

MINERAL REACTIONS WITH GASES FOUND ON VENUS SURFACES AT HIGH TEMPERATURES.

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Introduction:

The surface of Venus is a reactive chemical environment with temperatures near 460 °C, pressures ~92 bars, and a mixture of different O- and S-bearing gases in the atmosphere [1]. Many common rock forming minerals are not stable in this environment, and will react with the atmosphere to produce secondary minerals (see discussion in [2]). Critical to understanding the modern Venus surface and interpreting mission data from Venus is understanding how gas-solid reactions take place in the Venus environment. This involves knowing secondary mineral products, reaction mechanisms, and reaction rates for many mineral-gas reactions [e.g., 3].

The only chemical analyses we have of the Venus surface to date, combined with morphological evidence from orbit suggests the lowland plains are made of basalt [4]. Olivine is a common mineral in basalt, and likely important to weathering on Venus due to the large area of the plains (~80% of the surface). Weathering of this mineral has also been proposed to be a method for constraining the age of surface flows from orbital spectroscopy measurements [6]. This method relies on knowing the rate of olivine oxidation under Venus conditions, specifically how long it takes for olivine weathering to change the spectroscopic signature [6]. Mineral weathering rate has also been shown to be important to mineral preservation on Venus. Johnson and Fegley [7-9] discuss how unstable minerals may persist to the present day because of slow reaction rates.

In this work, we use high temperature furnaces with gas flow through setups to examine mineral-gas reactions in olivine and calcite when exposed to different Venus-relevant gas mixtures over different time-scales. These experiments are part of a larger effort to determine weathering rates of these minerals under Venus-like conditions.

Methods: The grains of olivine and calcite were handpicked from available samples to select the ones with the least visible inclusions and pre-existing surface alteration. Chips of olivine and calcite were cut using a diamond saw and DI water and polished to a 0.5µm finish. Mineral powders were made by wet grinding under DI water using an agate mortar and pestle. Powders were wet sieved to a grain size between 25 and 45 µm. The powders were ultrasonicated in DI water in a 20µm sieve, then rinsed in a vacuum filtration setup to remove adhered small particles. Samples were packed into quartz glass tubes and se-

cured with quartz wool on each side. Tubes were loaded into Thermo Fisher Scientific Lindberg/Blue M Mini-Mite horizontal tube furnaces, equipped with gas flow through setups. All experiments were run at 460 °C using premixed gases, and gas mixture compositions, samples, and run durations are found in Table 1.

Table 1: List of experiment conditions.

Experiment Name:	Minerals	Size	Tube Size	Gasses	Duration
V7	Olivine	Polished chips	¼"	SO ₂ , N ₂	63 Days
V10	Olivine & Calcite	Polished chips	½"	CO ₂ , SO ₂ , N ₂	14 Days
V11	Olivine & Calcite	25-45µm	¼"	SO ₂ , N ₂	14 Days
V12	Olivine & Calcite	25-45µm	½"	CO ₂ , SO ₂ , N ₂	14 Days

Upon experiment completion, samples were removed from glass tubes using tweezers and weighing paper to transfer to a clean vial and were stored in a desiccator until ready to be analyzed. Samples were then examined via Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometry (EDS) and Visible and Near Infra-Red Spectroscopy (VNIR).

Results: *Olivine:* Unreacted and reacted olivine chips appeared to have small loose particles on their surface when examined using SEM (Figure 1). In both the 14 day and 63-day experiment samples, these grains had smaller particles with more irregular shapes that were not present on the unreacted samples. These smaller brighter particles did have S in their EDS spectra (Figure 1). Sulfur generally wasn't present in the EDS spectra taken on the chip's flat surface despite the visible texture change of the majority of the sample surface in both V7 and V10 olivine chips.

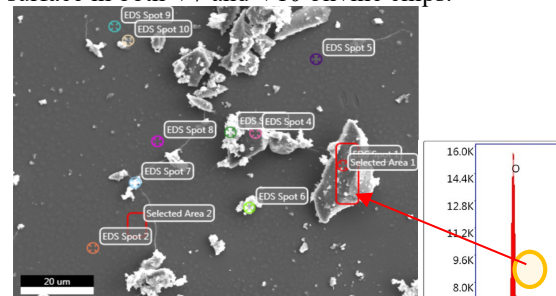


Figure 1: Secondary electron image of the surface of the olivine chip in experiment V7. On the right, an EDS spectrum measured on a surface particle area showing an S peak.

The brighter small particles seen in figure 1 show sulfur peaks but the darker surface areas, including

those on the larger loose particles do not. So it is likely the culmination of the small white particles in area 1 producing the measured sulfur absorption displayed to the right of the image. The powdered olivine samples showed a similar change from smooth surface to textured with an increase in tiny round nodules. Both V11 and V12 olivine powders had a very small peak of sulfur in the EDS spectra.

