

Basalt Alteration in a CO₂-SO₂ Atmosphere: Implications for Surface Processes on Venus

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Key Points:

- Basalts altered under Venus surface conditions and a CO₂-SO₂ atmosphere produce reaction products of Ca-, Na, and K sulfates, and Fe-oxides.
- Alteration products and reaction rates were strongly dependent upon the compositions of the reactants.
- The rates basalts altered in a hybrid CO₂-SO₂ atmosphere were greater than rates in either gas alone.

Abstract

Venus' surface and interior dynamics remain largely unconstrained, due in great part to the major obstacles to exploration imposed by its 470°C, 90 bar surface conditions and its thick, opaque atmosphere. Orbiter-based thermal emission data provide opportunities to characterize the surface composition of Venus. However, interpretations of such spectra depend on understanding interactions between the planet's surface basaltic rocks and its caustic, sulfur dioxide (SO₂)-bearing carbon dioxide (CO₂) atmosphere. Several studies, using remote sensing, thermodynamic modeling, and laboratory experiments, have placed constraints on basaltic alteration mineralogies and rates. Yet constraint with respect to SO₂-mediated reactions with basalts of contrasting compositions remains incomplete. Here, we present new data from a series of gas-solid reaction experiments, in which samples of two basalt compositions were reacted in an SO₂-bearing CO₂ atmosphere, at relevant Venus temperatures, pressure, and oxygen fugacity. We subjected reacted specimens to scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) analyses using sample cross-sections produced with focused ion beam (FIB) milling. Surface alteration products were characterized, and their abundances estimated; subsurface cation concentrations were mapped to show depth of alteration. We demonstrate that the initial rate of reaction in our experiments is very rapid. Alkaline basalt samples are coated by (meta)thenardite (Na₂SO₄) and amorphous calcium carbonate (CaCO₃) alteration products, and tholeiitic basalt samples are primarily covered by anhydrite (CaSO₄), Fe-oxide (Fe_xO_y; likely magnetite, Fe₃O₄), and other minor phases.

Plain Language Summary

Surface features on Venus, such as volcanic landforms, and their ages can be studied to infer the planet's interior properties. Venus' thick, opaque atmosphere and extreme surface temperature and pressure limit our ability to study its surface in detail. Fortunately, sensors aboard Venus-orbiting spacecraft can “see” its surface, using a few select wavelengths of light, to provide opportunities to interpret the composition of its surface. However, those interpretations can be made only if we first understand how quickly Venus' atmosphere chemically changes its surface rocks and what resultant mineral products may coat the rocks' surfaces. These are not fully understood, despite the results of several prior studies with objectives similar to ours. Here, we share the results from experiments that mimic these chemical reactions. We used rock types like those known to be on its surface and subjected them to relevant temperatures, pressure, and a blend of two reactive gases, carbon dioxide and sulfur dioxide, to model Venus' atmosphere. After the experiments, we examined the rocks with microscopic instruments that allowed us to characterize chemical changes from their surfaces to their interiors. Our interpretations suggest that these reactions occur at an initial high rate and that the compositions of the mineral coatings produced are dictated by the rocks' slightly different compositions.

1 Introduction

Unlike Mars, Mercury, and the Moon, Venus' opaque atmosphere precludes detailed study of its surface in visible and most infrared wavelengths (Esposito, 1984; Moroz, 2002). However, a handful of spectral windows, for light of near 1 μm wavelength, allow collection of emission spectra from orbit through the atmosphere; these spectra can be used to constrain surface composition (Carlson et al., 1991; Moroz, 2002; Hashimoto and Sugita, 2003; Mueller et al., 2008). Areas on Venus' surface of low infrared emissivity, observed with the Venus Express orbiter, have been interpreted as evidence of magnetite (Fe₃O₄) and/or hematite (Fe₂O₃)

alteration products coating Venus' rocks (Pieters et al., 1986; Smrekar et al., 2010; Kappel et al., 2016). Therefore, anomalously high infrared emissivities around some volcanic centers, such as the lava flows on the steep-sided dome and flanks of Idunn Mons, were proposed to represent unweathered basalt flows, possibly emplaced within the last 2.5 million to 250,000 years (Smrekar et al., 2010; Stofan et al., 2016; D'Incecco et al., 2017; Mueller et al., 2020). In contrast, more recent volcanic activity may be suggested by sharp spikes in the abundances of SO₂ in Venus' atmosphere above its cloud deck, as observed with NASA's Pioneer Venus orbiter in the 1980's and ESA's Venus Express orbiter in the 2000's (Esposito, 1984; Nimmo and McKenzie, 1998; Glaze, 1999; Marcq et al., 2012). Recent studies of basalt oxidation rates have similarly suggested that currently active volcanism is possible on Venus (Cutler et al., 2020; Filiberto et al., 2020; Tefeteller et al., 2021, 2022). Additionally, recent re-examination of Magellan radar data suggests topographic changes consistent with active volcanism during the mission (Herrick and Hensley, 2023). Confirmation of modern volcanism on Venus would herald a shift in our understanding of the planet's mantle state and thermal history, particularly within the last ~1000 Myr. Prospective emissivity measurements to be collected by upcoming DAVINCI and VERITAS (NASA) and EnVision (ESA) spacecraft may provide such a revelation only if we have a more complete understanding of alteration rates and the mineralogy of the alteration products likely coating its surface.

