SULFITES ON VENUS: THERMODYNAMIC EQUILIBRIUM WITH CARBONATES AND SILICATES.
V. F. Chevrier1 and N. Nawar1, 1Arkansas Center for Space and Planetary Simulations, University of Arkansas, Fayetteville, USA, (vchevrie@uark.edu).

Introduction: The sulfur cycle on Venus represents a dynamic and complex interplay of chemical processes within the planet's atmosphere, offering key insights into its unique and extreme climatic conditions [1]. Sulfur compounds, such as sulfur dioxide (SO2), play a pivotal role in this cycle, undergoing complex transformations driven by solar radiation and atmospheric interactions ([2]Fig. 1). SO2 is a major constituent detected in Venus' atmosphere [3,4] and acts as a precursor to sulfuric acid (H2SO4) cloud formation[2].

The second and less constrained part of this cycle is the interplay with the surface. It has long been suggested that sulfur bearing minerals such as pyrite (FeS2) or anhydrite (CaSO4) result from atmospheric sulfur gases reacting with the surface (Fig. 1). The formation of anhydrite requires reaction with silicates [5] or calcite [6] and is logically dependent on the oxygen fugacity, which remains poorly constrained. Alternatively, we propose that SO2 could react directly with surface minerals to form sulfites (such as CaCO3, Fig. 1), as it has been previously observed under martian conditions [7]. In this abstract, we explore the thermodynamics of sulfites equilibria with carbonates and silicates.

Methods: We modelled the stability of anhydrous sulfites with respect to carbonates and silicates based on the three basic thermodynamic equilibrium equations:

\[ \text{XSiO}_3 + \text{SO}_2 \leftrightarrow \text{XSO}_3 + \text{SiO}_2 \]  
\[ \text{XSiO}_3 + \text{CO}_2 \leftrightarrow \text{XCO}_3 + \text{SiO}_2 \]  
\[ \text{XSO}_3 + \text{CO}_2 \leftrightarrow \text{XCO}_3 + \text{SO}_2 \]

Where X represent a divalent cation such as Ca²⁺, Mg²⁺ or Fe²⁺. In this equilibrium system, the reaction is directly with SO2 and does not involve any redox reaction and is therefore independent on the oxygen fugacity. This abstract presents results on calcium and magnesium. Thermodynamic data were sourced from [8] except for wollastonite CaSiO3 from [9]. The results are presented as either pCO2 or pSO2 as a function of temperature. For each figure, the pressure (or fugacity) of the other gas has to be fixed. So for pCO2 we chose 95 bar (pressure at the mean surface radius) and 55 bar, pressure at the highest altitude above the surface. For SO2, we chose a low value close to the surface (10 ppm) and high concentration (100 ppm) more typical of the upper atmosphere [3]. Even though such high value is highly unlikely, the general variability of SO2 [3,4], and the evidence for active volcanism [10,11] could result in locally high abundances.

![Figure 1. Sulfur cycle on Venus [2]. Sulfur dioxide SO2 is a key player in this cycle and the most abundant sulfur compound in the atmosphere. We propose a new reaction with the surface, resulting in sulfite phases (in red), which is also independent from the O2 fugacity.](image1)

![Figure 2. Equilibrium phases in the calcium carbonate / silicate / sulfite system as a function of pCO2 and temperature, for two values of pSO2: 10 ppm and 100 ppm, which brackets the values expected at the surface of Venus. The two horizontal blue lines represent the values of pCO2 at the surface ranging from 55 bar (highest altitude) to 95 bar (mean radius). The green arrow represents the temperatures of Venus’ surface.](image2)

Results: Calcium system: The calcium triple points for carbonate / silicate / sulfite occur between 570 and 620 K and for CO2 partial pressures between 2 and 100 bar...
depending on the partial pressure of SO₂ (Fig. 2). Higher pSO₂ favors Ca-sulfite at the expense of both other phases. When looking at the same system but as a function of pSO₂ (Fig. 3), we observe similar results, although the temperatures are slightly higher, between 700 and 730 K for pCO₂ values of 55 to 95 bar, respectively. Similarly, increasing pCO₂ increases the stability field of Ca-carbonate to higher pSO₂ and T values. In both cases, increasing the pressure favors the volatile-based phase (carbonate or sulfite). Increasing the temperature favors the silicate at the expense of both other phases but favors Ca-carbonate at the expense of sulfite.

Figure 4. Equilibrium phases in the calcium carbonate / silicate / sulfite system as a function of pSO₂ and temperature, for two values of pCO₂: 55 bar and 95 bar, which correspond to high altitude and mean radius, respectively. The horizontal blue line represents a high SO₂ mixing ratio in the atmosphere (100 ppm). The green arrow represents the temperatures of Venus’ surface.

Magnesium system: In the case of magnesium phases, triple points occur at lower temperatures (around 460 K) but far lower partial pressures of SO₂ and CO₂, tens of orders of magnitude below the pressures observed for the calcium system (Fig. 4).

Discussion: In the case of the calcium system, the carbonate / silicate / sulfite triple point appears very close to the Venusian surface conditions (Fig. 2 and 3). Although the temperatures on Venus are slightly too high (Fig. 2) or the partial pressure of SO₂ is slightly too low (Fig. 3) to land in the stability field of CaSO₃, the conditions are nonetheless very close, and local high peaks of SO₂ following an eruption could lead to local accumulations of Ca-sulfite, especially if sufficient calcium is available in silicate or carbonate phases. However, normal Venusian conditions rather suggest equilibrium along the carbonate – silicate boundary (wollastonite – calcite buffer), which confirms previous thermodynamic observations about the surface of Venus.

The situation for magnesium is quite surprising, as the extremely low SO₂ partial pressures at the triple points suggest that magnesium sulfite should be the stable phase under Venustian surface conditions.

One important point to consider is that sulfite is usually unstable with respect to sulfate. On Earth the only sulfite known to naturally occur is Hannebachite CaSiO₃·0.5H₂O. However, Mg-sulfite has not been observed in nature or any simulation experiment. It is highly likely that it oxidizes very rapidly into sulfate.

Figure 4. Equilibrium phases in the magnesium carbonate / silicate / sulfite system as a function of pSO₂ and temperature, for two values of pCO₂: 55 bar and 95 bar, which correspond to high altitude and mean radius, respectively.

Conclusions: Our results show that sulfite could be considered as a potential stable phase on the surface of Venus, especially in regions of high calcium abundances (ancient terrains), colder and with high SO₂ abundances. Future work will further constrain the magnesium system, test similar equilibria for iron (if possible) and test the effect of O₂ fugacity on the stability of sulfites.