

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

Justin Filiberto<sup>1</sup> and Molly C. McCanta<sup>2</sup>

<sup>1</sup> ARES (XI3) NASA Johnson Space Center, Houston, TX 77058.

[Justin.R.Filiberto@NASA.gov](mailto:Justin.R.Filiberto@NASA.gov)

<sup>2</sup> Department of Earth and Planetary Sciences, University of Tennessee at Knoxville, Knoxville, TN 37996.

[mmccanta@utk.edu](mailto:mmccanta@utk.edu)

## **Abstract:**

The surface of Venus is in contact with a hot (~470° C), high pressure (92 bars), and caustic (CO<sub>2</sub> with S, but little H<sub>2</sub>O) 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<sub>2</sub> with S, but little H<sub>2</sub>O) 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<sub>2</sub>O) 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  $\mu\text{m}$  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  $\mu\text{m}$  emissivity measurements (Smrekar et al. 2010; D’Incecco 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’Incecco 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  $\sim 470^\circ\text{C}$ , 92 bars,  $\text{CO}_2$ -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  $\text{CO}_2$  atmosphere (Fegley et al. 1995; Teffeteller et al. 2022; Zhong et al. 2023), and alteration under a  $\text{CO}_2$  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 ( $T$ ,  $P$ ,  $f\text{O}_2$ ,  $f\text{S}_2$ ,  $X\text{H}_2\text{O}$ , and  $X\text{CO}_2$ ). 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<sub>2</sub> dominated atmosphere at ambient pressure (Fegley et al. 1995; Johnson and Fegley 2002; Zhong et al. 2023); C) alteration under a pure CO<sub>2</sub> 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<sub>2</sub> 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  $\rightarrow$  rutile + magnetite  $\rightarrow$  hematite and from pyrite  $\rightarrow$  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  $\mu\text{m}$ , 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  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  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<sub>2</sub> atmosphere:*

Alteration of tholeiitic and alkali basalt have also been conducted a pure CO<sub>2</sub> 1-bar atmosphere (Zhong et al. 2023), an oxidized mixed CO/CO<sub>2</sub> 1-bar atmosphere (Fegley et al. 1995; Johnson and Fegley 2002), and pure CO<sub>2</sub> high pressure (92-bar) atmosphere (Teffeteller et al. 2022). Oxidation experiments on olivine crystals with a range of Mg#s in a CO<sub>2</sub> atmosphere at 1-bar produced magnesioferrite, magnetite, laihunite, hematite and maghemite at 470 °C and hematite, magnetite, magnesioferrite and amorphous SiO<sub>2</sub> 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<sub>2</sub> atmosphere show discontinuous formation of iron-oxide crystals on the surface of the basalt and conversion of Fe<sup>2+</sup> to Fe<sup>3+</sup> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>-bearing runs were also conducted with an added magnetite-hematite oxygen fugacity buffer. To generate atmospheric SO<sub>2</sub> a pyrite source was added that decomposed throughout the run in the presence of CO<sub>2</sub> (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<sub>2</sub>-only atmosphere, the SO<sub>2</sub>-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<sub>2</sub>SO<sub>4</sub>), 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 *f*O<sub>2</sub>. 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<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub>) 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,  $fO_2$ ,  $fS_2$ , 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 thenardite 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  $f\text{O}_2$  than changes in  $f\text{S}_2$  (Figure 1). Changes in  $f\text{S}_2$ , within the expected conditions for the surface of Venus, stay largely in the sulfate region and only at the highest  $f\text{S}_2$ , correlated with the lowest  $f\text{O}_2$ , does pyrite become the dominate S-bearing mineral. On the other hand, small changes in  $f\text{O}_2$  will cause a change from the magnetite (+/- ilmenite) stability field to the hematite (+/- rutile) stability field. Further, increasing  $f\text{O}_2$ , while keeping  $f\text{S}_2$  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  $f\text{O}_2$  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  $f\text{O}_2$  near the hematite-magnetite buffer (e.g., Fegley et al. 1995; 1997; Zolotov 2018), but should be conducted at  $f\text{O}_2$  above and below because as of now, the exact  $f\text{O}_2$  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  $f\text{O}_2$  or  $f\text{S}_2$ , 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  $f\text{O}_2$  and to a lesser extent, on  $f\text{S}_2$ .

