

SO₂ VAPOR EQUILIBRIUM WITH OXIDIZED SURFACE ROCKS. T. Widemann^{1,2}, J. W. Head³, J. Helbert⁴, S. Smrekar⁵, ¹Observatoire de Paris – LESIA UMR CNRS 8109, 92190 Meudon, France, ²Université Versailles St-Quentin - DYPAC EA 2449, France (thomas.widemann@obspm.fr), ³Dept. of Earth, Environmental and Planetary Sciences, Brown University, Providence RI, U.S.A., ⁴Institute for Planetary Research, DLR, Rutherfordstrasse 2, 12489 Berlin, Germany, ⁵Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena CA, 91109.

Background : The geochemistry and mineralogy of Venus are strongly coupled with the trace gas chemistry of the lower atmosphere. Weathering reactions on Venus' surface can be characterized from orbit using band ratios from thermal emissivity data [1] in combination with radar emissivity [2]. Sulfur dioxide on Venus has been discussed extensively over four decades for (1) its spatial and long-term variability at cloud tops, coupling chemistry and transport [3, 4], (2) its importance for the microphysics and global maintenance of the H₂SO₄ cloud cover, (3) the radiative budget in the lower and middle atmosphere, and (4) complex lithosphere-atmosphere interactions such as surface weathering and volcanism [5, 6]. Attempts to determine a geochemical sulfur cycle to explain the replenishment of atmospheric sulfur have included pyrite (FeS₂), pyrrhotite (Fe₇S₈), or anhydrite (CaSO₄) [6, 7, 8].

Ground-level SO₂ : Venus' nightside near infrared emission has provided a valuable method to investigate atmospheric trace gases in the deep atmosphere of Venus [9]. Absorption features from H₂O, HDO, CO, HCl, hydrogen fluoride (HF), SO₂, and OCS have been measured using Earth-based telescopes in the Venusian atmospheric nIR windows, providing a means to quantify their abundances in the Venusian lower atmosphere at 30-50 km [10-13]. Closer to Venus' surface, sulfur dioxide was detected *in-situ* by instruments carried by the Pioneer Venus (PV), Venera 11/12 and Vega-1/2 entry probes [14-16]. Those SO₂ measurements are not only scarce but they also strongly differ from one another: at 22 km above Navka Planitia close to Phoebe Regio (4.4N, 304E), the Pioneer-Venus Large Probe gas chromatograph (GC) data indicated a mixing ratio of 185±43 ppm; Venera 11/12 GC data 130 ± 35 ppm at 42 km, while local UV spectroscopy on board Vega-1, which landed north of Aphrodite Terra at (7.5N, 177.7E) indicated a decreasing mixing ratio of 38 ppm at 22 km and 25 ± 12 ppm at 12 km [16].

Radar bright materials in the highlands : Pyrite and carbonate/anhydrite have very different reflectance spectra, so their emissivity spectra can be distinguished in the NIR [17]. It has been long argued that the Venus lower atmosphere contains a significantly higher concentration of SO₂ than the equilibrium value with sur-

face rocks. Fegley and Treiman [5] explored how the SO₂ equilibrium value with calcite CaCO₃ and anhydrite CaSO₄ is about 3 ppm at 740K, increasing with temperature. Pyrite (FeS₂) has also long been suggested to account for the high radar reflectivity of the Venus highlands, due to its high electrical conductivity [20]; in this scenario, it controls the atmospheric SO₂ abundance through the so-called pyrite-magnetite buffer : $3\text{FeS}_2 + 16\text{CO}_2 = \text{Fe}_3\text{O}_4 + 6\text{SO}_2 + 16\text{CO}$ [7, 19], suggesting the forming of hematite by heating the basalt in a CO-CO₂ mixture. Laboratory measurements and thermochemical modeling have shown that the presence of atmospheric SO₂ also inhibits the oxidation of pyrite, increasing its stability under Venusian temperature conditions in the highlands, at lower temperatures (380°C) than the plains (460°C), while pyrrhotite is thought to remain unstable [5,6]. This has been recently addressed by new laboratory experiments [7, 8]. Suggested alternatives to pyrite-magnetite radar-bright materials in the highlands are semi-conducting metal 'frosts' that would account for the anomalous radar reflectivity [18].

Combining near-infrared and radar emissivity : We conclude that complex weathering reactions, addressing the long term stability of Venus' climate over geological timescale, can be studied by a combination of (1) infrared emissivity data on the nightside, (2) integrated analysis of SAR backscatter and emissivity measurements to determine surface dielectric and physical properties, and (3) an *in-situ* local characterization of trace gases chemistry in the lower atmosphere. An illustration of this complex inter-dependency is the weathering of basalt, first reacting with SO₂ and CO₂ and then oxidizing, its emissivity transitioning from high to low. Interaction between basalt and the atmosphere therefore produces a succession of minerals, most likely culminating in the breakdown of primary olivine and pyroxene minerals to hematite (possibly magnetite in the low plains). Hematite has an extremely characteristic infrared signature seen as a strongly negative slope from 860 to 1020 nm, as evidenced by recent laboratory measurements [21]. Relative permittivity of near-surface materials can be inferred from their microwave emissivity, itself a derivative of the radar brightness temperature, measured by using a SAR antenna as a radiometer.

Conclusion : Integrated multidisciplinary studies of the atmosphere, surface and atmosphere/surface interactions are a key pathway forward in understanding the current state and overall evolution of Venus, the most Earth-like planet yet discovered.

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