Revision 1: Characterizing Basalt-Atmosphere Interactions on Venus: A Review of Thermodynamic and Experimental Results

Justin Filiberto1 and Molly C. McCanta2
1 ARES (XI3) NASA Johnson Space Center, Houston, TX 77058.
Justin.R.Filiberto@NASA.gov
2 Department of Earth and Planetary Sciences, University of Tennessee at Knoxville, Knoxville, TN 37996.
mmccanta@utk.edu

Abstract:

The surface of Venus is in contact with a hot (~470° C), high pressure (92 bars), and caustic (CO_2 with S, but little H_2O) atmosphere, which should cause progressive alteration of the crust in the form of sulfate and iron-oxide coatings; however, the exact rate of alteration and mineral species are not well constrained. Different experimental approaches, each with its own limitations, are currently being used to constrain mineralogy and alteration rate. One note is that no experimental approach has been able to fully replicate the necessary conditions and sustain them for a significant length of time. Further, geochemical modeling studies can also constrain surface alteration mineralogy, again with different assumptions and limitations. Here we review recent geochemical modeling and experimental studies to constrain the state of the art for alteration mineralogy, rate of alteration, open questions about the surface mineralogy of Venus, and what can be constrained before the fleet of missions arrive later this decade.

Combining the new results confirm that basalt on the surface of Venus should react quickly and form coatings of sulfates and iron-oxides; however, the mineralogy and rate of alteration is dependent on physical properties of the protolith (including bulk composition, mineralogy, and crystallinity), as well as atmospheric composition, and surface temperature. Importantly, the geochemically modelling results show that the mineralogy is largely controlled by atmospheric oxygen fugacity, which is not well constrained for the near surface environment on Venus. Therefore, alteration experiments run over a range of oxygen and sulfur fugacities are needed across a wide range of Venus analog materials with varying mineralogy and crystallinity.

1.0 Introduction:

The surface of Venus is in contact with a hot (~470° C), high pressure (92 bars), and caustic (CO_2 with S, but little H_2O) atmosphere, which should cause progressive alteration of the crust (e.g., Zolotov 2018; Volkov et al. 1986; Johnson and Fegley 2002). Alteration should form mainly thin rock coatings, since water is not stable on the surface to make clay minerals (e.g., Zolotov et al. 1997; 1998; Johnson et al. 2000; McCanta and Dyar 2014; Zolotov 2018). Such coatings are consistent with coatings of red hematite on the surface of rocks and regolith at the Venera 9 and 10 landing sites (e.g., Pieters et al. 1986). It has been previously proposed that these alteration surface coatings could be used to age date different lava flows, since the amount and thickness of the alteration rind should correlate with the age of the rock exposed to the atmosphere (e.g., Fegley et al. 1995; Fegley and Prinn 1989; Filiberto et al. 2020). However, there are still significant uncertainties with what alteration minerals form from different rock and mineral protoliths, the rates at which alteration minerals form and how they may fluctuate over alteration time periods, and if the alteration minerals can form a thick enough rind to affect orbital measurements (both spectroscopic and radar) (e.g., Dyar et al. 2021).

Due to the caustic nature of the Venus atmosphere and high surface temperatures, we do not have the same compositional and mineralogical data for the surface of Venus that we have for Mars, the Moon, or Mercury. Only three landed missions have measured the bulk major element composition of three rocks and radioactive element abundances for five rocks (e.g., Surkov et al. 1984; Kargel et al. 1993; Treiman 2007; Filiberto 2014), with the longest mission lasting for only 127 minutes (Venera 13). Conversely, on Mars there have been rovers active for over a decade that have measured the bulk chemistry and mineralogy of numerous rocks in various sites across the planet (e.g., Bell 2012). Overall, the few measurements show that Venus rocks are consistent with terrestrial tholeiitic and alkalic basalts, but the measurements have large error bars with some important elements (MgO) at detection limits at 2-sigma uncertainty and other important elements (Na_2O) were not measured (e.g., Surkov et al. 1984; Kargel et al. 1993; Treiman 2007; Filiberto 2014).

Further, orbital measurements cannot be used to image the surface or for reflectance spectroscopy to constrain mineralogy, bulk chemistry, or geomorphology like what has been done for Mars, the Moon, Mercury, and Pluto (e.g., Campbell 2002; Bishop et al. 2019) because of the thick opaque cloud deck. Instead, orbital night-time emissivity in the 1 μm region and radar measurements can give clues about the rock-types, and associated mineralogy, of the Venus surface (e.g., Gilmore et al. 2017; Dyar et al. 2020; Helbert et al. 2020; Treiman et al. 2021a). These orbital measurements have shown that the surface of Venus is largely consistent with basaltic rocks that have undergone various amounts of alteration (e.g., Mueller et al. 2008; Smrekar et al. 2010; Gilmore et al. 2017). Variations in both radar properties and emissivity show that some areas are consistent with very fresh and likely unweathered basalt, while other regions are consistent with either very weathered basalt, metamorphic rocks, or evolved (felsic) igneous rocks (Hashimoto et al. 2008; Mueller et al. 2008; Gilmore et al. 2015). In addition, certain mountain tops have high radar reflectivity consistent with a range of both common and very rare, and importantly as of yet not constrained, minerals (e.g., Klose et al. 1992; Schaefer and Fegley 2004; Treiman et al. 2016; Kohler 2016; Gilmore et al. 2017; Port et al. 2020; Semprich et al. 2020; Strezoski and Treiman 2022).

Large volcanic provinces are particularly interesting because of the variation in radar properties and emissivity associated with different lava flows (Smrekar et al. 2010; D'Incecco et al. 2017; 2020; 2021a, b; Filiberto et al. 2020; Brossier et al. 2020; 2021; Brossier and Gilmore 2021). Idunn Mons is perhaps the most well studied volcano on Venus because we have both orbital radar and 1 μm emissivity measurements (Smrekar et al. 2010; D'Incecoo et al. 2017; 2020; 2021a,b; Filiberto et al. 2020; Lopez et al. 2022). These data sets are consistent with fresh, relatively young lava flows on the top and eastern flank of the volcano (Smrekar et al. 2010; D'Incecoo et al. 2017; 2020; 2021a,b; Lopez et al. 2022), which has been suggested to represent active or very recently active eruptions. Similarly, radar properties of different lava flows at Maat Mons, Theia Mons, and Rhea Mons are also consistent with relatively young and possibly active volcanism (Brossier et al. 2020; 2021; Brossier and Gilmore 2021).

In the next decade, we will have extensive new data for the surface of Venus from the upcoming accepted and potential missions to Venus – NASA's DAVINCI (Garvin et al. 2022) and VERITAS (Smrekar et al. 2022) missions, ESA's EnVision mission (Ghail et al. 2016; 2020), Roscosmos' Venera-D mission (Zasova et al. 2019), China's VOICE mission (Wang et al. 2022), ISRO's Shukrayaan-I mission (Sundararajan 2021), and the privately funded Venus Life Finder mission (Seager et al. 2022). These will largely be orbital missions with new higher resolution radars and spectrometers, as well as atmospheric probes to measure the chemistry of the atmosphere and clouds and image the surface once the probe is below the opaque clouds.

In preparation for the decade of Venus exploration, multiple groups are using different experimental approaches over a range of parameter space to constrain the alteration mineralogy of the Venus surface with the main goals of determining original rock and mineral compositions and reaction rates. Experimentally it is difficult to replicate and sustain the conditions (combined ~470° C, 92 bars, CO_2-dominated atmosphere with reactive S) of Venus for long duration because of the caustic nature of the experiment (e.g., Santos et al. 2021; Treiman et al. 2021b). Due to these challenges, as well as different goals of each experimental study, different experimental approaches have been used to investigate and constrain the mineralogy: oxidation at elevated temperatures for long duration (Johnson and Fegley 2002; Filiberto et al. 2020; Cutler et al. 2020), alteration under a pure CO_2 atmosphere (Fegley et al. 1995; Teffeteller et al. 2022; Zhong et al. 2023), and alteration under a CO_2 atmosphere with S present (Berger et al. 2019; Reid 2021; Esvan et al. 2022; Radoman-Shaw et al. 2022; Santos et al. 2023). Similarly, while thermodynamic modeling can cover a much larger range of parameter space, it is limited by the available thermodynamic databases (Zolotov 2018; 2019; Semprich et al. 2020). Thermodynamic modelling also typically assumes equilibrium conditions of alteration, which may not be fully applicable to all locations on Venus, or during all geologic epochs.