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  $\text{CO}_2$ - $\text{SO}_2$  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.

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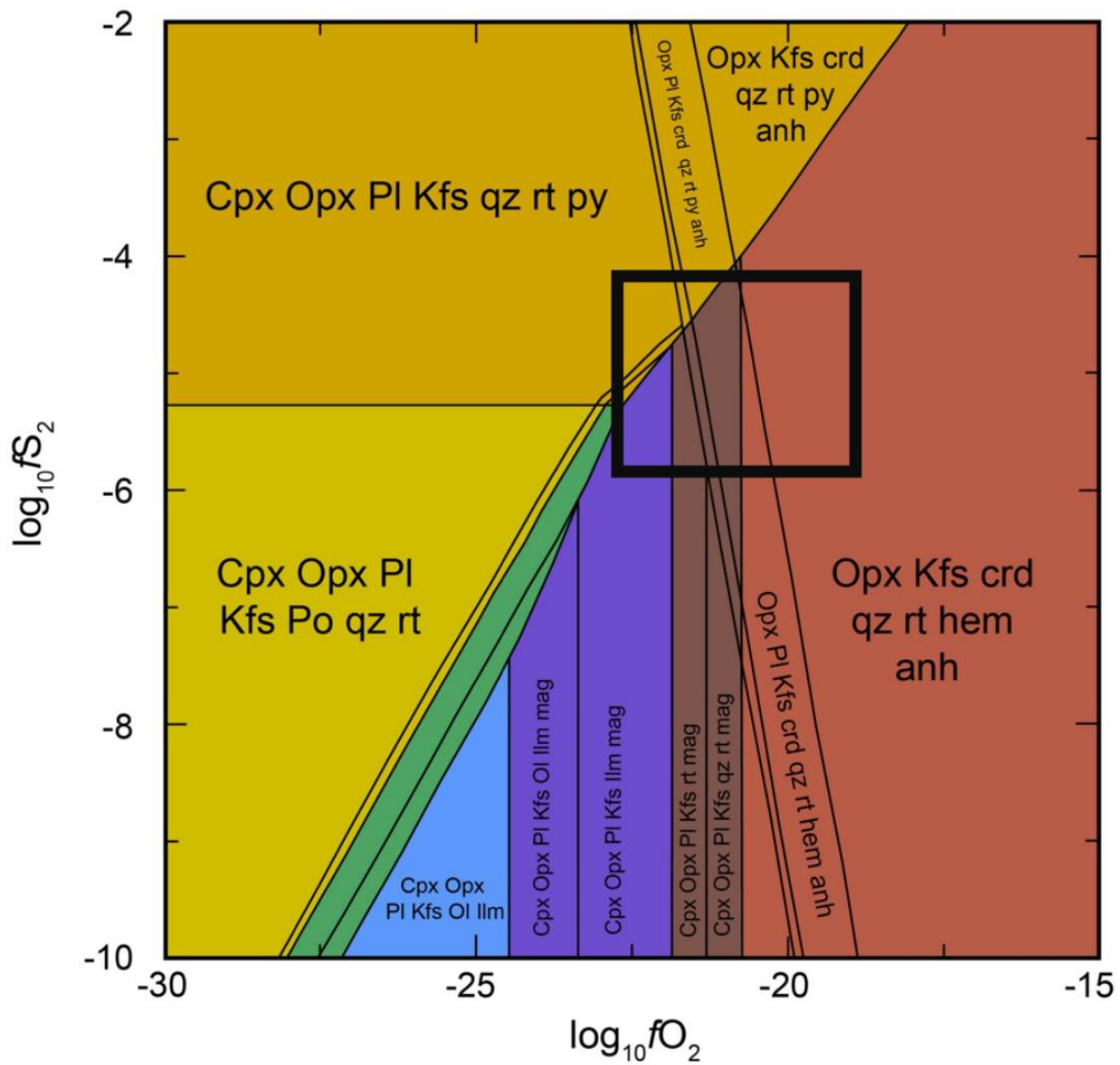
## Figure captions

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.