Although Venus is similar in size, mass, and bulk chemistry to Earth, its atmospheric composition and surface conditions are quite different. Its departure from a common evolutionary arc with Earth, sometime before it was likely catastrophically resurfaced approximately 300–600 Ma (Nimmo and McKenzie, 1998; Taylor and Grinspoon, 2009; Kane et al., 2019), has generated a predominantly basaltic surface (Head et al., 1992; Basilevsky et al., 2007) that is immersed in a dense, caustic atmosphere composed of 96.5% carbon dioxide, 3.5% nitrogen, and other trace gas species, including ~150 ppmv sulfur dioxide (Barsukov et al., 1982; Seif et al., 1985; Bézard and de Bergh, 2007), and buffered near the magnetite-hematite (MH) oxygen fugacity (f_{O_2}) buffer (Pieters et al., 1986; Fegley et al., 1995; Fegley et al., 1997). Collectively, the planet's 470°C and ~92 bars surface conditions (Seif et al., 1985) and reactive atmosphere have likely altered the rocks at the Venus surface over the ensuing several hundred million years. Such conditions have likewise restricted opportunities to collect surface data. Despite these limitations, three successful in-situ X-ray fluorescence (XRF) analyses were collected in Venera 13–14 and Vega 2 lander missions (Barsukov et al., 1982; Surkov and Barsukov, 1985). Although the analyses are quite uncertain and mineralogy was not constrained, the analyzed compositions are consistent with those of terrestrial alkaline and tholeiitic basalts, each having reacted with Venus' sulfur-bearing atmosphere (Barsukov et al., 1982; Surkov and Barsukov, 1985; Treiman, 2007; Filiberto, 2014). Venus' atmosphere is very dry in comparison to the Earth's (~30 ppm H₂O; Marcq et al., 2018; Zolotov, 2018). Therefore, it is unlikely that its trace water participates in basalt alteration under such extreme temperatures (Surkov and Barsukov, 1985). Basalt alteration is, nonetheless, chemically favorable to producing secondary mineral coatings of magnetite ± hematite and anhydrite (Barsukov et al., 1982; Surkov and Barsukov, 1985; Pieters et al., 1986; Fegley and Treiman, 1992; Treiman, 2007; Zolotov, 2018). However, it has been proposed that alteration rates are likely significantly slower than on Earth (Fegley and Treiman, 1992).

Foundational experimental work (Cook et al., 1990; Cooper et al., 1996) has established that high temperature alteration of basalt in terrestrial, sulfur-free atmospheres occurs via oxidation of iron at the surface. Oxidation is accompanied by the diffusive migration of network-modifying

cations (i.e., Fe^{2+} , Mg^{2+} , Ca^{2+} , and Na^{1+}) from the interior to the free surface, forming oxide phases at the solid-gas interface and generating a gradually thickened alteration layer in the subsurface of the sample body. Diffusive cation migration in basalt glass is induced by the oxidation potential created by the contrasting $f\text{O}_2$ of the oxidizing reactant compared to that of the glass, which was quenched at a more reduced $f\text{O}_2$ (e.g., Cook et al., 1990). The rate of alteration was shown to proceed in inverse proportion to the square root of time (e.g., Crank, 1980; Cook et al., 1990).

Using this rate principle, measurements from further experimental alteration of basaltic materials at Venus' surface conditions (i.e., T , P , $f\text{O}_2$) in pure CO_2 atmospheres led to estimates that Venus' volcanic activity could have occurred only a few hundred thousand to a few hundred years before the present (Teffetteller et al, 2020, 2021a, b). In contrast, Cutler et al. (2020) and Filiberto et al. (2020) proposed that alteration rates, derived experimentally using basalt glass and olivine grains and reacted at 600°C and 900°C, under terrestrial air and surface P and $f\text{O}_2$ conditions, indicate that Venus' volcanic activity may have occurred as recently as a few years to a few months before it was detected. Collectively, these experiments showed that Fe-oxide reaction products coat oxidized specimens and provide valuable data of likely reaction mechanisms and rates in SO_2 -free atmospheres. However, Venera and Vega geochemical analyses are consistent with SO_2 participation in surface-atmosphere alteration, in contrast to these experimental atmospheres. Moreover, only experiments conducted by Teffetteller et al. (2020, 2021) used T , P , and $f\text{O}_2$ relevant to the Venus surface.

Experiments in the literature have shown that basaltic rocks and glasses, at high temperatures, react readily with SO_2 -bearing (Berger et al., 2019) and pure SO_2 atmospheres (Henley et al., 2015; King et al., 2018; Palm et al., 2018; Renggli and King, 2018; Renggli et al., 2018, 2019). As with oxidation experiments, reactions between basalt and SO_2 -bearing gas were proposed to be rate-limited by the diffusive migration of cations, although rates were not constrained. Depending on the basalt composition, these experiments produced alteration phases of anhydrite, magnetite $\pm$ hematite, and less commonly, metathenardite and glauberite [$\text{Na}_2\text{Ca}(\text{SO}_4)_2$]; these are among the phases that have been documented on Hawaiian basalts that were altered by SO_2 -rich gases at an active volcanic vent (McCanta et al., 2014). However, while one experiment from Berger et al. (2019) was conducted with a Venus atmospheric SO_2 concentration (140 ppm) and T and P conditions analogous to Venus' surface, $f\text{O}_2$ was buffered at the more reduced nickel-nickel oxide buffer. Experiments employing pure SO_2 gas (Henley et al., 2015; King et al., 2018; Palm et al., 2018; Renggli and King, 2018; Renggli et al., 2018, 2019) also used temperatures $\geq 600^\circ\text{C}$, which are atmospheres and temperatures unlike those found on Venus. Therefore, it remains unclear if the results from these SO_2 -bearing studies are analogous to reactions at the Venus surface.