Here we review recent geochemical modeling and experimental studies to constrain the state of the art for alteration mineralogy, rate of alteration, open questions about the surface mineralogy of Venus, and what can be constrained before the fleet of missions arrive later this decade.

2.0 Sources of Data:

2.1 Modeling: As thermodynamic modeling is dependent on the input database that is used, we therefore focus on the recent studies of Zolotov (2018; 2019) and Semprich et al. (2020) that have utilized up-to-date databases. Both studies used thermodynamic modeling to calculate the equilibrium alteration mineralogy of the Venus crust using Venus-relevant compositions and conditions (T, P, fO_2, fS_2, XH_2O, and XCO_2). Semprich et al. (2020) used the Gibbs free energy minimization software Perple_X 6.8.6 (Connolly, 2005) using the internally consistent thermodynamic data set of Holland and Powell (2011). Zolotov (2018) took a thermodynamic reaction by reaction approach to constrain possible surface mineralogy; however, Zolotov (2018) also reviewed the extensive literature surrounding the proposed reactions. In this work, we focus on the calculations applicable to the basaltic plains using tholeiitic and alkalic basaltic compositions, because these can be directly compared to experiments on similar rock compositions.

2.2 Experimental: Experiments have been conducted in a range of experimental apparatus - (see **Table 1** for a summary of the experimental approaches, their capabilities, and their limitations): A) high-temperature oxidation in a box furnace under terrestrial atmospheric conditions and composition (Filiberto et al. 2020; Cutler et al. 2020); B) oxidation in a CO_2 dominated atmosphere at ambient pressure (Fegley et al. 1995; Johnson and Fegley 2002; Zhong et al. 2023); C) alteration under a pure CO_2 92-bar atmosphere either 1) in cold-seal pressure vessels with oxygen fugacity buffered at hematite-magnetite (Teffeteller et al. 2022) or 2) in an autoclave-France® bolt-closure reactor with the fO_2 buffered at the Ni-NiO mineral buffer (Berger et al. 2019; Esvan et al. 2022), and D) alteration under a CO_2 atmosphere with S present in either 1) cold-seal pressure vessels with a hematite-magnetite oxygen fugacity buffer (Reid 2021); 2) an autoclave-France® bolt-closure reactor at the Ni-NiO mineral buffer (Berger et al. 2019; Esvan et al. 2022); or 3) the GEER Chamber at NASA Glenn Research Center (Radoman-Shaw et al. 2022; Santos et al. 2023). We have excluded a discussion of those experiments done with water, as they are not pertinent to modern day relatively dry Venus atmosphere (e.g., Johnson and De Oliveira 2019), but may be applicable to ancient Venus (Way and Del Genio 2020; Izenberg et al. 2021).

3.0 Results:

3.1 Modeling: Modeling results show that secondary alteration mineralogy is dependent on bulk composition, oxygen fugacity (fO_2), sulfur fugacity (fS_2), and XCO_2 of the atmosphere (Zolotov 2018; 2019; Semprich et al. 2020). For the most Venus-relevant conditions, alteration produces a sulfur-bearing phase (pyrite at low fO_2 and high fS_2 and anhydrite at higher fO_2) and an oxide phase (magnetite at low fO_2 and hematite at high fO_2) (Zolotov 2018; 2019; Semprich et al. 2020). An alkali basalt starting composition results in a similar mineralogy to the tholeiitic basalt (Semprich et al. 2020). Calcite is only stable up to almost 773 K for the alkalic basalt composition and at high XCO_2 and in the absence of sulfur (Semprich et al. 2020). Interestingly, the alteration assemblage (both oxides and the sulfur-bearing phase) is more affected by small changes in fO_2 and is relatively insensitive to changes in fS_2 (**Figure 1**). At the average conditions relevant for the basaltic plains, the assemblage does not drastically change with changes in fS_2 as evidenced by the nearly vertical mineral stability fields (Semprich et al. 2020); however, small changes in fO_2 have much more significant effects on the mineralogy as demonstrated by the close spacing of the mineral stability fields. Small changes in fO_2 result in phase changes that progress from ilmenite + magnetite → rutile + magnetite → hematite and from pyrite → anhydrite in less than five log units of fO_2 space.

3.2 Experimental: All experimental results, no matter the experimental approach or parameter space investigated, show that alteration on Venus should begin quickly. However, there are differences in both rate and resulting mineralogy depending on the experimental approach. We will take each approach (**Table 1**) individually and focus on the high-level results.

3.2.1 Oxidation in Terrestrial Air:

High temperature (room pressure) oxidation experiments are the simplest experiments to run (Haggerty and Baker 1967; Cooper et al. 1996; Knafelc et al. 2019; Filiberto et al. 2020; Cutler et al. 2020). These experiments can be run on any size sample for long duration, but are run under a terrestrial atmospheric composition, which is orders of magnitude more oxidizing than the lower atmosphere of Venus is believed to be (e.g., Fegley et al. 1997; Zolotov 2008). Therefore, these experiments have largely focused on rate of oxidation and not the exact secondary alteration mineralogy (Filiberto et al. 2020; Cutler et al. 2020). For Venus-relevant temperatures, the results of oxidation experiments show that Fe migrates to the sample surface to produce assorted iron oxides in a discontinuous coating (**Figures 2a, 3a**; Haggerty and Baker 1967; Knafelc et al. 2019; Cutler et al. 2020). Rapid olivine oxidation and alteration is observed at Venus surface temperatures, forming magnetite first and hematite as oxidation progresses, a phase progression which is associated with a change from paramagnetic to ferromagnetic behavior (Knafelc et al. 2019). Magnetite and hematite nucleate along dislocations and impurities in the crystal structure, along with forming surface coatings and crack filling in olivine crystals (Knafelc et al. 2019). Further, with progressive alteration the VNIR reflectance feature near 1 μm, characteristic of olivine, weakens and eventually disappears being replaced by a hematite signature (Filiberto et al. 2020). Pyroxene oxidation did not produce coatings but mainly oxidized Fe^{2+} to Fe^{3+} within the crystal structure along with small iron oxides forming on cracks in the sample or on iron-rich rims (McCanta and Dyar 2020; Cutler et al. 2020). However, the rate of the migration of Fe to the surface, oxide formation, and change in spectroscopic properties is dependent on the original igneous mineralogy with Fe-bearing olivine and glass reacting faster than pyroxene (Cutler et al. 2020).

3.2.2 Alteration under a CO_2 atmosphere:

Alteration of tholeiitic and alkali basalt have also been conducted a pure CO_2 1-bar atmosphere (Zhong et al. 2023), an oxidized mixed CO/CO_2 1-bar atmosphere (Fegley et al. 1995; Johnson and Fegley 2002), and pure CO_2 high pressure (92-bar) atmosphere (Teffeteller et al. 2022). Oxidation experiments on olivine crystals with a range of Mg#s in a CO2 atmosphere at 1-bar produced magnesioferrite, magnetite, laihunite, hematite and maghemite at 470 °C and hematite, magnetite, magnesioferrite and amorphous SiO2 at 900 °C; increasing temperature and iron-content accelerated the oxidation rate (Zhong et al. 2023). Similar to the oxidation under terrestrial atmosphere experiments (Filiberto et al. 2020), oxidative coatings quickly eliminate spectral characteristics of olivine (Zhong et al. 2023). The experiments with the mixed CO/CO_2 atmosphere show discontinuous formation of iron-oxide crystals on the surface of the basalt and conversion of Fe^{2+} to Fe^{3+} in the pyroxene (Fegley et al. 1995), which is similar to the oxidation under terrestrial atmosphere experimental results (McCanta and Dyar 2020; Filiberto et al. 2020; Cutler et al. 2020). Synthetic tholeiitic basalt glass and a natural alkali basalt were altered under a pure CO_2 92-bar atmosphere at the magnetite-hematite oxygen fugacity buffer using cold-seal pressure vessels (Teffeteller et al. 2022) (**Figure 3b**). The resulting alteration zones showed an enrichment of divalent cation species moving from the interior of the sample to the surface – not only of just Fe, as in the oxidation-only experiments (**Figure 2a)**. Instead, Ca was enriched by ~5 wt% and Fe was enriched by ~1–2 wt%, which favored the production of iron (Fe) oxide(s) and carbonates (calcite on the alkalic basalt and siderite on the tholeiitic basalt) as discontinuous coatings on all reacted samples in two weeks duration. Interestingly, this work showed similar alteration front thicknesses developed for samples of different starting composition and crystallinity suggesting that the alteration front advancement is rate-limited by the ability for divalent cation species to flux through the glass (Cooper et al., 1996; Teffeteller et al. 2022). However, experiments run in a dry CO_2 atmosphere at lower fO_2 and/or shorter timescales (less than 1 week) did not show any sign of alteration; this changed with an increase in pH_2O, which aided with the production of iron-oxides (Berger et al. 2019).

