

Thermodynamic Modeling of Alterations During Climate Transition Reveals Evidence of Past Temperate Conditions on Venus

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Abstract

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Thermodynamic Modeling of Alterations During Climate Transition Reveals Evidence of Past Temperate Conditions on Venus

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Key Points:

- We show that the interaction between the venusian crust, atmosphere, and paleo-ocean can reproduce the present-day atmosphere of Venus.
- The evolution of various atmospheric gases is consistent with rising surface temperatures.
- Our model's resulting mineral parageneses may be indicative of past temperate conditions.

Abstract

We modeled the thermodynamic evolution of the venusian crust in the presence of an atmosphere and paleo-ocean during a potential climate transition to its present uninhabitable state. We show that the present-day atmospheric composition of Venus is reproduced by the interaction between a paleo-ocean and crust during a runaway greenhouse. The evolution of oxygen fugacity with increasing surface temperatures converges with the present-day value (10^{-20} bar) at current temperatures (400-500°C). Other atmospheric species (CO, CH₄, H₂S, SO₂) show varying behavior depending on RedOx, but are consistent with increasing oxygen fugacity. Low-pressure conditions result in the genesis of unique mineral parageneses, including tremolite and zeolites, that could survive on Venus over geological timescales and are indicative of stable liquid water in the past if detected by future missions. Therefore, the resulting venusian mineralogy in our models could be markers of past habitable conditions that were altered by a significant greenhouse effect.

Plain Language Summary

The possibility of habitable conditions with abundant liquid water and cooler temperatures in the history of Venus remains a long-standing question in the exploration of Earth's twin sister. Studying Venus' transition to its present uninhabitable state is critical to understanding terrestrial planet evolution and whether these planets can become habitable. However, how this transition occurred is not well understood, as Venus' thick atmosphere and recent volcanic activity obscures the planet's surface. Here, we use a mathematical model that calculates the chemical reactions between the venusian crust, atmosphere, and paleo-ocean. Our model demonstrates that the interaction between Venus' crust and paleo-ocean can reproduce the present-day atmosphere. These interactions also produced unique minerals that could be evidence of past temperate climates and stable liquid water if detected by future missions. We show that present-day Venus conditions could have resulted from a past habitable climate that experienced increasing temperatures induced by a potential climate transition.

Keywords: *Venus, Climate Transition, Thermodynamic Modeling, Paleoclimate, Habitability*

1 Introduction

Venus is the hottest planet in our solar system, with surface pressures and temperatures unsuitable for life. However, early in the Solar System's history, when the Sun was 30% dimmer, Venus resided comfortably in the Sun's habitable zone (Kasting, 1993; Kopparapu et al., 2013). Venus' favorable location and the similarities between Earth's and Venus' global compositions have caused many to speculate whether Venus was once habitable. Several models demonstrated that Venus could have maintained habitable temperatures and pressures for much of its history (Kasting, 1988; Way & Del Genio, 2020; Krissansen-Totton et al., 2021). Evidence for stable liquid water from elevated D/H ratios also supported early habitability, implying a shallow reservoir in the past that was progressively lost to space through hydrogen escape (Donahue & Russell, 1997; De Bergh et al., 2006).

Studies of the planet's surface composition, interactions with the atmosphere, and geophysical processes in the interior have revealed about the surface mineralogy. Although

surface mineralogy has never been directly analyzed, *in situ* X-ray fluorescence and gamma-ray spectroscopy from Venera landers have acquired the elemental compositions of some locations (Surkov et al., 1984), from which modal abundances were derived. Previous thermodynamic models and theoretical calculations have shown that some hydrous minerals might remain stable under Venus's current surface conditions (Zolotov et al., 1997; Semprich et al., 2020). However, little research has been done to examine the effect of a runaway greenhouse on the composition of the various surface reservoirs (atmosphere, crust, and hydrosphere). This work presents the results of a global thermodynamic model of Venus' geochemical evolution during a major climate transition from temperate (terrestrial-like pressure and temperature) to present-day Venusian (average P, T = 95 bar, 460°C).