Santos et al., (2023) reacted a variety of natural geologic materials under temperature and pressure conditions and an atmospheric composition that closely replicate those at the Venus surface. After a 30-day run, their MORB basalt glass yielded a near-continuous coating of primarily micron-scale Ca- and S-bearing secondary products and sporadic Fe, O and Fe, S phases. Their more alkaline basalt showed apparent reaction with Fe-Ti oxides to produce an Fe, S secondary phase, while primary mineral phases showed no obvious reaction. However, Santos et al., (2023) proposed that the rate of reaction of both basalt samples was rapid.

To date, constraints on the mineralogy of Venus' primary surface rocks, their alteration products, and the rates at which they alter remain incomplete. As the compositions of surface igneous

rocks are the sole means available to interpret Venus' interior state, additional experimental work that addresses these parameters is needed. Results of such work will aid in interpreting both past and future remote sensing data accurately and would thereby unlock crucial data points to deducing Venus' geodynamic evolution. Previous laboratory experiments have begun to answer these uncertainties but have yet to consider the collective effects of Venus' CO₂+SO₂ atmosphere and its surface temperature, pressure, and oxygen fugacity.

Here, we isolate the effect of SO₂ on gas-solid reactions via a series of experiments using materials, atmospheres, and conditions that simulate those at Venus' surface, and comparison of results with data from previous work. The results of these experiments place constraints on alteration products, thicknesses, and effects on emissivity and provide new means of interpreting geochemical data returned by DAVINCI, VERITAS, and EnVision missions.

2 Materials and Methods

2.1 Starting materials

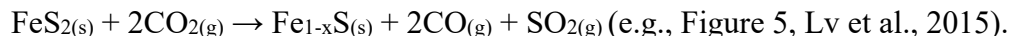
We investigate alteration of two samples of basaltic glass, chosen for their chemical similarity to the rocks analyzed on Venus' surface (Table 1), and consistency with earlier work on S-free alteration of Venus basalt compositions (Teffetteller et al., 2021, 2022). Composition A is a natural alkaline basalt containing crystalline phases, from Sverrefjell volcano, Svalbard, Norway (Skjelkvåle et al., 1989). It is compositionally similar to the Venera 13 volcano plume basalt (Barsukov et al., 1982; Surkov and Barsukov, 1985; Barsukov et al., 1986; Treiman, 2007), and consists mostly of basaltic glass with micro-phenocrysts of olivine, plagioclase, and pyroxene, and rare grains of CaCO₃ and FeCO₃. Composition B is a synthetic glass (Filiberto, 2014), modeled after the chemical analyses of the Venera 14 and VEGA 2 basalts of Venus' global plains surfaces (Barsukov et al., 1982; Surkov and Barsukov, 1985; Barsukov et al., 1982; Treiman, 2007). Due to the large uncertainties of the Venera 13, 14 and VEGA 2 bulk analyses, as well as sodium not being measured by any lander, adjustments were made to ambiguous element abundances to produce the synthetic glass based on experimental and thermodynamic studies of basaltic melts (Surkov and Barsukov, 1985; Treiman, 2007; Filiberto, 2014). This tholeiitic glass was prepared using reagent grade oxides and homogenized and fused at 1300°C, 1 atm, at the quartz-magnetite-fayalite (QFM) f_{O_2} buffer. The melt was rapid-quenched and broken into fragments suitable for inclusion in cold-seal pressure vessels.

2.2 Experimental Setup

Three experiments (VS-1, VS-3, and VS-4) were run in cold-seal pressure vessels in the experimental petrology laboratory at Brown University. Experimental conditions for samples VS-1 (A and B) were 700°C, 90 bars and a 14-day duration. The durations of the two remaining experimental runs, conducted at Venus' surface conditions, 470°C, 90 bars, were as follows: VS-3 (A and B), 22 days, and VS-4 (A and B), 30 days (Table 2). The 470°C temperature was selected to approximate Venus' surface temperature at low elevations and to isolate the effect of time, while the 700°C temperature was chosen to increase the rate of alteration while remaining below the ~725°C glass transition temperature, thereby minimizing devitrification (Bender et al., 1978; Ryan and Sammis, 1981).

A powdered mineral assemblage containing magnetite and hematite was used to buffer the

experimental oxygen fugacity to approximately Venus' surface $f\text{O}_2$ (MH buffer). Powdered pyrite (FeS_2) was added to produce SO_2 gas via the decomposition reaction:



Samples and buffer assemblages were inserted in gold tubing, which was crimped but not sealed, and encased in a cold-seal pressure vessel. The system was subsequently pressurized with pure CO_2 gas and heated to the experimental run temperature for the pre-selected duration. At the conclusion of each run, the buffer assemblages were checked to verify that the buffer assemblage (magnetite + hematite + pyrite) had not been exhausted over the duration of the runs.

2.3 Analytical methods

2.3.1 Surface characterization using SEM

Following each run, the surfaces of the samples were characterized using backscatter electron (BSE) images collected using the Phenom Pro scanning electron microscope (SEM) at the University of Tennessee, Knoxville, to assess the mineralogy and abundance of alteration products present. Specifically, each sample was imaged in a transect of 25 individual frames, each with a field of view of $\sim 50 \mu\text{m}$. Phases (and aggregates of phases) in each image were then characterized using energy dispersive X-ray spectroscopy (EDS) and visual assessment of their morphologies and z-contrasts to determine their mineralogies. The percentages of surface area covered by the alteration phases were estimated by visually comparing them with a chart of modal abundances (e.g., Terry and Chilingar, 1955). Finally, the estimates from the 25 images were averaged to produce overall abundance estimates of the alteration phases for the samples, expressed in percent. In addition, surface analyses were used to identify regions on the samples suitable for creating cross sections to be used in micro- and nano-scale analyses. To contrast the effect of the added SO_2 gas to the reactive environment, these steps were repeated using identical samples from a companion study (Teffetteller et al., 2021, 2022) in which two sets of samples—VEN-4 (A and B) and VEN-5 (A and B)—were run for two weeks in pure CO_2 , at MH $f\text{O}_2$ and 700°C and 470°C .