3.2.3 Alteration under a sulfur-bearing CO_2 atmosphere:

Experiments have recently been conducted on the same alkali partially crystalline natural basalt and tholeiitic basaltic glass starting compositions from Teffeteller et al. (2022) but with sulfur added to the atmosphere (Reid et al. 2021; Reid 2021). As with the Teffeteller et al. (2022) experiments, these SO_2-bearing runs were also conducted with an added magnetite-hematite oxygen fugacity buffer. To generate atmospheric SO_2 a pyrite source was added that decomposed throughout the run in the presence of CO_2 (Lv et al., 2015); the source was examined after each run to make sure it was not fully consumed during the experiment. Unlike the experiments with a CO_2-only atmosphere, the SO_2-bearing runs generate alteration phases more rapidly and showed significant differences between the alkalic partially crystalline natural basalt and the glassy synthetic tholeiitic basalt, with the alkalic basalt reacting much more quickly (**Figure 2b)**. For example, after 3 weeks at 470° C, the alkalic basalt is covered by ~35% alteration products compared with ~1% for the tholeiitic basalt, suggesting that the diffusive mobility of the 1+ alkali cations to the surface is significantly faster than the divalent cation flux driving alteration in the tholeiite. For the alkalic basalt, the main reaction product is (meta)-thenardite (Na_2SO_4), along with rare iron oxides (**Figure 3c**). It is worth noting that the starting alkali basalt has a high sodium concentration thereby leading to thenardite as a reaction product; a potassium-dominated alkalic starting composition could have a very different alteration sulfate assemblage. Thenardite is mainly concentrated on the glass with less dense alteration occurring on olivine, and nearly no alteration on pyroxene and plagioclase. For the tholeiite, the main reaction product is anhydrite, which occurs as a surface coating in association with Fe-oxides (either as single grains ≤ 1 μm, or as aggregate spheroid masses ~1–3 μm in diameter).

A complementary set of experiments were run on a range of basaltic precursor materials in an autoclave-France® bolt-closure reactor at the Ni-NiO mineral buffer (Berger et al. 2019; Esvan et al. 2022). These results make a nice comparison with Reid (2021) and Reid et al. (2021), which were done at higher fO_2. Berger et al. (2019) and Esvan et al. (2022) showed that basaltic glass reacts with the atmosphere to make a range of sulfate materials - anhydrite on basaltic glass and obsidian, anhydrite + (meta)thenardite + glauberite ($Na_2Ca(SO_4)_2$) on pumice. Alternatively, olivine reacts with the Venus atmosphere gas to produce an iron oxide coating instead of sulfates (Berger et al. 2019). A cross section through the alkali basalt glass shows the sulfate coating with dendrites of Fe, Mg, and Ti in the glass matrix (Berger et al. 2019). This is consistent with Ca, Mg, and Na migration towards the surface of glass, while Fe, Mg, and Ti form clusters within the glass instead; however, within olivine, Fe migrates to the surface to form iron-oxides (Berger et al. 2019; Esvan et al. 2022). Interestingly, iron-oxides do not precipitate from the glass but do form on the olivine in the basaltic samples (Berger et al. 2019; Esvan et al. 2022); comparatively, at higher fO_2, iron-oxides are similarly not the dominant mineral but do occur regularly on the tholeiitic basaltic glass (**Figure 3c**; Reid et al. 2021; Reid 2021).

Experiments on a wide range of starting materials have recently been run at the Glenn Extreme Environment Rig (GEER) at NASA John Glenn Research Center (Radoman-Shaw et al. 2022; Santos et al. 2023). The GEER laboratory benefits from a large reaction chamber where the exact gas composition can be changed from experiment to experiment, the atmospheric composition can be measured during an experiment, and the atmosphere is repumped during the experiment to account for leakages and reactions; however, the GEER chamber is currently not buffered or monitored for oxygen fugacity, the fS_2 appears higher than what is currently thought for the surface of Venus, and the chamber is built for engineering, so science experiments conducted thus far have piggy backed on those set for testing equipment (Santos et al. 2023). This means that the chamber atmosphere is reacting with all rocks, minerals, and equipment (test article or chamber fixture) at the same time, which can affect the local atmosphere around each sample and change the resulting secondary mineralogy (Radoman-Shaw et al. 2022; Santos et al. 2023). Santos et al. (2023) calculated $\log fO_2 = -21.6$ and $\log fS_2 = -4.2$ for the started gas composition, but the alteration mineralogy, specifically anhydrite plus Fe-sulfide stability, constrained the actual fS_2 and/or fO_2 to be substantially higher. Results from GEER experiments show that Ca- and Fe- bearing minerals and glasses react with the atmosphere to produce S-, O-, and Cl-bearing secondary minerals with sulfur being the dominant driver of mineral reactions in the experiments. Secondary mineralization on basaltic glasses was exceptionally fast (weeks to months) producing anhydrite, thenardite, transition metal (i.e., Cu, Cr) sulfates, an Fe-S-phase, and/or an Fe-oxide depending on the composition of the atmosphere and starting material (Radoman-Shaw et al. 2022; Santos et al. 2023). Ca-bearing pyroxenes reacted to form anhydrite in some experiments (Radoman-Shaw et al. 2022) but did not react at all in others (Santos et al. 2023). Olivine showed minimal reactivity and plagioclase and alkali feldspar did not react at all (Radoman-Shaw et al. 2022; Santos et al. 2023).

4.0 Implications:

All experiments show that alteration is fast and happens on experimental time scales. Therefore, the surface of Venus should be subjected to near-continuous alteration. To exemplify how caustic the Venus surface conditions are, no experimental approach has been able to fully replicate the necessary conditions and sustain them for a significant length of time. Each experimental approach provides important snap shots of reactions conducted at different conditions. Each approach has significant caveats and differences that need to be addressed before these results can be broadly applied to understanding the Venusian surface (as described in **Table 1**). Therefore, in order to wholistically constrain Venus surface alteration mineralogy and rates of reactions, we need extensive experiments over a broad parameter space conducted using different approaches combined with thermochemical modeling to further expand the parameter space, in order to understand how to synthesize all of the results into an understanding of Venus weathering. For all approaches, the assumptions being made (such as starting composition, material, fO2, fS2, temperature, what to leave out, what to include etc) and limitations of the approach must well documented and understood. While we have estimates for the surface-atmosphere conditions on Venus, we need to explore reactions over a large parameter space (including those outside our current estimates), to determine the effects of different variables on reactions, since there are still many unknowns about the surface-atmosphere conditions on Venus.