2 Methods: Geochemical Modeling

To model the geochemical evolution of Venus, we use the *Geochemist's Workbench 17*® software, specifically the *React* module, to simulate the equilibrium parageneses between various crust models, a primitive ocean, and the atmosphere as a function of temperature. We used three different models of crust: a tholeiitic basalt based on Venera 13's *in situ* measurements of the surface (Surkov et al., 1984), and two models of ancient terrains, the so-called tesserae: a granodiorite and an anorthosite, based on emissivity observations (Gilmore et al., 2015). We used standard terrestrial seawater as an ocean composition (Alanezi & Hilal, 2007). For the atmosphere, we used two CO₂ surface pressures: 1 bar to represent an ancient terrestrial "habitable" Venus and 100 bar to replicate current surface conditions. RedOx potential is not fixed in the model as there is no constraint on oxygen fugacity (*f*O₂) in the atmosphere of Venus. Instead, we consider global crust-ocean interaction that would buffer the atmosphere and the resulting *f*O₂ evolution. Initial oxidizing conditions are set to pE = 13.05 based on the iron RedOx couple (Fe²⁺/Fe³⁺, e.g. Chevrier & Morrison, 2020) that is prevalent on the surface of Venus. We then simulated the evolution of equilibrium parageneses as a function of temperature between 25 and 300°C (the highest temperature achievable by the thermodynamic database). For more information on the model's parameters and how to run it, see the Supporting Information and refer to White (2024).

3 Results

Overall, the alteration of our three models of primary crust results in globally similar mineral parageneses and a variety of phases as a function of temperature (Fig. 1). Table S1 in the Supporting Information section provides an exhaustive list of the minerals present in the results, along with their composition. Quartz is the most abundant phase at high pressure, while quartz, dolomite, mesolite, calcite, and corundum (in order of increasing temperature) are the dominant phases at low pressure. However, quartz is the dominant phase in both pressure models of granodiorite. At low pCO₂, we observe roughly three regions for mineral assemblages as a function of temperature: below 100°C, between 100 and 200°C, and above 200°C. At higher pCO₂, we only observe two regions, with a transition around 150°C. Low temperatures (< 100°C) show similar assemblages at both low and high pressures, composed of quartz, carbonates, phyllosilicates, and diaspore. At low pressure, the intermediate temperature (100-200°C) paragenesis is quite complex but is essentially composed of zeolite (mesolite), phyllosilicates (smectites and micas), and feldspar. At high temperatures, noticeable mineralogical differences are observed between the low- and high-pressure simulations. Some

phases are common to both pressures, such as corundum, microcline, and saponite-Na. However, several high-temperature silicates only appear at low pressure, including tremolite, diopside, tephroite, and andradite.