2.3.2 Cross-section sample preparation

The focused ion beam (FIB) *in-situ* milling technique was used to produce a microscale cross-section (foil) of the body of a sample, which allowed analyses of both its surface and subsurface with minimal damage to the sample. Surface products were preserved using carbon deposition. The FIB foils were designed for analyses using transmission electron microscopy (TEM); i.e., electron transparent ($\sim 80\text{-}100 \text{ nm}$ thick; Wirth, 2009). Cross-section foils in this study were milled using the FEI Quanta 3D FEG instrument at Johnson Space Center, Houston, Texas.

2.3.3 Transmission electron microscopy

After FIB preparation, samples were characterized utilizing the JEM-2500SE scanning transmission electron microscope (STEM), which provided elemental analyses of the samples at high spatial resolution (i.e., on the nanometer scale). Qualitative data, using energy dispersive x-ray spectroscopy (EDS) elemental mapping (via x-ray counts produced from each element), were collected to identify chemically altered regions of the samples by depicting—on the micron

scale—the distribution of cations. Thereafter, nanometer scale traverses in EDS were used to quantitatively analyze the elemental chemistry of the selected region; quantification was achieved by the Cliff-Lorimer method (Cliff and Lorimer, 1975), comparing the intensities of characteristic elemental x-ray emissions with those of standard materials. Apparent high abundances of Na at and near the samples' surfaces are not real, and represent X-ray emissions from gallium used in preparing the FIB foils; NaK α radiation is at 1.04 keV and GaL α is a 1.08 keV, which are essentially indistinguishable with the available EDX detector. These analyses, expressed as oxides and normalized to 100% of all elements analyzed, were used to characterize the nature of diffusive migration of cations from within the sample to the free surface. Crystalline reaction products ranging from a few nanometers to tens of microns in diameter on the surface and near-surface were then characterized using selected area electron diffraction (SAED), from which we determined the crystal symmetry and characteristic lattice parameters (e.g., d-spacings) of the reaction products.

3 Results

All experimental run products exhibited evidence of alteration, both element diffusion in the products and deposition of alteration phases on the products' surfaces. Alteration products, including Ca- and Na-sulfates and Fe-oxides, were observed on both alkaline and tholeiitic starting compositions, although the amounts and sulfate mineralogies differed. CaCO₃, though indicated on the alkaline sample, was also present on unreacted samples. Sample surfaces showed small rare grains of materials that were not abundant in the original samples or gas, including phases containing nickel (Ni), chromium (Cr), gold (Au), silver (Ag), and platinum (Pt). These are interpreted as products of slight volatilization of materials in the experimental setup. The Ni and Cr likely originated from the cold-seal pressure vessel (e.g., Beckman and Woodford, 1988; Berger et al., 2019). The precious metals likely originated from the sample containment tubes. Subsurfaces of two samples had regions of cation enrichment and depletion, indicating alteration proceeded inwards from the surface.

3.1 Basalt Surface Alteration in the Presence of SO₂ Gas

3.1.1 Alkaline Basalt

After a run of 3 weeks at 470°C, 90 bars, the surface of sample VS-3A (Fig. 1a, Table 2) was partially coated (40%) by submicron, uniformly dispersed phases and scattered larger grains. Isolated subhedral thenardite grains ~1–5 μ m in diameter and aggregates of such grains, up to ~20 x 10 μ m, covered another 1% of the sample. Trace glauberite [Na₂Ca(SO₄)₂] was also present. The submicron grains were too small to collect individual EDS spectra; however, the presence of S, Ca, and C, morphology, and z-contrast suggest they include sulfates (possibly thenardite, Fig. 1b) and carbonates. Primary olivine, pyroxene, and plagioclase microphenocrysts on the surface exhibited distinct grain boundaries (Fig. 1b, white arrows) and showed no obvious evidence of reaction. Fe-oxides were present as rare (<<0.1%), randomly dispersed, submicron sized grains. The total reaction products covered ~41% of the surface (Table 2). Rare particles of Pt, Au, and Ag were noted.

VS-4A, after reaction at 470°C, 90 bars for 4 weeks, exhibited only a 20% surface coating of evenly-dispersed, submicron phases (Table 2). Grains were too small to resolve using EDS;

however, spectral peaks of S, Ca, and C suggest they are possibly thenardite and calcite. Randomly distributed iron oxide phases $<1\text{--}3\text{ }\mu\text{m}$ (Fig. 1c, Table 2) covered 0.3% of the surface. Similar to VS-3A, only rare nanoscale grains were observed on microphenocrysts of olivine, pyroxene, and plagioclase. Siderite (FeCO_3) and magnesite (MgCO_3) were indicated in two instances—both occurring in surface vesicles. Minor Fe metal and Au were observed, suggesting possible reaction with the sample capsule material and experimental assemblage. Additionally, Ni-bearing phases were noted in several EDS analyses, often accompanied by minor sulfur concentrations. Other rare grains exhibited spectra consistent with pure silica and silica with alumina.

Thenardite dominated the alteration assemblage on the surface of VS-1A (700°C , 90 bars) at 70% coverage (Fig. 1d; Table 2). Thenardite grains ranged in size from approximately $1\text{ }\mu\text{m}$ to $>30\text{ }\mu\text{m}$ in diameter with acicular, tabular, and prismatic habits that covered and obscured most of the surface (Fig. 1d). Acicular thenardite crystals $\sim 1\text{--}5\text{ }\mu\text{m}$ long were thinly dispersed, however, coating microphenocrysts of olivine, pyroxene, and plagioclase. Iron oxides covered approximately 0.1% of the surface (Table 2) and occurred as randomly distributed grains $<1\text{ }\mu\text{m}$ in diameter.