Alteration mineralogy from all experiments and thermodynamical modeling are consistent with the formation of sulfates (anhydrite or thenadite depending on the precursor material) with lesser iron-oxides (hematite or magnetite depending on the oxygen fugacity and/or length of experiment). The exact nature of the alteration minerals including their composition, structure, and texture (including grain size) is dependent on fO_2, fS_2, starting material, gas composition, and temperature. The effect from starting material includes crystallinity, grain size, and composition (e.g., Berger et al. 2019; Cutler et al. 2020; Teffeteller et al. 2022; Reid et al. 2021; Reid 2021; Zhong et al. 2023), but the effect may also depend on what materials are near each other (Esvan et al. 2022). For example, olivine is one of the most reactive minerals in some experiments and does not substantially react unless it is near basaltic glass in other experiments. Conversely, pyroxene rarely reacts beyond oxidation of iron in the crystal structure in most experiments, but in isolated experiments Ca-rich pyroxene produces anhydrite.

Importantly, the experimental results show that while sulfur may be the most reactive species in the atmosphere, modeling results show that the surface alteration mineralogy is more dependent on small changes in fO_2 than changes in fS_2 (Figure 1). Changes in fS_2, within the expected conditions for the surface of Venus, stay largely in the sulfate region and only at the highest fS_2, correlated with the lowest fO_2, does pyrite become the dominate S-bearing mineral. On the other hand, small changes in fO_2 will cause a change from the magnetite (+/- ilmenite) stability field to the hematite (+/- rutile) stability field. Further, increasing fO_2, while keeping fS_2 stable, will go from the pyrite stability field to the sulfate stability field. Therefore, it is critical for future experiments to either measure or preferably buffer fO_2 in each experiment using either solid state buffers (as done in Teffeteller et al. 2021 and Reid et al. 2021) or with gas mixing (as done in Fegley et al. 1995; 1997). Experiments should be done over a range of fO_2 near the hematite-magnetite buffer (e.g., Fegley et al. 1995; 1997; Zolotov 2018), but should be conducted at fO_2 above and below because as of now, the exact fO_2 at the surface-atmosphere boundary is not well constrained. Oxygen fugacity through the lower atmosphere will be measured with the VfOx (a novel ceramic device design) instrument on the DAVINCI probe mission (Isenberg et al. 2021), which will give us precise measurements at one location, above Alpha Regio, on Venus (Garvin et al. 2022). DAVINCI will also measure the atmospheric composition with Venus Tunable Laser Spectrometer (VTLMS), Venus Mass Spectrometer (VMS), and Vfox, which can be combined with experimental and modeling results to constrain mineral stability fields (Garvin et al. 2022).

Textures of alteration minerals beyond surface coatings are important and have been less investigated. For example, alteration does not only produce surface coatings on the experimental run products but can also produce 1) secondary alteration minerals within existing igneous crystals and on cracks within a sample and 2) amorphous clusters within the substrate (e.g., Berger et al. 2019; Knafelc et al. 2019; Filiberto et al. 2020; Zhong et al. 2023). Alteration rinds are also not always crystalline but can be seen as a migration of cations within the substrate towards the surface (Teffeteller et al. 2022; Reid et al. 2021; Reid 2021). These alteration cation-rinds can be microns thick in only weeks at Venus-surface conditions (Teffeteller et al. 2022; Reid et al. 2021; Reid 2021; Zhong et al. 2023) Therefore, it is vital to investigate the interiors of experimental run products and not just the surface changes alone.

Expected alteration mineralogy has also been constrained by thermodynamic modeling (see reviews Zolotov 2018; 2019 and recent work by Semprich et al. 2020), with their own sets of limitations. Models are limited based on assumptions such as pre-alteration mineralogy, and input parameters such as thermochemical constants, e.g., Gibbs Free energy of a reaction and kinetics of mineral formation. This information is gained from observations, analog experiments, and experimental results for thermochemical data (e.g., Holland and Powell 2011). Despite their limitations, models can cover a much larger parameter space than any given experimental approach. Experiments also need assumptions on starting conditions and are limited by such things as material stability (such as the glass transition temperature) and duration of the experimental run, but they deliver samples that can be observed in great detail. It is also important to note that, in general, experimental reactions observed at low temperatures may be inconsistent with equilibrium thermodynamics, which are often based on high temperature experiments required to reach equilibrium conditions. Therefore, the accuracy of extrapolating high temperature experimentally generated thermodynamic data to model Venus surface conditions at lower temperatures has not been verified, as no databases to date are calibrated for Venus-surface conditions. Therefore, each approach, experiments and models, have their own set of strengths and limitations. Combining both approaches is therefore critical to constrain surface mineralogy on Venus as best as currently possible, and neither approach should discount the other. Further, experiments over a wide range of parameter space are needed to obtain analog observations, and thermochemical databases require expansion based on these experimental results for future models.

Alteration rate has been proposed as a mechanism for age dating the surface of Venus (Fegley et al. 1995; Filiberto et al. 2020; Dyar et al. 2021); however, for alteration rate to be used to calculate an exact age of the surface, experimental results are needed to constrain the rate of surface alteration and to determine how changing mineralogy may affect orbital measurements. The experimental results to date show that alteration happens on experimental time scales, and therefore the surface should be altering in real time. However, the experimental results described above show that the rate of alteration and production of surface coatings is not linear with time and depends on the starting material (i.e., composition, mineralogy, porosity, and/or crystallinity), surface temperature, and exact atmospheric composition. Interestingly, the rate of alteration to first order does not seem to significantly depend on either fO_2 or fS_2, at least within the ranges of experiments done to date (but more experiments are needed to confirm if this is true), even though the exact alteration mineralogy is highly dependent on $f\mathrm{O}_2$ and to a lesser extent, on $f\mathrm{S}_2$.

Extensive experiments are still needed to cover the range of possible parameter space including atmospheric composition, oxidation state, temperature, and protoliths – including mineralogy, composition, crystallinity, and porosity. One important unknown required to apply the experimentally determined alteration rate to constrain Venus is the mineralogy, composition, and crystallinity of basalts on the Venusian surface (e.g., Surkov et al. 1984; Kargel et al. 1993; Treiman 2007; Filiberto 2014). As this is poorly constrained at best, it is currently impossible to use experimental results to directly calculate the exact age of any surface feature measured from orbit. Instead, relative ages can be calculated and since all experiments show incredibly fast alteration, any surfaces showing unweathered signatures must be young – less than 10s of thousands of years as a maximum and days at a minimum. Further, in situ measurements of unaltered surface materials on Venus, such as with X-ray diffraction (Blake et al. 2021), Raman spectroscopy (Sharma et al. 2010), Mossbauer for iron-mineralogy (Klingelhöfer and Fegley 2000), and/or high precision geochemistry (Treiman et al. 2020), are needed to relate alteration phases to future remotely collected data.

5.0 Conclusions:

Combining experimental results and modeling calculations suggests that basalt rocks on Venus should react quickly with the CO_2-SO_2 atmosphere to produce an alteration assemblage consisting mainly of sulfates with iron-oxides. However, the exact mineralogy and rate of alteration is dependent on the bulk chemistry, mineralogy, and crystallinity of the surface material, atmospheric composition, and surface temperature. Further, the results show that the exact sulfur-bearing and Fe-oxide mineralogy is largely controlled by the atmospheric oxygen fugacity. Therefore, any direct application of alteration rate to extract the age of lava flows should be interpreted with great caution. Future alteration experiments should be conducted on a wide range of Venus analog materials with varying mineralogy and crystallinity to constrain the effect of these parameters on things such as reaction rates, alteration mineralogy, and orbital measurements. Geochemical modeling, specifically including non-equilibrium processes, is critical to bridge between experimental results and cover a larger parameter space. In addition, experiments are needed as input parameters to make geochemical modeling more accurate and applicable to Venus surface conditions.

Acknowledgements: The authors acknowledge partial support from NASA Grant 80NSSC17K0766. Partial support for this research was provided by NASA's Planetary Science Division Research Program, through ISFM and DAVINCI. We would like to thank S.P. Schwenzer for helpful discussions and A. Santos and N. Johnson for reviews that helped clarify the manuscript.

References:

Bell, J. (2012). Mars exploration: Roving the red planet. *Nature*, *490*(7418), 34-35.

Berger, G., Cathala, A., Fabre, S., Borisova, A. Y., Pages, A., Aigouy, T., ... & Pinet, P. (2019). Experimental exploration of volcanic rocks-atmosphere interaction under Venus surface conditions. Icarus, 329, 8-23.