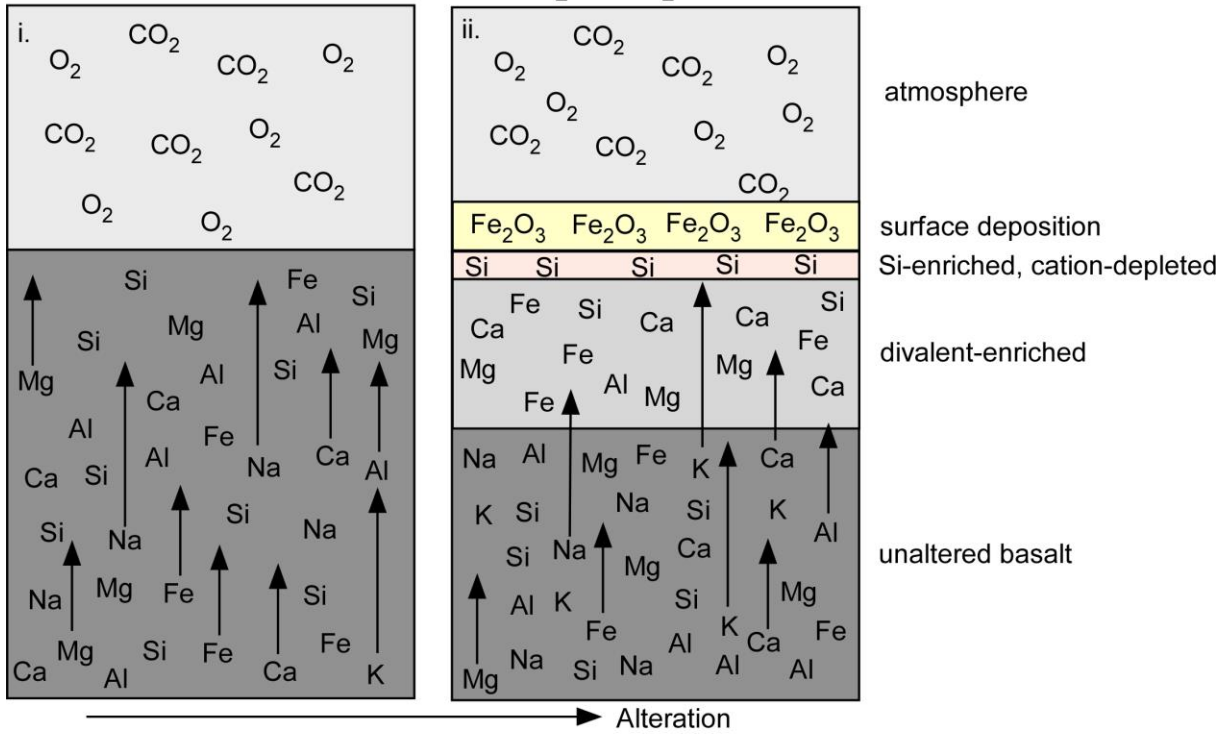
Figure 2. Progression of geochemical alteration under various Venus atmospheric conditions from experimental data. A) O<sub>2</sub> or CO<sub>2</sub>-only atmosphere i. Unaltered basalt in contact with O<sub>2</sub> or CO<sub>2</sub> atmosphere. Elemental fluxes are shown as different length arrows based 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 diffusional flux. At some depth, unaltered basalt is still present. B. SO<sub>2</sub>+CO<sub>2</sub> 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<sub>2</sub>-only atmosphere (Cutler et al., 2020). B) Surface coating on an alkaline basalt in a CO<sub>2</sub>-only atmosphere, 90 bars, 700°C (Teffeteller et al., 2022). C) Surface coating on an alkaline basalt in a SO<sub>2</sub>+CO<sub>2</sub> atmosphere, 90 bars, 700°C (Reid et al., 2021; submitted).