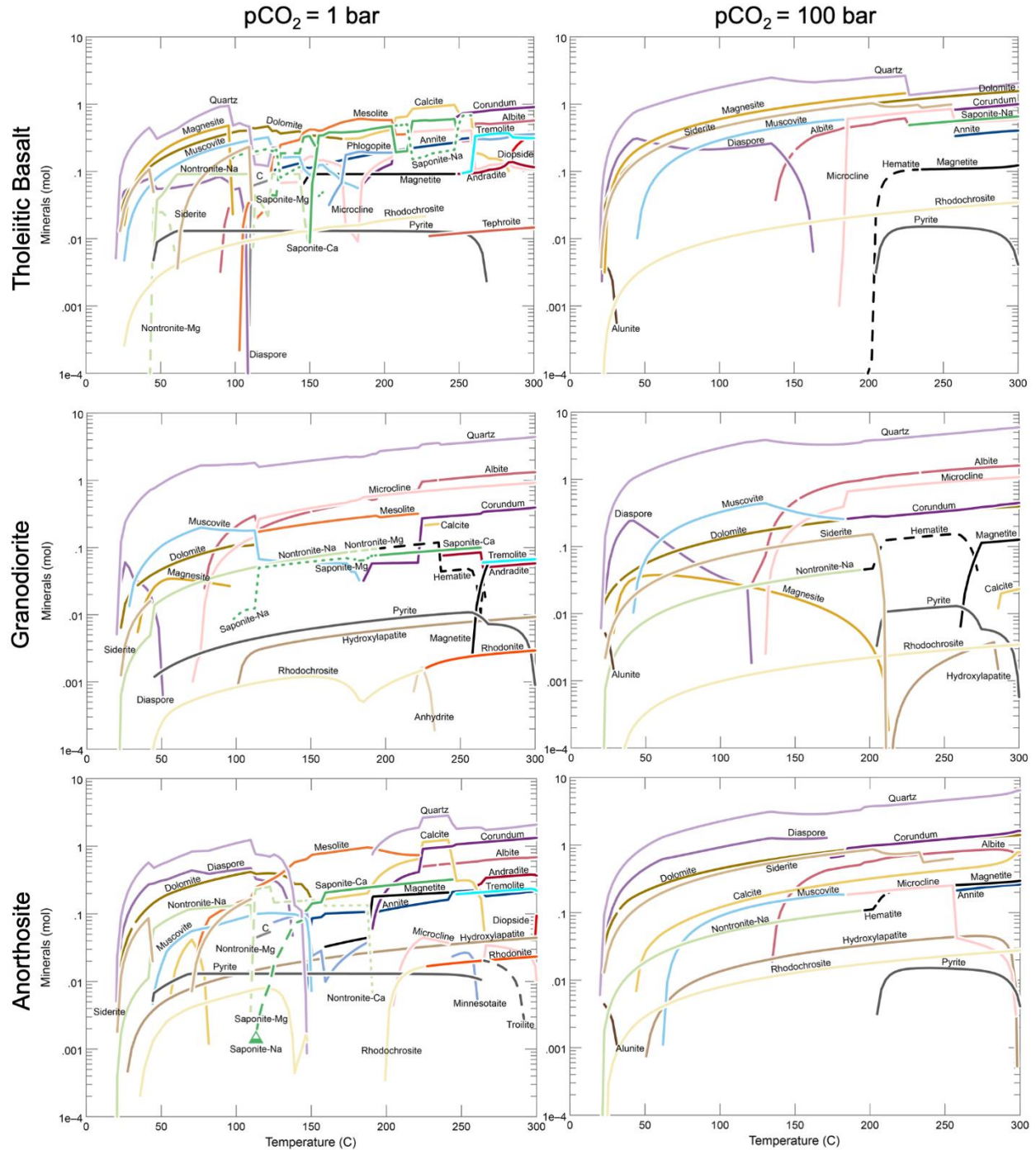


Figure 1: Evolution of mineral assemblages as a function of temperature for tholeiitic basalt (Surkov et al., 1984), granodiorite tessera (Hu et al., 2014), and gabbroic anorthosite tessera (Mukherjee et al., 2005) under initial oxidizing conditions ($pE = 13.05$). Lines denote a specific mineral's evolution that result from the interaction of the crust with the paleo-ocean and atmosphere. Dashed and dotted lines differentiate minerals with similar chemical formulas.

Mineral groups and sub-groups are divided by similar color shades: Nesosilicates, Pyroxenoids = red; Zeolites = orange; Carbonates = yellow; Smectites = green; Micas, Talc, Amphiboles = Blue; Aluminum and Silica Oxides = purple, Feldspars = pink; Sulfates, Phosphates = Brown. Sulfides, Native Elements = gray; Iron Oxides = black.

Regarding iron-bearing minerals, low-temperature, and low-pressure conditions show siderite and various nontronites. At high temperatures, nontronite typically destabilizes into iron oxide magnetite and, finally, into andradite garnet. At high pressure, nontronite destabilizes into iron oxides hematite, then magnetite. At low pressure, the iron sulfide pyrite is stable at most temperatures, but at high pressure, it only appears at high temperatures.