In VNIR spectra (Figure 2), the 1000 nm feature in the San Carlos olivine due to Fe^{2+} ions [3] remains relatively constant. There is a reduction in overall reflectance. Ratioing of the reacted and unreacted samples shows an increase in ferric iron bands in the 400-600 nm range, indicating oxidation. The absorption at 630 nm is greater in V11 than V12 suggesting that the $\text{CO}_2/\text{SO}_2/\text{N}_2$ present in the V11 experiment may be an more oxidizing environment than the SO_2/N_2 in V12.

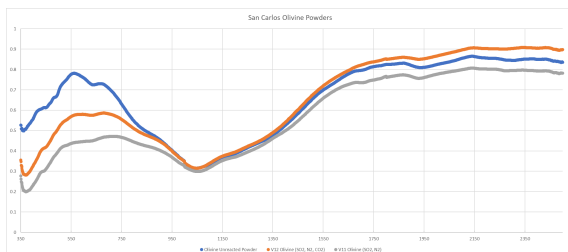


Figure 2: VNIR spectra from unreacted olivine powder (blue line), V12 olivine powder (orange line), and V11 olivine powder (gray line).

Calcite: In the reacted calcite there were generally notable sulfur reactions in many visibly different areas. In the V10 calcite chip, there were lines of brighter rectangular material that seemed reoriented in a pattern along with other rounder particles which combined to create lines across the surface not seen in the unreacted sample. Both of these pattern forming objects possessed a small peak of sulfur. Unlike the olivine, the calcite chips seem to show a reaction with sulfur in many locations rather than just those with irregular growth on loose particles.

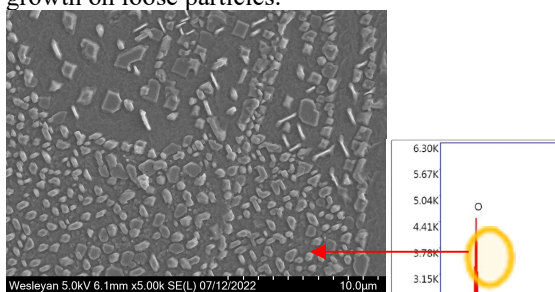


Figure 3: Secondary electron image of the surface of calcite chip in experiment V10. On the right, an EDS spectrum measured on a surface particle area showing an S peak. The rows of particles and brighter rectangles can be seen in the top half of the image.

The calcite powders seemed to have a very small potential increase in lighter nodules along rippled edges on grains. These are present in some of the unreacted samples so it is difficult to confidently confirm they are due to reaction although, the composition reports show an increase in sulfur in those areas indicating a possibility for very small amounts of reactions. Overall the calcite powders were less densely covered by secondary minerals than the calcite chips.

VNIR spectroscopy on calcite samples found the changes pictured in Figure 4. Ratioing of the reacted and unreacted samples shows a decrease in the strength of water bands at ~1000, 1400, 1900 nm, indicating some dehydration of the sample. There is also a decrease in the strength and broadening of the ~2300 band may indicate a reorientation of the calcite lattice.

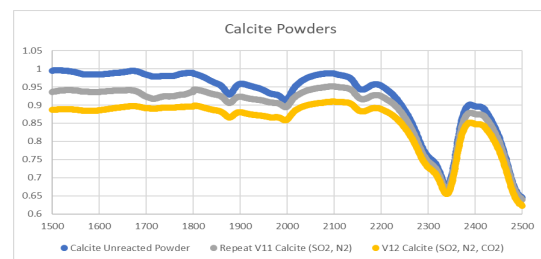


Figure 4: VNIR spectra from unreacted calcite powder (Blue line), V11 calcite powder (gray line), and V12 calcite powder (yellow line).

Discussion: Our results show sulfur reacting with calcite to form secondary minerals through gas-solid reactions. This is consistent with observations from other experiments where calcite was seen to react with sulfur-bearing gas to produce anhydrite [4]. Olivine did not develop an obvious coating of secondary minerals, but did contain sulfur.

These mineral-gas interactions are crucial in developing an understanding of the complex reactions occurring in the past and present on Venus's surface (discussion in [5]). Further experiments are needed to better constrain the rates and mechanisms of these mineral-gas reactions.

References: [1] Lodders K. and Fegley B. (1998) *The Planetary Scientist's Companion*. Oxford University Press. [2] Zolotov M.Yu. (2018) *RIMG 84*, 351-392. [3] King P.L. et al. (2018) *RIMG 84*, 1-56. [4] Treiman A.H. (2007) *Exploring Venus as a Terrestrial Planet*. AGU. p.7-22. [5] plains ref [6] Feiliberto J. et al. (2020) *Science Adv.*, 6, eaax7445. [7] Johnson N.M. and Fegley B. (2000) *Icarus*, 146, 301-306. [8] Johnson N.M. and Fegley B. (2002) *Planetary Atmospheres*, Pergamon-Elsevier. [9] Johnson N.M. and Fegley B. (2003) *Icarus*, 164, 317-333.