Bishop, J. L., Bell III, J. F., Bell, J., & Moersch, J. E. (Eds.). (2019). Remote Compositional Analysis: Techniques for Understanding Spectroscopy, Mineralogy, and Geochemistry of Planetary Surfaces (Vol. 24). Cambridge University Press.

Brossier, J. F., Gilmore, M. S., & Toner, K. (2020). Low radar emissivity signatures on Venus volcanoes and coronae: New insights on relative composition and age. Icarus, 343, 113693.

Brossier, J., Gilmore, M. S., Toner, K., & Stein, A. J. (2021). Distinct mineralogy and age of individual lava flows in Atla Regio, Venus derived from Magellan radar emissivity. Journal of Geophysical Research: Planets, 126(3), e2020JE006722.

Brossier, J., & Gilmore, M. S. (2021). Variations in the radiophysical properties of tesserae and mountain belts on Venus: Classification and mineralogical trends. Icarus, 355, 114161.

Campbell, B. A. (2002). Radar remote sensing of planetary surfaces. Cambridge University Press.

Connolly, J.A.D. (2005). Computation of phase equilibria by linear programming: A tool for geodynamic modeling and its application to subduction zone decarbonation. Earth and Planetary Science Letters. 236(1), 524-541.

Cooper, R.F., J.B. Fanselow, and D.B. Poker (1996). The mechanism of oxidation of a basaltic glass: chemical diffusion of network-modifying cations. Geochimica et Cosmochimica Acta,. 60(17), 3253-3265.

Cutler, K. S., Filiberto, J., Treiman, A. H., & Trang, D. (2020). Experimental investigation of oxidation of pyroxene and basalt: Implications for spectroscopic analyses of the surface of Venus and the ages of lava flows. The Planetary Science Journal, 1(1), 21.

D'Incecco, P., Filiberto, J., López, I., Gorinov, D. A., Komatsu, G., Martynov, A., & Pisarenko, P. (2021a). The young volcanic rises on Venus: a key scientific target for future orbital and in-situ measurements on Venus. Solar System Research, 55(4), 315-323.

D'Incecco, P., Müller, N., Helbert, J., & D'Amore, M. (2017). Idunn Mons on Venus: Location and extent of recently active lava flows. Planetary and Space Science, 136, 25-33.

D'Incecco, P., Filiberto, J., López, I., Gorinov, D. A., & Komatsu, G. (2021b). Idunn Mons: Evidence for Ongoing Volcano-tectonic Activity and Atmospheric Implications on Venus. The Planetary Science Journal, 2(5), 215.

D'Incecco, P., López, I., Komatsu, G., Ori, G. G., & Aittola, M. (2020). Local stratigraphic relations at Sandel crater, Venus: Possible evidence for recent volcano-tectonic activity in Imdr Regio. Earth and Planetary Science Letters, 546, 116410.

Dyar, M.D., Helbert, J., Cooper, R.F., Sklute, E.C., Maturilli, A., Mueller, N.T., Kappel, D. and Smrekar, S.E., (2021). Surface weathering on Venus: Constraints from kinetic, spectroscopic, and geochemical data. Icarus, 358, p.114139.

Dyar, M. D., Helbert, J., Maturilli, A., Müller, N. T., & Kappel, D. (2020). Probing Venus surface iron contents with six-band visible near-infrared spectroscopy from orbit. Geophysical Research Letters, 47(23), e2020GL090497.

Esvan, J., Berger, G., Fabre, S., Bêche, E., Thébault, Y., Pages, A., & Charvillat, C. (2022). Mechanism of olivine and glass alteration under experimental H2O-CO2 based supercritical gas: Application to modern and ancient Venus. Geochimica et Cosmochimica Acta, 335, 124-136.

Fegley, B., & Prinn, R. G. (1989). Estimation of the rate of volcanism on Venus from reaction rate measurements. Nature, 337(6202), 55-58.

Fegley Jr, B., Klingelhöfer, G., Brackett, R. A., Izenberg, N., Kremser, D. T., & Lodders, K. (1995). Basalt oxidation and the formation of hematite on the surface of Venus. Icarus, 118(2), 373-383.

Fegley Jr, B., Zolotov, M. Y., & Lodders, K. (1997). The oxidation state of the lower atmosphere and surface of Venus. Icarus, 125(2), 416-439.

Filiberto, J. (2014). Magmatic diversity on Venus: Constraints from terrestrial analog crystallization experiments. Icarus, 231, 131-136.

Filiberto, J., Trang, D., Treiman, A. H., & Gilmore, M. S. (2020). Present-day volcanism on Venus as evidenced from weathering rates of olivine. Science Advances, 6(1), eaax7445.

Garvin, J. B., Getty, S. A., Arney, G. N., Johnson, N. M., Kohler, E., Schwer, K. O., ... & Zolotov, M. (2022). Revealing the Mysteries of Venus: The DAVINCI Mission. The Planetary Science Journal, 3(5), 117.

Ghail, R., Wilson, C., Widemann, T., Bruzzone, L., Dumoulin, C., Helbert, J., ... & Burtz, L. J. (2017). EnVision: understanding why our most Earth-like neighbour is so different. arXiv preprint arXiv:1703.09010.

Ghail, R. Wilson, C., Widemann, T., Titov, D., Ansan, V., Bovolo, F., Breuer, D., Bruzzone, L., Campbell, B., Dumoulin, C., Helbert, J., Hensley, S., Kiefer, W., Komatsu, G., Le Gall, A., Marcq, E., Mason, P., Robert, S., Rosenblatt, P., Vandaele, A.C., (2020). The science goals of the EnVision Venus orbiter mission. EPSC2020-599, Europlanet Science Congress 2020.

Gilmore, M. S., Mueller, N., & Helbert, J. (2015). VIRTIS emissivity of Alpha Regio, Venus, with implications for tessera composition. Icarus, 254, 350-361.

Gilmore, M., Treiman, A., Helbert, J., & Smrekar, S. (2017). Venus surface composition constrained by observation and experiment. Space Science Reviews, 212(3), 1511-1540.

Hashimoto, G. L., Roos-Serote, M., Sugita, S., Gilmore, M. S., Kamp, L. W., Carlson, R. W., & Baines, K. H. (2008). Felsic highland crust on Venus suggested by Galileo near-infrared mapping spectrometer data. Journal of Geophysical Research: Planets, 113(E5).

Haggerty, S. E., & Baker, I. (1967). The alteration of olivine in basaltic and associated lavas: Part I: High temperature alteration. Contributions to Mineralogy and Petrology, 16, 233-257.

Helbert, J., Maturilli, A., Dyar, M. D., & Alemanno, G. (2021). Deriving iron contents from past and future Venus surface spectra with new high-temperature laboratory emissivity data. Science Advances, 7(3), eaba9428.

Holland, T. J. B., & Powell, R. (2011). An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids. Journal of metamorphic Geology, 29(3), 333-383.

Izenberg, N. R., Gentry, D. M., Smith, D. J., Gilmore, M. S., Grinspoon, D. H., Bullock, M. A., ... & Słowik, G. P. (2021). The Venus life equation. Astrobiology, 21(10), 1305-1315.

Johnson, N. M., & Fegley Jr, B. (2002). Experimental studies of atmosphere-surface interactions on Venus. Advances in Space Research, 29(2), 233-241.

Johnson, N. M., & de Oliveira, M. R. (2019). Venus atmospheric composition in situ data: A compilation. Earth and Space Science, 6(7), 1299-1318.

Johnson, N. M., & Fegley Jr, B. (2000). Water on Venus: new insights from tremolite decomposition. Icarus, 146(1), 301-306.

Kargel, J. S., Komatsu, G., Baker, V. R., & Strom, R. G. (1993). The volcanology of Venera and VEGA landing sites and the geochemistry of Venus. Icarus, 103(2), 253-275.

Klingelhöfer, G., & Fegley Jr, B. (2000). Iron Mineralogy of Venus' Surface Investigated by Mössbauer Spectroscopy. Icarus, 147(1), 1-10.