4 Discussion

In addition to the mineralogical transformation of the crust, the atmospheric composition also undergoes significant changes with increasing temperature. The most important parameter controlling atmospheric composition is the fugacity of oxygen (fO_2), which was calculated by our model as a function of temperature. Each model's fO_2 significantly increases with temperature from 10^{-60} bar at 25°C to 10^{-30} bar at 300°C (Fig. 2). There is also no significant variation of fO_2 between the three models we tested (Fig. 2). fO_2 values typically spread over five orders of magnitude, which is relatively small compared to the 30 orders of magnitude change of fO_2 over the entire modelled temperature range. Carbon species buffer the atmospheric fO_2 of Venus since CO_2 constitutes 96% of the atmosphere (Oyama et al., 1980). Sulfur species could only contribute to a small fraction of the atmospheric fO_2 . Therefore, the fO_2 is probably the least susceptible to fluctuations, as shown by the limited variability of our fO_2 modelled data (Fig. 2). Although our simulations do not extend beyond 300°C, the resulting fO_2 likely follows a steady trend because the mineral parageneses remain unchanged at higher temperatures (being dominated by anhydrous silicates or oxides similar to what would be present in a rock crystallized at high temperature). In those conditions, the fO_2 values depend on temperature rather than redox equilibria. At temperatures above 300°C, the paleo-ocean was most likely completely vaporized into the atmosphere. The water would be in a supercritical state but continue to react with the surface; thus, oxidation would continue, and fO_2 would keep rising (Zheng et al., 2020). Therefore, the fugacity data for each model were extrapolated via simple exponential fit up to the present-day value of $fO_2 \sim 10^{-20}$ (Fegley et al., 1997). All the resulting equilibrium temperatures are comprised between 400 and 500°C, which is very close to Venus' main surface temperature of 465°C. The 1 bar basalt, 100 bar granodiorite, and 1 bar anorthosite models show the most accurate predictions.

