may be less volcanically active than the Earth.

Calcite acts as a net sink for SO_2 on Venus by incorporating it into the crust through the net reaction[1-4]

$$CaCO_3\ \text{(calcite)} + SO_2 \rightarrow CaSO_4\ \text{(anhydrite)} + CO \qquad (1)$$

which proceeds to the right because the observed SO_2 abundance on Venus is ~100 times higher than the value in equilibrium with coexisting calcite and anhydrite[4]. Calcite is also predicted by several authors to be present on the Venus surface because it appears to be capable of buffering the CO_2 abundance on Venus through the Urey reaction ($CaCO_3 + SiO_2 = CaSiO_3 + CO_2$)[10-13]. These predictions concerning possible roles for calcite on Venus, the exemplary nature of reaction (1), and the availability of high-purity $CaCO_3$ in several forms led us to study reaction (1) as an example of SO_2 removal processes. However, as Fig. 1 illustrates, SO_2 also reacts with other calcium minerals (such as, diopside, $CaMgSi_2O_6$), which are believed to be present on the surface of Venus[14,15]. The kinetics for these alternative reactions are also being measured and will be reported later.

Reaction (1) was studied by heating clear calcite crystals (Iceland spar) of known impurity content (~350 p.p.m. total impurities from analysis by inductively coupled plasma emission spectroscopy), weight and surface area in SO_2-bearing gas streams for varying time periods at three different temperatures. Experiments were done at temperatures of 600–850 °C and ambient atmospheric pressures with SO_2-CO_2 gas mixtures nominally containing 1% (by volume) SO_2. Thus, the molecular number density of SO_2 is about the same as that at the surface of Venus, where the atmospheric pressure is ~100 times larger but the SO_2 volume mixing ratio is ~100 times smaller[16]. The mixtures also typically contained <1 p.p.m. O_2 and $\leqslant$10 p.p.m. H_2O as impurities. Experiments were also done with gas mixtures containing up to 100 p.p.m. O_2; however, the rates were independent of oxygen fugacity (and thus of the CO/CO_2 ratio) within this range of O_2 content. Standard techniques were used to monitor and control gas flow and temperature (to better than ±5 °C). The rate of reaction (1) was determined by three independent methods: (1) measuring the weight gain at the end of reaction, (2) using scanning electron microscopy (SEM) to measure the porosity and thickness of the reacted surface layers from micrographs of external and fracture surfaces (see, for example, Fig. 1), and (3) SO_4^{2-} analyses of reacted samples by ion chromatography. SEM examination of many samples (in combination with X-ray line scans and energy-dispersive spectroscopy (EDS) on the SEM) showed that $CaSO_4$ layers covered
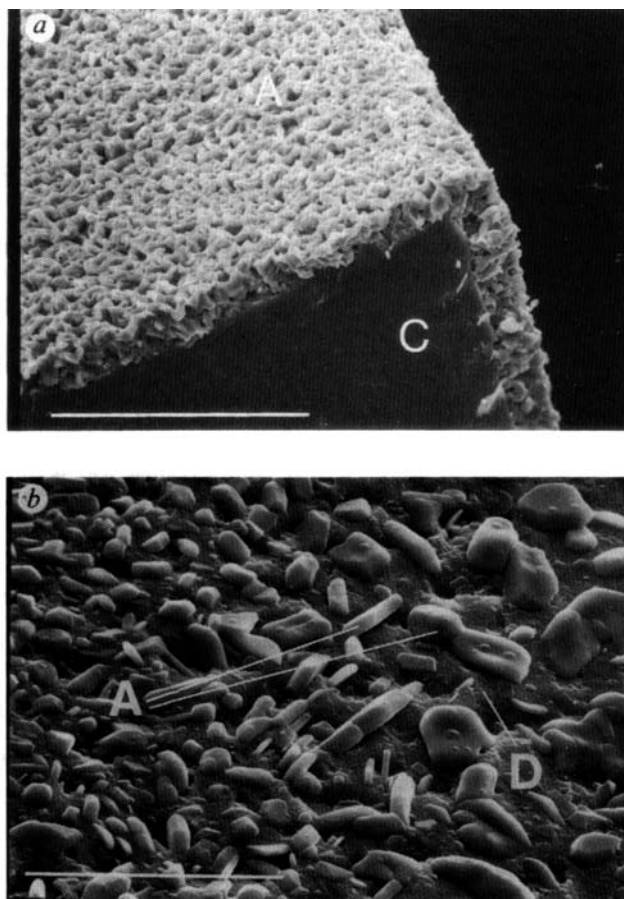
Fig. 1 Scanning electron micrographs of chemically reacted samples. *a*, Fracture surface, showing a $CaSO_4$ (anhydrite) layer (A) completely covering a partially reacted calcite crystal (C) (850 °C for 192 h) *b*, Top surface, showing $CaSO_4$ (A) growing on a partially reacted diopside crystal (D) (833 °C for 48 h). Scale bars indicate 100 μm (*a*) and 50 μm (*b*).