3.1.2 Tholeiitic Basalts

The surface of VS-3B (Fig. 2a), reacted for 3 weeks at 470°C , 90 bars, exhibited scattered, discrete anhydrite grains that covered 0.1% of the surface. These anhydrite crystals were acicular, $\sim 1\text{--}10\text{ }\mu\text{m}$ long, and surrounded by a fringe of nanometer-sized phases having spectral peaks of Ca, Fe, and S, that contributed 0.1% surface coverage (Fig. 2b, Table 2). Fe-oxides (0.2%) were randomly distributed on the surface as single grains $\leq 1\text{ }\mu\text{m}$, or in aggregate spheroid masses $\sim 1\text{--}3\text{ }\mu\text{m}$ in diameter. Anhydrite and Fe-oxides contributed approximately equally to the alteration phase coverage on the sample.

After reaction at 470°C , 90 bars for 4 weeks, sample VS-4B (Fig. 2c; Table 2) exhibited a $<<0.1\%$ abundance of S-rich grains, $\sim 2\text{--}4\text{ }\mu\text{m}$ in diameter (i.e., 3 discrete grains over the entire transect). Grains having z-contrast consistent with sulfates $<1\text{ }\mu\text{m}$ in diameter covered $<<0.1\%$ of the specimen (Fig. 2c). Fe-oxides (0.2%) were rare single grains $<1\text{ }\mu\text{m}$ or were grains clustered with sulfates in heterophase aggregates $3\text{--}8\text{ }\mu\text{m}$ (Fig. 2c). Trace Ni + S phases were also present.

VS-1B, altered at 700°C , 90 bars for 2 weeks, was covered with a nearly-continuous (23.8%) frost-like coating of grains smaller than $1\text{ }\mu\text{m}$ (Fig. 2d; Table 2), that were visually consistent with being anhydrite. $\sim 6.2\%$ of the surface was covered by larger, twinned euhedral to subhedral anhydrite masses ranging from $\sim 1\text{--}10\text{ }\mu\text{m}$ in diameter (Fig. 2d). Rare grains of Fe-oxide (0.8%) appeared either as isolated grains $<1\text{ }\mu\text{m}$, as aggregates of such grains, or with anhydrite grains heterophase clusters (Fig. 2d). Anhydrite contributed 97% of the alteration phase coverage and Fe-oxides 3%. Rare Au and Pt grains were observed.

3.2 Surface Alteration in a Pure CO_2 Atmosphere at 90 Bars, Magnetite-Hematite $f\text{O}_2$

3.2.1 Alkaline basalt

SEM analyses of the surface of VEN-5A (470°C) revealed a 3% abundance (Table 2) of Fe-

oxides and siderite (FeCO_3), occurring together in aggregates of grains less than $1\text{ }\mu\text{m}$ to $>5\text{ }\mu\text{m}$ in diameter, which were thinly, but evenly, dispersed (Fig. 3a); however, grain morphologies and sizes ($\leq 1\text{ }\mu\text{m}$) smaller than EDS spot size made them difficult to distinguish. Therefore, Fe-oxide and siderite abundances were combined. Also observed were isolated Fe and Fe-Cr metal grains.

VEN-4A (700°C) exhibited a 0.2% surface coverage of Fe-oxides (Table 2), observed as rare discrete grains or clusters $\leq 1\text{ }\mu\text{m}$ in diameter (Fig. 3c). EDS indicated that rare clusters contained possible siderite. Patches of Fe metal and Fe-Cr alloy, as well as occasional phases of Au and Pt metal were noted.

3.2.2 Tholeiitic basalt

After reaction at 470°C , VEN-5B abundances of Fe-oxides and siderite were 2% (Table 2) and occurred as small clusters ($\sim 1\text{ }\mu\text{m}$) and aggregates of nanoscale phases that were distributed discontinuously on the glassy surface (Fig. 3b) and accumulated preferentially along cracks and ridges. Aggregate grain patches occasionally covered surface areas up to $\sim 20 \times 50\text{ }\mu\text{m}$, and EDS indicated greater abundances of siderite than those inferred on the other samples. Sporadic grains of a Fe-Cr metal were also present.

The surface of sample VEN-4B, which was reacted at 700°C , had a dominantly vitreous texture (Fig. 3d). SEM analyses determined that a coating of Fe-oxides and plausible siderite covered 0.1% of the sample (Table 2), appearing as randomly distributed clusters of grains $< 1\text{ }\mu\text{m}$ to $\sim 2\text{ }\mu\text{m}$ (Fig. 3d). Rare Fe metal and Fe-Cr alloy were also noted.

3.3 Sub-Surface Alteration in the Presence of SO_2 Gas

3.3.1 Alkaline basalt

The FIB foil of composition A was examined by TEM, and EDX spectra were collected along two traverses, each several hundred nanometers long, extending from the sample interior to its surface. Chemical analyses from these traverses are shown in Figure 4, and elements maps are shown in Figure 5. For convenience, we divided the traverse into five zones of consistent or distinctive chemistries, and discuss them first in reference to traverse 1, Figure 4a. Unaltered basalt, Zone 5, is present at the deepest parts of the traverse, until $\sim 580\text{ nm}$ below the original sample surface. At that point, moving towards the surface, we enter Zone 4 where Si concentrations begin decreasing (from ~ 45 to $\sim 35\%$ wt SiO_2), in concert with abundances of Al, Ca, Fe, and Mg. These decreases are compensated by increasing abundances of K and Na, which peak at 17 wt. % and 12 wt. %, respectively. Zone 3, next toward the sample surface, is the opposite of Zone 4: increasing abundances of Si, Fe, and Ca, and diminution of Na and K toward the surface. Moving to the sample's original surface, Zone 2, one sees a pronounced enrichment in SiO_2 , compensated for by decreasing abundances of all other elements (Fig. 4a). At and above the sample's original surface (Fig. 4a, Zone 1), Ca increases and peaks to define a secondary phase crystallizing there (see also Fig. 5). Na is not plotted in Zone 1, as apparent enrichment in Na above the surface is not real, but represents Ga metal used in preparing the TEM foil (see above). The mottled texture visible in the brightfield images (Fig. 5) is present throughout the entire FIB cross-section and appears to coarsen and become modestly enriched with Ca, Fe, and