Figure 1



A. Experimental basalt alteration in O<sub>2</sub> or CO<sub>2</sub> atmosphere



B. Experimental basalt alteration in SO<sub>2</sub>+CO<sub>2</sub> atmosphere

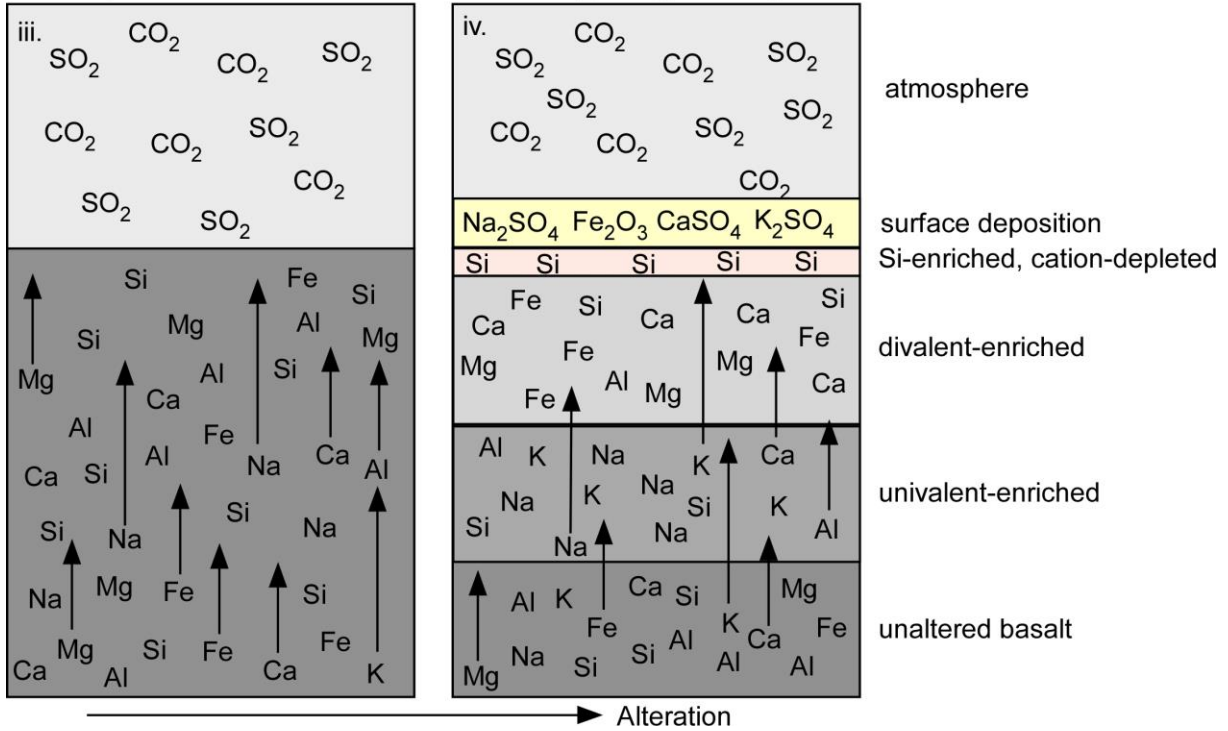


Figure 2.