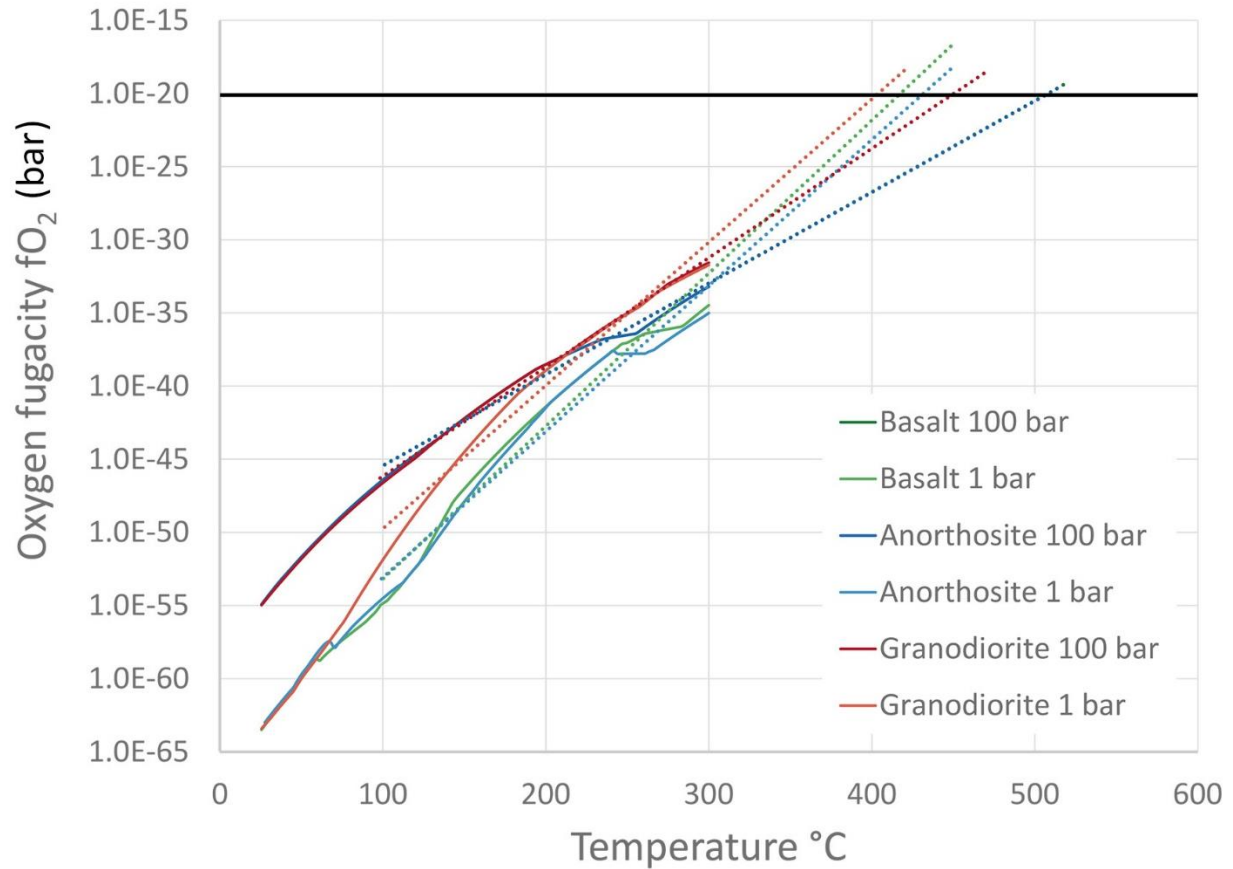


Figure 2: Oxygen fugacity (f_{O_2}) of the system. The plot combines results from each crustal model under oxidizing conditions at high and low pressure, which are denoted by different colored lines. Colors are grouped by crustal model. The 100 bar anorthosite and basalt models produce very similar gas fugacities, as a result, their lines are identical. The black line is the predicted f_{O_2} at current Venus temperatures calculated from CO observations by Pioneer and Venera spacecraft (Fegley et al., 1997), but we plot it at all temperatures. Dotted lines denote the extrapolation of each model.

We also determined the evolution of various important gas fugacities in the atmosphere of Venus: methane CH_4 , carbon monoxide CO, hydrogen sulfide H_2S and sulfur dioxide SO_2 (Fig. 3). All four species' fugacities increase with temperature but not necessarily monotonously. Nonetheless, as a test of our f_{O_2} extrapolation, we also extrapolated the gas fugacities based on the data in the range 100-300°C to their present-day measured value. The fugacity of reduced species (CH_4 and H_2S) tends to increase faster with temperature compared to oxidized species (SO_2 and CO). Reduced species show low equilibrium temperatures at present-day atmospheric fugacities, e.g., 100-300°C for CH_4 and 150-200°C for H_2S . Therefore, these low values indicate that these species are currently undersaturated compared to equilibrium fugacity values. On the other hand, oxidized species (CO, SO_2) show higher equilibrium temperatures between 300 and 450°C for CO and between 400 and 600°C for SO_2 , in both cases quite close to the mean Venusian surface temperatures. Moreover, the fugacity of reduced species is strongly affected by

the pressure of CO₂, where both CH₄ and H₂S have fugacities at 1 bar of CO₂ that are 10¹⁵ orders of magnitude above the values at 100 bar, but only for temperatures below 100°C. The fugacity values for both pressures converge with increasing temperature. The fugacity values of CH₄ converges to the present atmospheric concentration of 980 ppm (Donahue & Hoffman, 1993) typically from 250-300°C. The 1 bar granodiorite converges at 660°C (Fig. 3A), although the low p_{CO2} CH₄ fugacities seem to plateau and reach a maximum value above 100°C. In all low-pressure models, CO fugacity values increase sharply below 100°C but then exhibits a decrease in fO₂ increase rate above (Fig. 3B). The 1 bar models converge with the present-day concentration of 28 ppm at 350-450°C, which is closer to Venus' current surface temperatures compared to the 100 bar model predictions which converge around 300°C (Hoffman et al., 1980a). H₂S is interesting as it shows no variation of fugacity with the nature of the crust but extreme differences with CO₂ pressure (Fig. 3C). Akin to CH₄, H₂S fugacity values at p_{CO2} = 100 bar are 10 to 15 orders of magnitude lower than their 1 bar counterpart, but all values converge to the present day H₂S atmospheric abundance of 3 ppm (Hoffman et al., 1980b) at temperatures around 200°C. Finally, the evolution of SO₂'s fugacity differs depending on the nature of the crust (Fig. 3D). Basalt and anorthosite's SO₂ fugacity peaks from 200-300°C while granodiorite consistently increases. The 1 bar models show significant fluctuations at 100°C and 300°C, while the 100 bar models and granodiorite model show a rapid and monotonous increase. These fluctuations result in a higher variability in the final equilibrium temperatures, which are nonetheless in the range 400-600°C for an average SO₂ surface concentrations of 25 ppm (Bézard et al., 1993).