Al within ~200-300 nm of the sample surface.

The second traverse across the composition A foil (Fig. 4b) shows similar zones of changing cation concentrations beginning at ~530 nm deep. In contrast to the first traverse, however, Ca concentrations increase sharply in a region from ~100 nm deep (Fig. 4b, Zone 2) to the surface. Zone 1 is distinguished by an enrichment of Ca and Fe which indicate products on the surface. One grain of the sample that was characterized using HRTEM and SAED; it shows polycrystalline goethite (α -FeO(OH)) that is encased in amorphous CaCO₃. EDX elemental maps (Fig. 5) are consistent with this conclusion, showing Fe-, Ca-, and C-rich phases on the surface, as well as the regions of cation enrichment in the subsurface. CaCO₃ was also observed in a crack ~ 2 μ m beneath the surface and has a diffraction pattern consistent with aragonite.

3.3.2 Tholeiitic Basalt

The alteration pattern in the tholeiitic basalt sample is significantly different from that of the alkaline basalt. The tholeiite's alteration zone is much thinner than for the alkaline basalt - ~90 nm versus 580 nm (Figs. 4,6). The unaltered tholeiitic glass, Zone 3, of Figure 6a extends until ~90 nm below the surface, and alteration appears in Zone 2 as slowly increasing abundances of Na₂O and SiO₂ coupled with slightly decreasing abundances of CaO, MgO, and FeO. Abundances of the latter elements are more variable in Zone 2 than in the unaltered glass of Zone 3. Zone 2 terminates at the original sample surface. Above the original sample surface, in Zone 1, one can distinguish two apparent materials, one enriched in Ca (possibly a sulfate) and another enriched in Fe. As before, Na₂O data are excluded in Zone 1.

Our TEM EDX maps (Fig. 7) do not have enough precision to show the small changes in elemental concentration across Zone 2. However, they show the surface reaction deposits clearly. Discrete mineral grains on the surface of the reacted tholeiite are rich in Ca and S (Figs. 7), and are interpreted as a calcium sulfate, likely anhydrite. There is an increase in iron as well that suggests the presence of an Fe-rich phase such as magnetite.

A second traverse from a nearby region (Fig. 6b) shows similar changes in cation concentrations beneath the sample surface. EDX maps (Fig. 7, Map 2), also show two nanometer-scale grains on the sample surface, like the grains in the first transect, that are enriched in S, Fe, and Ca. HRTEM imaging shows lattice fringes that are consistent with a spinel structure, likely of magnetite. The grains may be aggregates of both magnetite and anhydrite.

One element map of a FIB foil, Figure 8, shows a euhedral crystal of ~1 μ m in diameter, which has elevated concentrations of S and Ca with a lesser abundance K. The distribution of elements suggests the crystal is possibly an aggregate of anhydrite and arcanite (K₂SO₄) or syngenite (K₂Ca (SO₄)₂) and, given the presence of goethite on VS3-A, may be partially hydrated. Nanometer-size grains covering the sample surface in Figure 8, that were too small to quantify using SEM-EDS (i.e., Fig. 2B), and having elevated Fe, S, and Ca concentrations are interpreted as Fe-oxides and Ca-sulfates.

4 Discussion

Run durations, temperatures, and basalt compositions were varied to contrast their effects on the mineralogies and abundances of alteration products and subsurface alteration. The surface

coverages of total alteration products and the depth of reaction were then used to place qualitative constraints on alteration rates. Analysis of the run products and subsurface alteration data from identical samples reacted in pure CO₂ (Teffetteller et al., 2021, 2022) afforded a further comparison with reaction in a SO₂-free reactive atmosphere—Figure 9 summarizes reaction at Venus surface conditions. Sulfate and Fe-oxide reaction products in all SO₂-bearing experiments were consistent with those predicted by thermodynamic calculations (Fegley et al., 1997; Treiman, 2007; Zolotov, 2018; Semprich et al., 2020) and with the results of other SO₂-basalt experiments (King et al., 2018; Palm et al., 2018; Renggli and King, 2018; Berger et al., 2019; Renggli et al., 2018, 2019). Additionally, they confirmed the successful decomposition of pyrite to produce a sulfur-bearing gas that included SO₂. Interpretation of the mineralogy of alteration phases, including sub-micrometer sized grains, was based on the collective analysis of EDS spectra, grain morphology, and BSE z-contrast, and selected analyses of single grains using TEM techniques. All sample surfaces, including the CO₂ run products, exhibited a widely dispersed scattering of metal grains, similar to those described by Berger et al. (2019), that originated from gas interaction with parts of the experimental apparatus and the powdered buffer minerals.