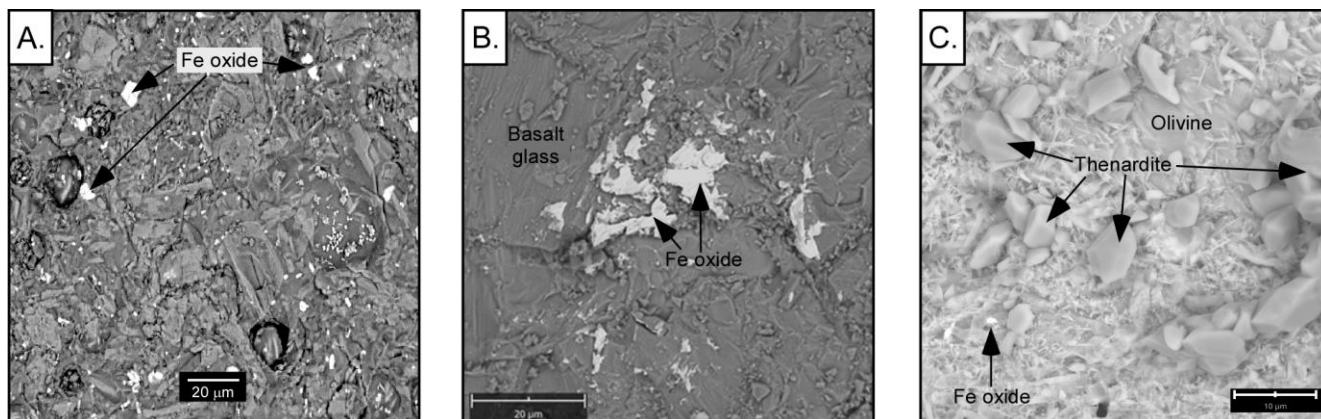


Table 5. List of experimental approaches and their capabilities and limits

Experimental Approach	Pressure	Atmosphere Composition	Control/CO <sub>2</sub>	Control/Fe	Sample References	Other notes
Box Furnace	1 bar	Terrestrial atmosphere	No ~ QFM +10	No	Filberts et al. (2020); Cutler et al. (2021)	Can be run for long duration and large samples, but is useful for rate and oxidation only
Gas Mixing Furnace	3 bar	Simple mixed gas species	Yes	No	Pagley et al. (1995); Zhong et al. (2020)	Control of CO <sub>2</sub> is tied to controlling atmospheric composition
Autoclave	controlable	Simple mixed gas species	No	No	Beger et al. (2018); Owen et al. (2022)	CO <sub>2</sub> is at the low end of the range expected for the Venus surface (190-450; Beger et al. 2018; Owen et al. 2022), but the exact fO <sub>2</sub> is dependent on the specific alloy used for the vessel
Cold Seal Apparatus	controlable	Simple mixed gas species	Yes with solid buffers	No	Taylor et al. (2021); Hild et al. (2021)	Standard experimental petrology approach changed to pressurizing with CO <sub>2</sub>
GEER Chamber	controlable	Complex mixed gas species	No	No	Radoman-Shaw et al. (2022); Santos et al. (2023)	Samples react with everything in the chamber; select atmospheric gas species can be measured <i>in situ</i> ; atmospheric gas can be adjusted during the experiment
Venus In-Situ Chamber Investigations at Goddard	3-90 bars	pure CO <sub>2</sub> or Fe <sub>2</sub> may include SO <sub>2</sub> at ppm levels	Not specified	No	Köhler and Johnson (2021)	
Other individual chambers as custom built					Santos et al. (2022) for a review of other facilities	

### Supplementary Table 1. Mineral formula

#### Mineral

Olivine  
 Pyroxene  
 Plagioclase  
 Alkali Feldspar  
 Ilmenite  
 Rutile  
 Magnetite  
 Hematite  
 Maghemite  
 Magnesioferrite  
 Laihunite  
 Anhydrite  
 (meta)-Thenardite  
 Glauberite  
 Pyrite  
 Pyrrhotite

#### Mineral Formula

$(\text{Mg, Fe})_2\text{SiO}_4$   
 $\text{XY}(\text{Si, Al})_2\text{O}_6$   
 $\text{NaAlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8$   
 $(\text{Na, K})\text{AlSi}_3\text{O}_8$   
 $(\text{Fe, Ti})_2\text{O}_3$   
 $\text{TiO}_2$   
 $\text{Fe}_3\text{O}_4$   
 $\text{Fe}_2\text{O}_3$   
 $\text{Fe}_2\text{O}_3$   
 $\text{MgFe}_2\text{O}_4$   
 $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SiO}_4)_2$   
 $\text{Ca}(\text{SO}_4)$   
 $\text{Na}_2\text{SO}_4$   
 $\text{Na}_2\text{Ca}(\text{SO}_4)_2$   
 $\text{FeS}_2$   
 $\text{Fe}_{(1-x)}\text{S}$

X = Ca, Na, Fe<sup>2+</sup>, Mg, Mn, Li

Y = Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mg, Al, Cr, Ti, Mn