Klose, K. B., Wood, J. A., & Hashimoto, A. (1992). Mineral equilibria and the high radar reflectivity of Venus mountaintops. Journal of Geophysical Research: Planets, 97(E10), 16353-16369.

Knafelc, J., Filiberto, J., Ferré, E. C., Conder, J. A., Costello, L., Crandall, J. R., ... & Schwenzer, S. P. (2019). The effect of oxidation on the mineralogy and magnetic properties of olivine. American Mineralogist: Journal of Earth and Planetary Materials, 104(5), 694-702.

Kohler, E. (2016). Investigating mineral stability under Venus conditions: A focus on the Venus radar anomalies. University of Arkansas.

López, I., D'Incecco, P., Filiberto, J., & Komatsu, G. (2022). The volcanology of Idunn Mons, Venus: The complex evolution of a possible active volcano. Journal of Volcanology and Geothermal Research, 421, 107428.

Lv, W., Yu, D., Wu, J., Zhang, L., & Xu, M. (2015). The chemical role of CO_2 in pyrite thermal decomposition. Proceedings of the Combustion Institute, 35(3), 3637–3644. https://doi.org/10.1016/j.proci.2014.06.066

McCanta, M. C., & Dyar, M. D. (2020). Effects of oxidation on pyroxene visible-near infrared and mid-infrared spectra. Icarus, 352, 113978.

Mueller, N., Helbert, J., Hashimoto, G. L., Tsang, C. C. C., Erard, S., Piccioni, G., & Drossart, P. (2008). Venus surface thermal emission at 1 μm in VIRTIS imaging observations: Evidence for variation of crust and mantle differentiation conditions. Journal of Geophysical Research: Planets, 113(E5).

Pieters, C.M., Head, J.W., Pratt, S., Patterson, W., Garvin, J., Barsukov, V.L., Basilevsky, A.T., Khodakovsky, I.L., Selivanov, A.S., Panfilov, A.S. and Gektin, Y.M. (1986). The color of the surface of Venus. Science, 234(4782), 1379-1383.

Port, S. T., Chevrier, V. F., & Kohler, E. (2020). Investigation into the radar anomaly on Venus: The effect of Venus conditions on bismuth, tellurium, and sulfur mixtures. Icarus, 336, 113432.

Radoman-Shaw, B. G., Harvey, R. P., Costa, G., Jacobson, N. S., Avishai, A., Nakley, L. M., & Vento, D. (2022). Experiments on the reactivity of basaltic minerals and glasses in Venus surface conditions using the Glenn Extreme Environment Rig. Meteoritics & Planetary Science, 57(10), 1796-1819.

Reid, R. B., McCanta, M. C., Filiberto, J., Treiman, A. H., Keller, L., & Rutherford, M. (2021, March). Assessment of the Effect of Bulk Composition on Basalt Weathering on Venus' Surface. In 52nd Lunar and Planetary Science Conference (No. 2548, p. 1293).

Reid, R. B. (2021). Experimental alteration of Venusian surface basalts in a hybrid CO2-SO2 atmosphere.

Santos, A. et al. (2023) Experimental weathering of rocks and minerals at Venus conditions in the Glenn Extreme Environments Rig (GEER). Journal of Geophysical Research: Planets. In press.

Santos, A., Filiberto, J., Ganesh, I., Gilmore, M., Lewis, J. A., & Treiman, A. H. (2021). Venus Petrology: The Need for New Data. Bulletin of the American Astronomical Society, 53(4), 177.

Schaefer, L., & Fegley Jr, B. (2004). Heavy metal frost on Venus. Icarus, 168(1), 215-219.

Seager, S., Petkowski, J. J., Carr, C. E., Grinspoon, D. H., Ehlmann, B. L., Saikia, S. J., ... & Venus Life Finder Mission Team. (2022). Venus life finder missions motivation and summary. Aerospace, 9(7), 385.

Semprich, J., J. Filiberto, and A.H. Treiman (2020) Venus: A phase equilibria approach to model surface alteration as a function of rock composition, oxygen- and sulfur fugacities. Icarus, 346: p. 113779.

Sharma, S. K., Misra, A. K., Clegg, S. M., Barefield, J. E., Wiens, R. C., & Acosta, T. (2010). Time-resolved remote Raman study of minerals under supercritical CO2 and high temperatures relevant to Venus exploration. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 368(1922), 3167-3191.

Smrekar, S., Hensley, S., Nybakken, R., Wallace, M. S., Perkovic-Martin, D., You, T. H., ... & Mazarico, E. (2022). VERITAS (Venus emissivity, radio science, InSAR, topography, and spectroscopy): a discovery mission. In 2022 IEEE Aerospace Conference (AERO) (pp. 1-20). IEEE.

Smrekar, S. E., Stofan, E. R., Mueller, N., Treiman, A., Elkins-Tanton, L., Helbert, J., ... & Drossart, P. (2010). Recent hotspot volcanism on Venus from VIRTIS emissivity data. Science, 328(5978), 605-608.

Sundararajan, V. (2021). Tradespace Exploration of Space System Architecture and Design for India's Shukrayaan-1, Venus Orbiter Mission. In ASCEND 2021 (p. 4103).

Strezoski, A., & Treiman, A. H. (2022). The “Snow Line” on Venus’s Maxwell Montes: Varying Elevation Implies a Dynamic Atmosphere. The Planetary Science Journal, 3(12), 264.

Surkov, Y. A., Barsukov, V. L., Moskalyeva, L. P., Kharyukova, V. P., & Kemurdzhian, A. L. (1984). New data on the composition, structure, and properties of Venus rock obtained by Venera 13 and Venera 14. Journal of Geophysical Research: Solid Earth, 89(S02), B393-B402.

Teffeteller, H., Filiberto, J., McCanta, M. C., Treiman, A. H., Keller, L., Cherniak, D., ... & Cooper, R. F. (2022). An experimental study of the alteration of basalt on the surface of Venus. Icarus, 115085.

Treiman, A. H. (2007). Geochemistry of Venus' surface: Current limitations as future opportunities. *GEOPHYSICAL MONOGRAPH-AMERICAN GEOPHYSICAL UNION*, *176*, 7.

Treiman, A., Harrington, E., & Sharpton, V. (2016). Venus’ radar-bright highlands: Different signatures and materials on Ovda Regio and on Maxwell Montes. Icarus, 280, 172-182.

Treiman, A. H., Filiberto, J., & Rivera-Valentín, E. G. (2020). How Good is “Good Enough?” Major Element Chemical Analyses of Planetary Basalts by Spacecraft Instruments. The Planetary Science Journal, 1(3), 65.

Treiman, A., McCanta, M., & Filiberto, J. (2021b). Laboratory Studies in Support of Venus Exploration: Surface and Near-Surface. Bulletin of the American Astronomical Society, 53(4), 077.

Treiman, A. H., Filiberto, J., & Vander Kaaden, K. E. (2021a). Near-infrared Reflectance of Rocks at High Temperature: Preliminary Results and Implications for Near-infrared Emissivity of Venus's Surface. The Planetary Science Journal, 2(2), 43.

Wang, C., Song, T., Shi, P., Li, M., & Fan, Q. (2022). China's Space Science Program (2025–2030): Strategic Priority Program on Space Science (III). Chinese Journal of Space Science, 42(4), 514-518.

Way, M. J., & Del Genio, A. D. (2020). Venusian habitable climate scenarios: Modeling Venus through time and applications to slowly rotating Venus-like exoplanets. Journal of Geophysical Research: Planets, 125(5), e2019JE006276.

Volkov, V., M.Y. Zolotov, and I. Khodakovsky, Lithospheric-atmospheric interaction on Venus, in Chemistry and physics of terrestrial planets. 1986, Springer. p. 136-190.

Zasova, L. V., Gorinov, D. A., Eismont, N. A., Kovalenko, I. D., Abbakumov, A. S., & Bober, S. A. (2019). Venera-D: A design of an automatic space station for Venus exploration. Solar System Research, 53(7), 506-510.