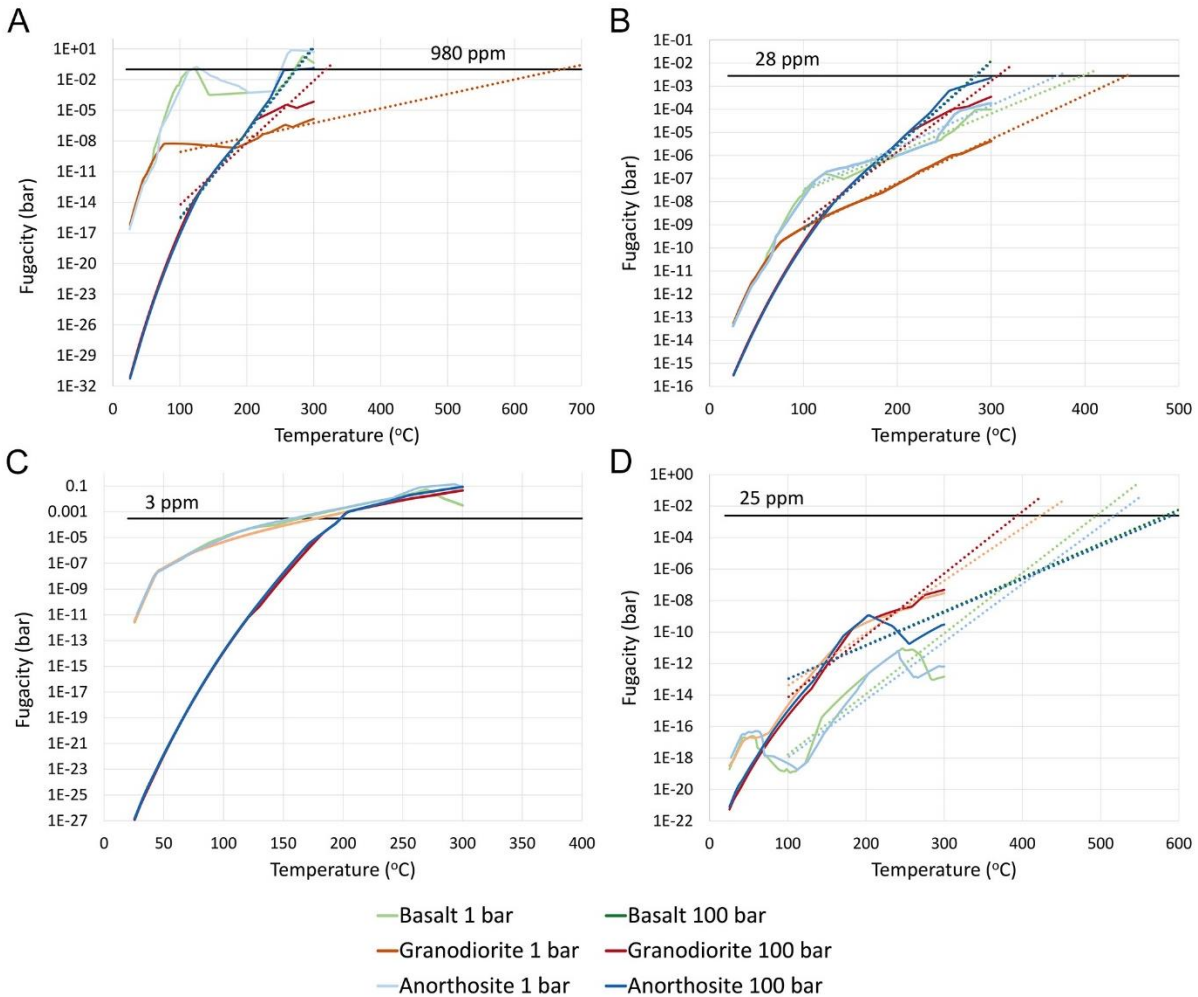


Figure 3: Fugacity of CH_4 (A), CO (B), H_2S (C), and SO_2 (D) under different partial pressures of CO_2 for each crust model (all models have initial oxidizing conditions). Plots use the same color key as Figure 2. Some trendlines are omitted if the model converges with modern-day observations. Black lines are the predicted present-day values based on spectroscopic observations, and have only been observed at present Venus temperatures ($\sim 465^\circ\text{C}$) but we show them across a wide temperature range (Donahue & Hodges, 1993; Hoffman et al., 1980a; Hoffman et al., 1980b; Bézard et al., 1993).

The difference in behavior between reduced and oxidized species and the respective low versus high temperatures reached at equilibrium with present-day atmospheric abundances are essentially due to oxygen fugacity. Our extrapolations do not consider the effect of increasing $f\text{O}_2$ on the abundance of reduced gas. It is highly likely that the fugacity of these gases would not significantly increase at high $f\text{O}_2$, as shown by the significant drop in rate for the fugacity of H_2S above 50°C for low pressure or 200°C for high pressure. The same observation can be made for CH_4 which plateaus at temperatures around 100°C in low p_{CO_2} simulations. Thus, CH_4 's and H_2S 's fugacity slopes become significantly shallower at high temperatures and could result in

higher equilibrium temperatures compared to our extrapolations, although if those species are indeed significantly undersaturated, this could also indicate an active source for those reduced gas species such as volcanism (Herrick and Hensley, 2023).

Our model focuses on equilibria in the presence of liquid water. However, other mechanisms could affect the concentrations of compounds in the atmosphere. Photochemistry in the upper cloud layer (60-70 km) oxidizes SO_2 into H_2SO_4 (Yung & Demore, 1982; Krasnopolsky, 2007), creating a continuous sink for SO_2 . In fact, the entire sulfur cycle could modify the atmospheric abundances resulting from surface alteration. Other sinks for sulfur and carbon species could be related to reactions with surface minerals. For example, the abundance of sulfur compounds could be affected by the formation of sulfides (pyrite in our model; Kohler, 2016) or sulfates (anhydrite; Zolotov, 2007). On the other hand, recent observations of active volcanism on Venus could provide sources for these gases (Filiberto et al., 2020; Herrick & Hensley, 2023). Those processes would systematically affect the equilibrium fugacities.