4.1 SO₂-Bearing Experiments

4.1.1 Effect of Starting Composition on Reaction

Alkaline and tholeiitic specimens were altered simultaneously in three experimental runs (i.e., VS-1, VS-3, and VS-4). In each run, independent of duration and temperature, reaction products were consistently more abundant on the alkaline composition (Fig. 1; Table 2), 70% vs 27%, 40% vs 0.3%, and 20% vs 0.2%. Thenardite (Na₂SO₄) and amorphous CaCO₃ on all alkaline basalts comprised >99% of the total alteration phases, with Fe-oxides accounting for the remainder. Additionally, maximum sulfate grain sizes on alkali samples were larger than those on corresponding tholeiitic samples in all runs but VS-4 (A and B). Discovery of CaCO₃ on the surface and in the subsurface of VS-3A confirms that it existed prior to reaction and that it could be metastable in the experimental conditions. However, it is unclear how much CaCO₃ is in fact the product of reaction. Goethite is a secondary product of magnetite that reacted with ambient water vapor in post experimental storage and handling.

Though thenardite has been predicted and observed in previous work, it has not been suggested to be a major alteration product of basalt-SO₂ reactions as observed in Figure 1 and illustrated in Figure 9. However, its prevalence on alkaline samples suggests that the speed of Na diffusion and resulting reaction rate in the alkaline glass are significantly more rapid than corresponding rates of Ca in the tholeiitic glass. This inference is consistent with the following:

- 1) Reaction of a SO₂-bearing model Venus atmosphere with basalt glasses (see Fig. 9) results in strong oxidation at the glass surface, and chemical potential gradients that drive diffusive migration of univalent and divalent cations to the glass surface (King et al., 2018; Palm et al., 2018; Renggli and King, 2018; Berger et al., 2019; Renggli et al., 2018, 2019);
- 2) In silicate glasses (An₆₀Ab₄₀) analogous to basalts, Na has a relatively large diffusion coefficient (D_{Na}) and that $D_{\text{Na}} > D_{\text{Ca}} > D_{\text{Mg}}$ (Behrens, 1992);
- 3) The availability of Na to react with SO₂ and form Na₂SO₄ on basalt glass is mediated by the

glass's $\text{Fe}^{3+}/\text{Fe}^{2+}$ and the participation of Na^{1+} in stabilizing network-forming Fe^{3+} during oxidation— $\text{Fe}^{3+}/\text{Fe}^{2+}$ may have been lower in the unreacted alkali specimens compared to the tholeiitic specimens (Cook et al., 1990; Cooper et al., 1996; Renggli and King, 2018; Berger et al., 2019); and

4) Crystalline thenardite ($53.34 \text{ cm}^3 \text{ mol}^{-1}$) has a greater volume per mole than magnetite ($44.53 \text{ cm}^3 \text{ mol}^{-1}$), hematite ($30.28 \text{ cm}^3 \text{ mol}^{-1}$), siderite ($29.38 \text{ cm}^3 \text{ mol}^{-1}$) and anhydrite ($45.94 \text{ cm}^3 \text{ mol}^{-1}$) (Robie and Bethke, 1962) that likely facilitates efficient surface coverage of crystallizing thenardite. Moreover, because thenardite requires two moles of Na per mole of sulfate, rapid migration of Na from depth to the surface may engender greater crystal sizes and quantities.

However, grain sizes and abundances of sulfate reaction products in the 4-week run (VS-4A; Fig. 1c) were less than those on the other alkali specimens. Reaction of CO_2 and SO_2 with the vessel over the extended duration may have changed the chemistry of the gases in the system, resulting in deposition of Ni, Fe, and C on the specimen surface. As gas composition was not monitored and the precise compositions of precipitant phases were not constrained, it is uncertain what caused this discrepancy. Pure crystalline thenardite has been shown to decompose in the presence of elemental carbon and a pure oxygen atmosphere, at a temperature of 500°C and ~ 1 bar pressure (Samadhi et al., 2003). A similar process may explain the lack of sulfate grains $\geq 1 \mu\text{m}$ observed on VS-4A. Testing this hypothesis would require more experimentation and the use of experimental techniques in which gas composition monitoring is possible, and therefore, falls outside of the scope of the present study.

The crystallinity of the alkali material permitted the additional assessment of concurrent mineral and glass alteration. In high temperature oxidation experiments (Cutler et al., 2020; Filiberto et al., 2020), the rate of secondary hematite production was observed to be fastest on olivine, followed by glass. However, in the present SO_2 -bearing experiments, microlites and microphenocrysts of olivine, pyroxene, and plagioclase phases exhibited zero to trace observable alteration products at 470°C (Fig. 1b-d). Similarly, the original surface of VS-1A (700°C) was visible only where phases of olivine, plagioclase, and pyroxene were present. Interstitial glass, on the other hand, was readily coated by sulfate phases in all three runs. Not only does this bimodal alteration exemplify the slower alteration of crystalline phases versus basaltic glass, but it also demonstrates that greater crystallinity in a basalt significantly slows the overall rate of surface sulfate production. A more crystalline alkali basalt (or gabbro) may, therefore, appear “younger” via its emissivity spectra than a glassier alkali basalt emplaced at the same time.

Sulfates (primarily anhydrite) and magnetite were produced in nearly equal trace amounts on tholeiitic samples (Fig. 2b and c; VS-3B and VS-4B), which were run at Venus' surface temperature (470°C); only the high temperature run produced abundant anhydrite (26%). Given the presence of goethite on VS-3A, sulfate products may have likewise hydrated during storage and handling to produce secondary bassanite ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), potassium sulfate hydrate ($\text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$), and syngenite ($\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$). Heterophase masses of CaSO_4 and magnetite were observed on all reacted tholeiitic specimens, but none were detected on the alkaline surfaces. The production of anhydrite and Fe-oxide secondary phases supports both thermodynamic and experimental results in previous SO_2 -basalt alteration studies (Barsukov et al., 1982; Surkov and Barsukov, 1985; Pieters et al., 1986; Fegley and Treiman, 1992; Treiman, 2007; Henley et al., 2015; King et al., 2018; Palm et al., 2018; Renggli and King,

2018; Berger et al., 2019; Renggli et al., 2018, 2019; Zolotov, 2018), but when considering the extent of the surfaces coated by alteration products, reaction rates inferred here (0.05–0.13% per week) are far slower than rates in comparable alkali alteration runs (5–13% per week).

