

ATMOSPHERE-SURFACE INTERACTIONS AT THE VENUS CONDITIONS: EXPERIMENTS AND MODELING. A. Cathala^{1,3}, G. Berger^{1,3}, G.S. Pokrovski^{2,3}, ¹Institut de Recherche en Astrophysique et Planétologie (IRAP), acathala@irap.omp.eu, ²Géosciences Environnement Toulouse (GET), ³Observatoire Midi-Pyrénées, Université Toulouse III - Paul Sabatier/CNRS, 14 Avenue E. Belin, 31400 Toulouse, France

Introduction:

Understanding chemical interactions between the near-surface atmosphere and the surface of Venus is a key for the comprehension of the planet's atmosphere chemistry and surface mineralogy [1], [2]. However, the chemical reactivity of basaltic materials prevailing at the Venus surface versus the hot atmospheric gases is still poorly known owing to a lack of both thermodynamic and kinetic direct data. We attempted to fill this gap by experiments at controlled conditions in a model modern Venus atmosphere (dry, CO₂-rich, sulfur-bearing) as well as in a humid early Venus environment using a Venusian chamber developed in Toulouse. Chemical exchanges between solids and the model atmosphere were monitored by in situ gas sampling during the experiments and high temperature and pressure, and by analyses of the solid samples after the runs.

Experimental and modeling details:

The chamber operates up to 500°C and 400 bars for an internal volume of 300 ml and is made of hastelloy C-276, a Ni-based alloy that minimizes chemical corrosion. The input CO₂ gas contains 3.5% vol N₂, 130 ppmv SO₂, 15 ppmv H₂S, and 15 ppmv CO. The experiments were run during 1 or 2 weeks at 470°C and 90 bar. Water was added in some runs up to 1:1 CO₂ to H₂O molar ratio.

Mineral transformations of the investigated rock samples, a natural crystallized basalt, a synthetic vitreous basalt and a natural obsidian, were analyzed at the end of the runs by SEM and XRD. The mass transfer between rocks and gas was measured during the run by sampling the supercritical gas directly into an alkaline solution, and then analyzing the condensate by ICP-MS, ICP-AES and colorimetry. Basalt in the form of slabs or powder were compared to check the effect of surface area on their reactivity (ranging from 10⁻³ to 5.4 m² in the chamber). Vitreous material was also tested with different amounts of H₂O.

The computer code HCh [3] together with data on the thermodynamic properties of minerals and gases [4]–[7], allowing chemical equilibrium calculations in multicomponent mineral-gas systems was used for modeling the element speciation and solubility in the gas phase and the resulting mineral compositions in the chamber assuming that a thermodynamic equilibrium was attained.

Experimental results:

Newly formed phases were observed in small amount at the surface of the altered materials. In a water-free gas, new minerals are mainly Na- and Ca-sulfates (Fig.1A) and Fe oxides. Some secondary phases are chemically related to the primary phase on which they grew up, reflecting a local reaction. For example, iron oxide coated the olivine surface (Fig.1B) while plagioclase and pyroxene showed sulfurization features and smoothly altered surfaces. However, some minerals have grown without chemical correlation with the substrate suggesting transfers through the gas.