all external surfaces of the reacted samples. X-ray powder patterns of samples and standards confirmed that the layers were anhydrite (in particular, there was no evidence for calcium sulphite) and that unreacted calcite was the only other phase present in the samples. The ion chromatography also verified the absence of anion impurities at levels $\geqslant$10 p.p.m.

The experimental run conditions and rate data are summarized in Table 1 and Fig. 2. Rate data using the weight-gain, SEM and SO_4^{2-} analysis methods for the same sample agree within the combined experimental uncertainties (1σ) shown in Table 1. A weighted linear least-squares fit to the data gives a rate equation $R = 10^{19.64(\pm 0.28)} \exp(-15,248(\pm 2,970)/T)$ molecules $cm^{-2}\ s^{-1}$, with a corresponding activation energy of $126.8 \pm 5.4\ kJ\ mol^{-1}$. The rate of reaction (1) was extrapolated downward to Venus surface temperatures (~660-750 K) using this equation and the Pioneer Venus radar-altimetry data[17] and atmospheric (P-T) profile[18] to take into account the altitude dependence of the rate. The derived global-mean SO_2 reaction rate is ~4.6×10^{10} molecules $cm^{-2}\ s^{-1}$, equivalent to ~1 μm of $CaSO_4$ being deposited per year. However, aeolian weathering[19] by the ~1.0-m s^{-1} winds on Venus[20] will probably remove this thin $CaSO_4$ layer on a shorter timescale, so the laboratory rate data for reaction (1) are applicable to Venus.

Chemical analyses of the Venus surface by the Venera 13, 14 and Vega 2 spacecraft[5,6] give a CaO content (by mass) of $7.90 \pm 0.51\%$ (weighted mean $\pm 1\sigma$); this is also taken as the areal percentage because of similar rock and oxide densities. Assuming that the experimental rate is representative of the rate

Sample	T (°C)*	Duration (hours)	Rate $\times 10^{-12}$ (molecules cm^{-2} s^{-1})†
R44-1	602	95	1.67 ± 0.19‡
R45-1	602	314	0.85 ± 0.77
			1.05 ± 0.12‡
R45-3	602	314	1.01 ± 0.11‡
R45-4	602	314	1.20 ± 0.51
			0.68 ± 0.48§
R36-1	746	96	8.43 ± 2.93
			13.6 ± 6.0§
R36-2	746	96	23.2 ± 6.2
			19.9 ± 11.0§
R50-1	747	192	9.19 ± 1.60
R50-3	747	192	10.5 ± 7.8
R51-1	748	96	13.2 ± 4.0
R51-2	748	96	10.3 ± 5.6
R43-1	848	91	60.4 ± 6.8
			57.1 ± 31.7§
R43-2	848	91	53.2 ± 7.0
			67.2 ± 43.4§
R43-3	848	91	58.1 ± 7.0
			48.4 ± 12.1§

* The estimated temperature uncertainty is ± 5 °C.