Zhong, S. S., Zhao, Y. Y. S., Lin, H., Chang, R., Qi, C., Wang, J., Mo, B. Wen, Y., Yu, W. Zhou D-S., Yu, X-W, Li, X, and Liu, J. (2023). High-Temperature Oxidation of Magnesium- and Iron-Rich Olivine under a CO_2 Atmosphere: Implications for Venus. Remote Sensing, 15(8), 1959.

Zolotov, M. Y., Fegley Jr, B., & Lodders, K. (1997). Hydrous silicates and water on Venus. Icarus, 130(2), 475-494.

Zolotov, M. Y., Fegley, B., & Lodders, K. (1998). Stability of micas on the surface of Venus. Planetary and space science, 47(1-2), 245-260.

Zolotov, M.Y., Gas-Solid Interactions on Venus and Other Solar System Bodies. Reviews in Mineralogy and Geochemistry, 2018. 48: p. 351-392.

Zolotov, M. (2019). Chemical weathering on Venus. In *Oxford Research Encyclopedia of Planetary Science*.

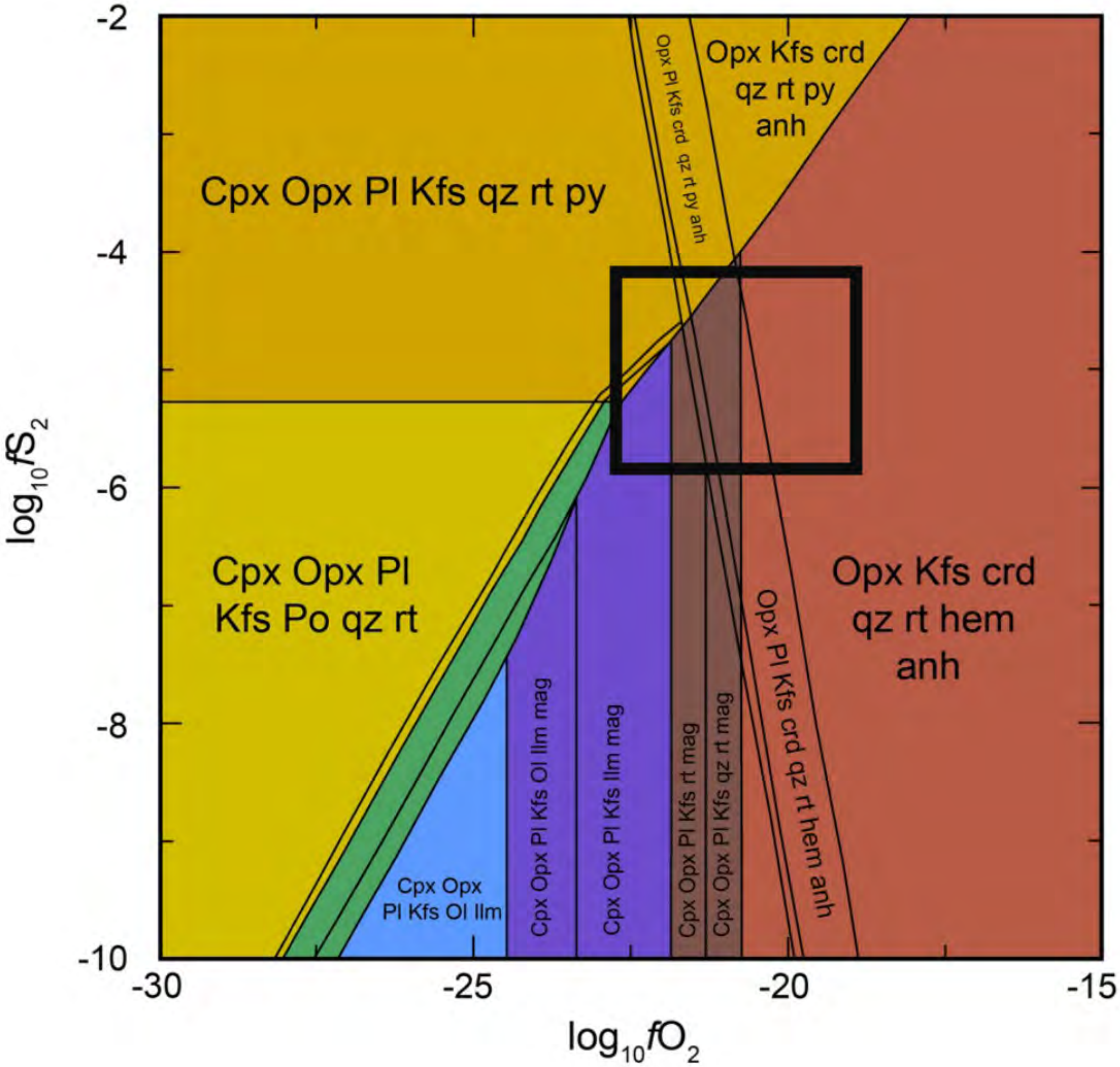
Figure captions

Figure 1. Metamorphic phase equilibria for a basalt composition as a function of oxygen and sulfur fugacities and at temperature-pressure conditions (470 °C, 96.6 bar) applicable to the Venus basaltic plains region, from Semprich et al. (2020). The black boxes represent the most likely fugacities (oxygen fugacity: 10^{-19}–10^{-23} bars and sulfur fugacity: $10^{-4.2}$ – 10^{-6} bars) for the basaltic plains based on Zolotov (2018). Hematite – red, magnetite – brown, pyrite – dark yellow, pyrrhotite – bright yellow, ilmenite + magnetite – purple, ilmenite – blue, ilmenite + pyrrhotite – green.

Figure 2. Progression of geochemical alteration under various Venus atmospheric conditions from experimental data. A) O_2 or CO_2-only atmosphere i. Unaltered basalt in contact with O_2 or CO_2 atmosphere. Elemental fluxes are shown as different length arrows based on diffusion rate within basalt glass (i.e., faster diffusion rate = longer arrow). ii. Progressively altered basalt after some experimental duration. Surface is coated in oxide phases based on diffusion rates and mineral stability. A Si-enriched layer is present directly below the surface due to the relative immobility of Si. Further from the surface-atmosphere interface, a divalent-enriched region is developed due to diffusionary flux. At some depth, unaltered basalt is still present. B. SO_2+CO_2 atmosphere. iii. Unaltered basalt. iv. Progressively altered basalt after some experimental duration. Surface is coated in sulfate and oxide phases based on diffusion rates and mineral stability. A Si-enriched layer is present directly below the surface due to the relative immobility of Si. Further from the surface-atmosphere interface, divalent- and univalent-enriched regions are developed based on diffusion rate differences between the two cation species. At some depth, unaltered basalt is still present.

Figure 3. Backscatter electron (BSE) images of surface coating as a function of atmospheric composition. A) Surface coating on an alkaline basalt in an O_2-only atmosphere (Cutler et al., 2020). B) Surface coating on an alkaline basalt in a CO_2-only atmosphere, 90 bars, 700°C (Teffeteller et al., 2022). C) Surface coating on an alkaline basalt in a SO_2+CO_2 atmosphere, 90 bars, 700ºC (Reid et al., 2021; submitted).