5 Conclusions

In the absence of any in situ identification of secondary phases, the mineralogical results presented in this study remain hypothetical. However, considering the strong arguments made by the atmospheric components and the oxygen fugacity, we can conclude that some specific phases that could survive geological timescales on the Venusian surface could be indicators of past environments. Most hydrated phases that precipitate at low temperatures would most likely not survive. However, phases like tremolite, a water-carrying amphibole, have been shown to remain stable in the current Venusian surface conditions but are characteristic of high temperatures and low CO_2 pressure. Mesolite (a zeolite) is a consistent tracer of intermediate temperatures and low CO_2 pressures. The detection of these phases by future spacecraft or landers/rovers would indicate a past environment with stable liquid water, lower pressures, and lower temperatures. This model does not reach current Venus's temperatures; consequently, some minerals (e.g., hydroxides) may destabilize in modern Venus conditions. However, our model predictions of gas and especially oxygen fugacities reproduced present-day observations and models. Therefore, we show that the current Venusian surface environment results from past habitable conditions that were altered by a significant greenhouse effect that increased temperatures and pressures. Modeling the atmospheric and mineralogical parageneses resulting from this transition helps constrain past conditions on the Venusian surface and identify signs of habitability on terrestrial planets and exoplanets.

Acknowledgments

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Open Research

The dataset containing the thermodynamic calculations used in this research is the thermo.com.V8.R6+.tdat available in Geochemist's Workbench format at: <https://www.gwb.com/thermo.php>. The data produced from these models are available online at (White, 2024).

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