† The number of SO$_2$ molecules reacted per cm^2 surface area per second. The rate is from weight gain measurements unless noted otherwise. The 1σ uncertainties are also listed.

‡ The rate from ion chromatography analyses of SO$_4^{2-}$ content of reacted sample

§ The rate from scanning electron microscope (SEM) measurements of anhydrite layer thickness and porosity.
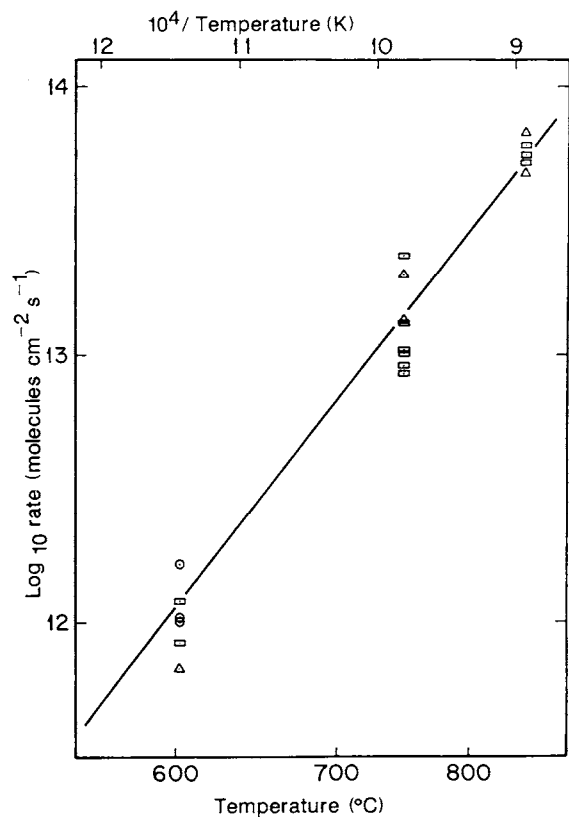
Fig. 2 Arrhenius plot of rate data from Table 1 against $1/T$. The line is a weighted linear least-squares fit, and indicates an activation energy of 126.8 ± 5.4 kJ mol^{-1}. Rates determined from independent methods (weight gain (rectangles), SEM (triangles), SO$_4^{2-}$ analyses (circles)) for the same sample agree within the 1σ experimental uncertainties.

at which SO$_2$ is depleted by reaction with calcium minerals on the Venus surface, the observed SO$_2$ column density (2.2×10^{23} molecules cm^{-2})[16] would be removed from the Venus atmosphere in $\sim 1.9 \times 10^6$ yr in the absence of a comparable sulphur source. However, maintenance of the global H$_2$SO$_4$ clouds, which are formed by the ultraviolet-sunlight-powered conversion of SO$_2$ into H$_2$SO$_4$ cloud particles[21], requires a comparable sulphur source. This source must be endogenic, because infalling cosmic material cannot supply enough sulphur. The calculated SO$_2$ removal rate on Venus is equivalent to $\sim 2.8 \times 10^{13}$ g sulphur per year. However, the measured terrestrial flux of infalling material, which is roughly applicable to Venus because of similar sizes and masses, is only $\sim 7.8 \times 10^{10}$ g yr^{-1} (ref. 22), or only $\sim 4.6 \times 10^9$ g S yr^{-1} assuming the most sulphur-rich CI chondrite composition[23].