Figure 1


-2
-4
-6
-8
-10
-30
-25
-20
-15
$\log_{10}fS_2$
$\log_{10}fO_2$
Cpx Opx Pl Kfs qz rt py
Opx Pl Kfs crd qz rt py anh
Opx Kfs crd qz rt py anh
Cpx Opx Pl Kfs Po qz rt
Cpx Opx Pl Kfs Ol Ilm
Cpx Opx Pl Kfs Ol Ilm mag
Cpx Opx Pl Kfs Ilm mag
Cpx Opx Pl Kfs rt mag
Cpx Opx Pl Kfs qz rt mag
Opx Pl Kfs crd qz rt hem anh
Opx Kfs crd qz rt hem anh

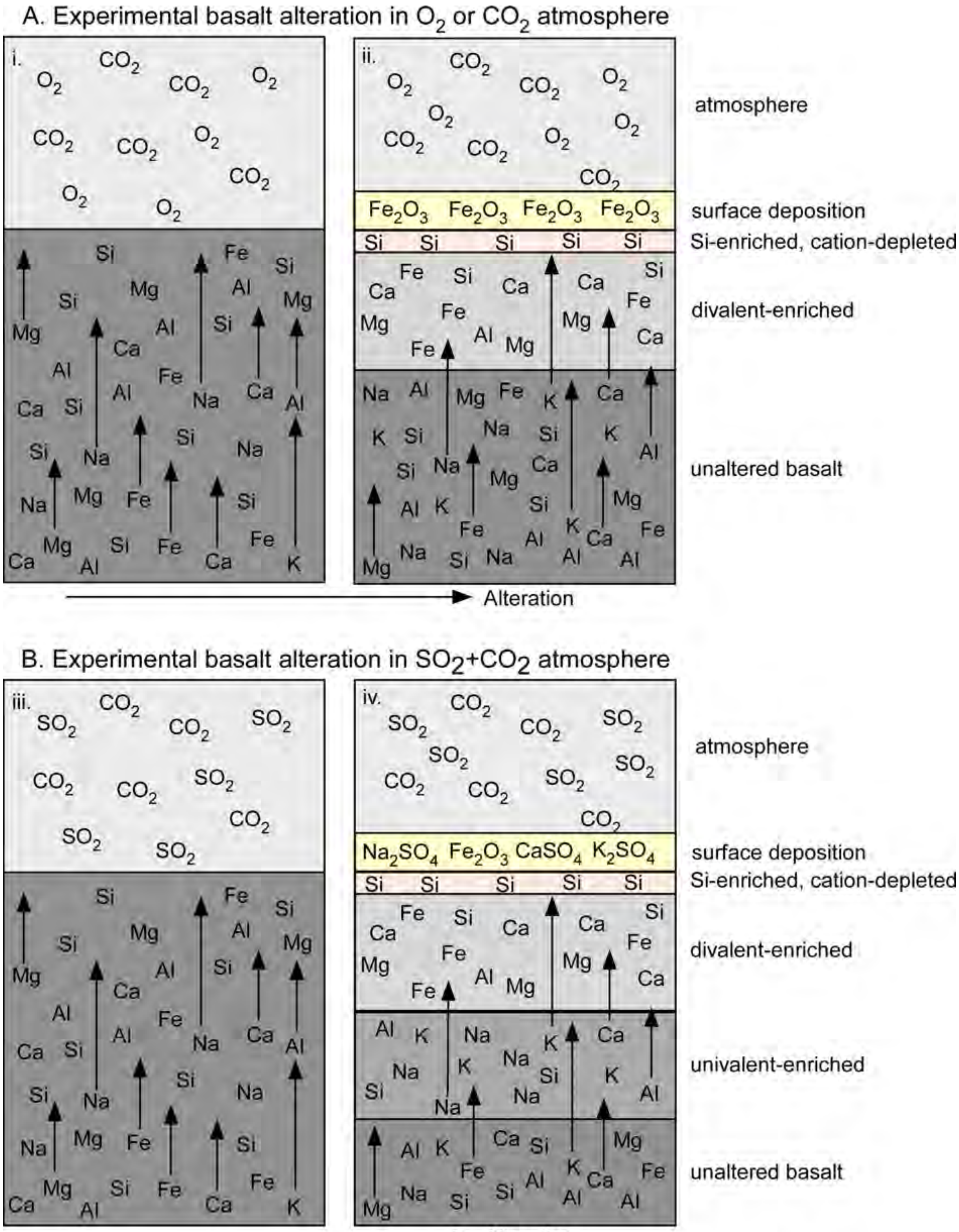

A. Experimental basalt alteration in O2 or CO2 atmosphere
i.
ii.
O2
CO2
atmosphere
Fe2O3 Fe2O3 Fe2O3 Fe2O3
surface deposition
Si Si Si Si Si
Si-enriched, cation-depleted
divalent-enriched
unaltered basalt
Ca Fe Si Mg Al Na K
Alteration
B. Experimental basalt alteration in SO2+CO2 atmosphere
iii.
iv.
SO2
CO2
atmosphere
Na2SO4 Fe2O3 CaSO4 K2SO4
surface deposition
Si Si Si Si Si
Si-enriched, cation-depleted
divalent-enriched
univalent-enriched
unaltered basalt
Alteration

Figure 2.

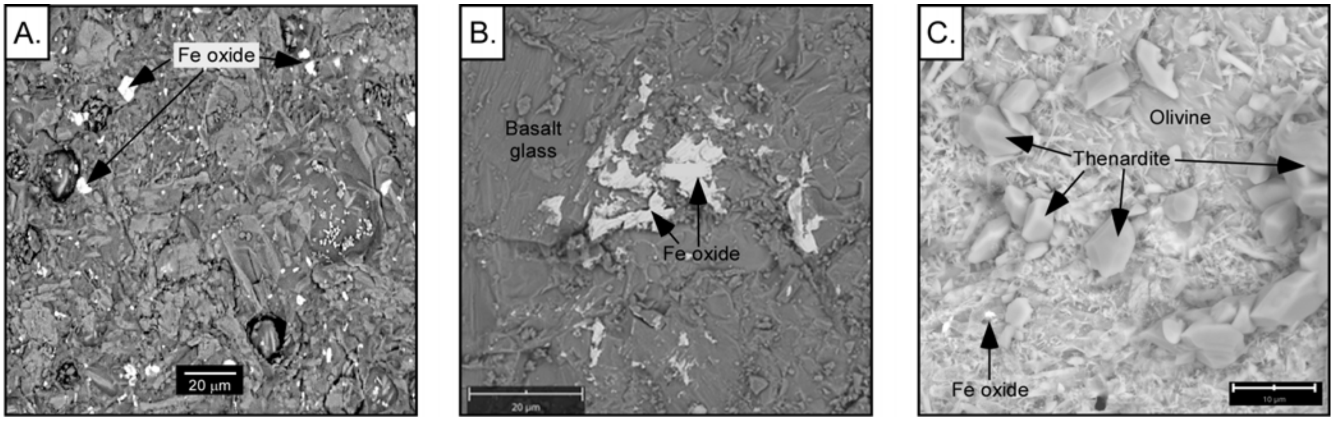

A.
Fe oxide
20 µm
B.
Basalt glass
Fe oxide
20 µm
C.
Olivine
Thenardite
Fe oxide
10 µm

Figure 3.

Table 1. List of experimental approaches and their capabilities and l

Experimental Approach	*Pressure*
Box Furnace	1 bar
Gas Mixing Furnace	1 bar
Autoclave	controlable
Cold Seal Apparatus	controlable
GEER Chamber	controlable
Venus In-Situ Chamber Investigations at Goddard	1-96 bars
Other idividual chambers as custom built	

limits

Atmosphere Composition	*Control fO_2*	*Control fS_2*
Terrestrial atmosphere	No ~ QFM +10	No
Simple mixed gas species	Yes	No
Simple mixed gas species	No	No
Simple mixed gas species	Yes with solid buffers	No
Complex mixed gas species	No	No
pure CO_2 or N_2, may include SO_2 at ppm levels	Not specified	No

Example References	*Other notes*
Filiberto et al. (2020); Cutler et al. (2021)	Can be run for long duration and large samples, b
Fegley et al. (1995); Zhong et al. (2023)	Control of $f\mathrm{O}_2$ is tied to controling atmospheric c
Berger et al. (2019); Esvan et al. (2022)	$f\mathrm{O}_2$ is at the low end of the range expected for th
Teffeteller et al. (2021); Reid et al. (2021)	Standard experimental petrology approach chan
Radoman-Shaw et al. (2022); Santos et al. (2023)	Samples react with everything in the chamber; se
Kohler and Johnson (2021)	
Santos et al. (2021) for a review of other facilities	

ut is useful for rate and oxidation only

omposition

e Venus surface (~Ni-NiO; Berger et al. 2019; Esvan et al. 2022), but the exact fO2 is dependent on the

ged to pressurizing with CO_2

elect atmospheric gas sepcies can be measured ex situ; atmospheric gas can be adjusted during the expe specific alloy used for the vessel

eriment