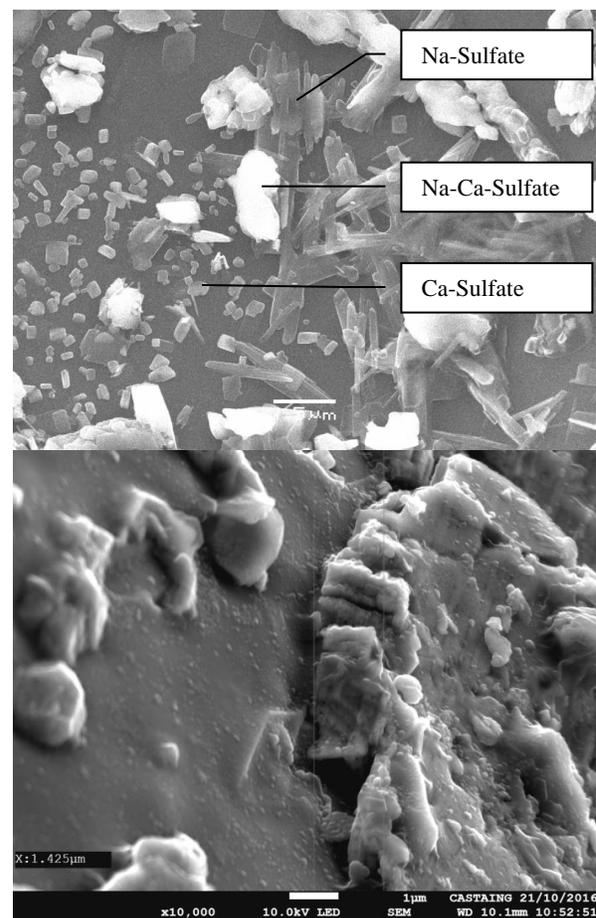


Figure 1: Newly formed phases. A (top): sulfates, likely metathenardite (Na₂SO₄), glauberite (Na₂Ca(SO₄)₂) and anhydrite (CaSO₄). B (bottom): iron oxide coating an olivine surface.

In the water-bearing system, alteration processes are far more pronounced with the formation of secondary silicates still under characterization. In the particular case of vitreous material, we found a clear correlation between the thickness of the altered layer and the partial pressure of water ($\sim 0.6 \mu\text{m}/\text{bar}$).

The intensity of alteration also depends on the exposed surface area, in particular in a wet atmosphere. When using a powder with a large surface area the thickness of the altered layer was much smaller than when using rock slabs with a low specific surface area. This finding suggests that the progression of the alteration has been limited by a chemical equilibrium with the gas. This conclusion is also supported by gas composition data. The most concentrated element in the experimented atmosphere is silicon at the level of few ppm Si in both wet and dry gas.

Numerical modeling results:

Our experimental results were compared to thermodynamic predictions assuming chemical equilibrium in the system. Calculations predict the complete transformation of fayalite member into magnetite, the excess of silica feeding the transformation of forsterite into enstatite in agreement with previous findings [8].

Pyroxene and plagioclase are also thermodynamically unstable, producing anhydrite in a dry system and hydrated silicates (mostly amphiboles and chlorites) in a wet system with a $\text{H}_2\text{O}:\text{CO}_2$ molar ratio above 10^{-4} .

Low rock-gas mass ratios ($< 6 \cdot 10^{-2}$) promote formation of a variety of secondary products (sulfates, sulfur, oxides) whereas at higher rock/gas ratios the breakdown of olivine is the only predicted reaction. In a wet gas, the amount of secondary H_2O -silicates decreases with increasing the rock/gas ratio. Most of these conclusions are consistent with our experimental observations, although enstatite was not clearly identified experimentally. By contrast, the transfer into the gas phase of significant amounts of elements from the primary rock is not well predicted except for Si in the form of $\text{Si}(\text{OH})_4$ in H_2O -rich gas (0.8 ppm Si).

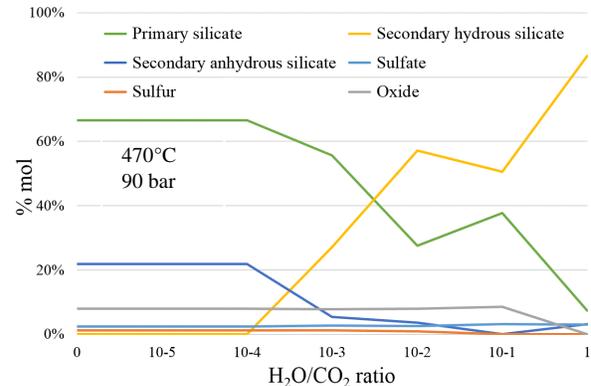


Figure 2: Mineralogical changes predicted versus $\text{H}_2\text{O}/\text{CO}_2$ ratio

Conclusions and perspectives:

Both experimental and numerical results allow better insight into the surface geochemistry of Venus. Under modern Venusian conditions, sulfates, sulfides and iron oxides (and probably enstatite) are expected to exist at the basalt surface. Under wet conditions assumed for early Venus, hydrous silicates may have formed above 40 ppm H_2O in the atmosphere that can be compared to the current H_2O concentration.

Work is in progress to a deeper investigation of the kinetics of gas-mineral reactions and a more quantitative assessment of element transfers by the gas phase.

References:

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