The most plausible endogenic source is volcanism, which has occurred on Venus in the past[24], and which may have led to increased SO$_2$ levels above the Venus cloud-tops observed by the PV orbiter[25,26]. The rate of volcanism required to balance SO$_2$ depletion by reactions with calcium minerals on the Venus surface depends on the sulphur content of the erupted material (gas and magma). If this material has an overall sulphur/silicon mass ratio of 0.03 (the weighted mean of the Venera 13, 14 and Vega 2 surface analyses[5,6]), the corresponding rate of volcanism is ~ 1 km^3 yr^{-1}. Figure 3 illustrates that this rate is ~ 20 times smaller than the terrestrial value[8,27]. Two other plausible models for the S/Si ratio of the erupted material on Venus are also shown: S/Si ≈ 0.1, as in ordinary chondrites[23], giving a rate of ~ 0.4 km^3 yr^{-1} and S/Si ≈ 0.004, as in the Earth's crust[28], giving a rate of ~ 11 km^3 yr^{-1}. All rates will scale as ε^{-1}, where ε is the sulphur degassing efficiency for erupted material ($0 < \varepsilon \leq 1$). However, ε is likely to be close to unity because sulphur gases are expelled directly into the atmosphere, and hot, reactive sulphur-bearing magmas will rapidly lose sulphur to the atmos-
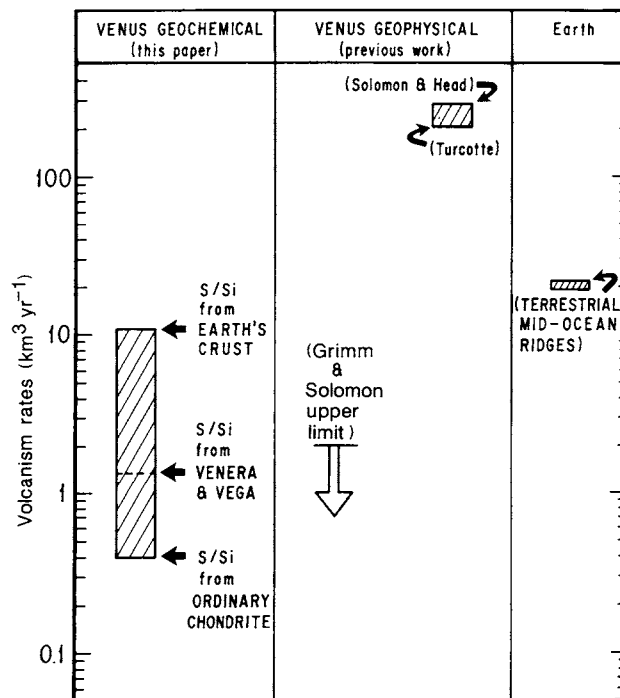
Fig. 3 Geochemical and geophysical estimates of the rate of volcanism on Venus, compared with the terrestrial rate. Three plausible models for the S/Si ratio of erupted material on Venus yield rates of ~ 0.4 to ~ 11 km^3 yr^{-1} (see text). Adopting the Venus surface S/Si ratio from Venera 13, 14 and Vega 2 analyses[5,6] yields a rate of ~ 1 km^3 yr^{-1}, or about 20 times less than the rate of volcanism on Earth. The terrestrial rate of ~ 20 km^3 yr^{-1} is based on a plate creation rate[27] of ~ 3 km^2 yr^{-1} and a crustal thickness of ~ 6 km.

phere. Our experiments on the chemical weathering by CO_2 of a possible magmatic sulphur-bearing mineral pyrite FeS_2 indicate complete loss of sulphur in hours at sub-magmatic temperatures ($\sim$980 °C).

Figure 3 also illustrates that widely discordant volcanism rates have been estimated by two different geophysical methods. Rates of $\sim$200–300 km^3 yr^{-1} are estimated by scaling terrestrial heat production to Venus and transporting the outward heat flux solely by volcanism[8,9], and an upper limit of 2 km^3 yr^{-1} is estimated by analysis of impact-crater areal densities on Venera 15, 16 radar images[7]. The present, geochemically derived volcanism rate is independent of these two methods and can be used, in principal, to test if either (or neither) is correct. In particular,

the values computed by the former geophysical method do not agree with our geochemical values. This work also suggests that on average Venus may be less volcanically active than the Earth. Finally, the geochemically estimated volcanism rate can also be used to constrain water loss on Venus through oxidation of FeO-bearing basalt[3]. This work is in progress and will be reported elsewhere.

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