Lower abundances, smaller grain sizes, and slower rates of reaction in the tholeiite run products may be explained by Na concentrations insufficient to charge-balance oxidizing Fe^{2+} to Fe^{3+} via inward diffusing electron holes, which forces divalent cations to participate in the charge-balancing role (Cook et al., 1990; Cooper et al., 1996; Renggli and King, 2018). Oxidizing Fe results in nucleation of subsurface Fe-oxides and Na-, Fe-, and Mg-, crystallites, as depicted in Figure 9. As subsurface crystallization proceeds, it depletes Na, Fe, and Mg cations in the matrix glass, limiting their diffusion to the surface. Ca diffuses to the surface at a slower rate than that of Na to form modest amounts of anhydrite. The 700°C temperature increases the energy of the system and elevates the reaction rate, which produces greater amounts and larger grain sizes of anhydrite.

The co-crystallization and superposition of Fe-oxide on the surface of anhydrite grains indicate that Fe can diffuse through both the glass and anhydrite media to form surface oxides (Fig. 2d). Dyar et al. (2020) propose that Venus' basaltic surfaces are likely coated by anhydrite $\pm$ calcite that decrease emissivity, and that hematite (Fe-oxides) has little to no effect. On the short timescales of the present study, however, Fe-oxides comprise a significant portion of the alteration assemblage on tholeiitic basalts. Therefore, it is possible that Fe-oxides make some contribution to VIRTIS emissivity contrasts.

4.1.2 Effect of Run Duration on Reaction Products and Coverage at 470°C, 90 Bars, and Magnetite-Hematite $f\text{O}_2$

Alkali basalt samples (VS-3A and VS-4A) were altered over 22- and 30-day durations (Table 2). Minor Fe-oxides (0.2% and 0.02%, respectively) were observed on both alkali samples (Fig. 1b and c). However, as Fe-oxide quantities were less than 1% and grain sizes $<1\ \mu\text{m}$, the effect that increased experimental duration had on Fe-oxide production is unclear, though their abundances decreased with time. Anhydrite has been predicted (Treiman, 2007; Zolotov, 2018) but it was not detected. Sulfate abundances and grain sizes were expected to increase with increasing duration; however, an increase was not observed (Fig. 1; Table 2). In addition to the evidence for the possible interaction of SO_2 gas with parts of the vessel, as previously discussed, the relatively low occurrence of sulfate phases on VS-4A may have been the result of the formation of an amorphous silica layer near the surface that inhibited further cation diffusion and reaction at the surface, as described in McCollum et al. (2013) and McCanta et al. (2014).

Tholeiite samples (VS-3B and VS-4B) retained much of their original vitreous surface textures (Fig. 2b and c), and had few alteration products overall (Table 2). VS-4B was reacted concurrently with VS-4A. Therefore, lower secondary product abundances observed on the sample likely reflect reaction that was also limited by interaction of SO_2 with parts of the experimental vessel, as well as the development of a subsurface amorphous silica layer.

The effect of duration on reactions in these systems may be observable on longer time-scales than the 3- and 4-week experiments conducted here. However, alteration phase abundances in both sets of run products, when considered together, offer support to the hypothesis that

chemisorption of SO₂ directly to the glass surface induces an instantaneous reaction with surface Na and Ca, producing an initially high abundance of sulfate phases, followed by far slower surface reactions governed by the diffusive transport mechanism (Henley et al., 2015; Renggli and King, 2018; Renggli et al., 2018). Therefore, sulfate product abundances generated in three weeks may not appear significantly different than those produced in four weeks of alteration, as depicted in Figure 2b and c.

4.1.3 Effect of Varying Run Temperature on Reaction Products and Coverage

Alkaline and tholeiitic samples (Figs. 1 and 2) were reacted in an SO₂-bearing CO₂ atmosphere under 90 bars pressure, near the MH f_{O_2} buffer at contrasting temperatures, 470°C for 22 days (VS-3A and VS-3B) and 700°C for 15 days (VS-1A and VS-1B) (Table 2). Though the run durations were not equal, it has been demonstrated above that reaction phenomena would be similar between 15- and 22-day runs at 470°C. As expected, the higher temperature exerted a more profound effect than run duration on alteration phase surface coverage and grain sizes on both basalt types that indicated higher diffusion rates; however, it had no discernable effect on alteration phase mineralogy. These results are consistent with the expectation that the 700°C temperature would increase the reaction rate beyond the rate at 470°C, and thereby provide a model of alteration beyond a 4-week duration. In this context and after alteration, it is apparent that the crystal size of sulfate secondary phases was an important factor to discerning a rate of reaction, which would likely become rate-limiting as crystal growth proceeded. Renggli et al. (2019) presented textural evidence that both SO₂ gas and cations from the glass diffuse through a sulfate layer at the surface to engender further sulfate crystallization and create a gradually thickening continuous mineral crust. Crystal growth would ultimately eliminate diffusion of SO₂, which would halt the chemical potential driver for cation diffusion. On both high temperature specimens, abundant sulfate grains ranging from <1–10 µm (VS-1B) and 1–30 µm (VS-1A) (Figs. 1d and 2d), suggest that such a threshold was not yet attained. It is, therefore, plausible that a crust of sulfate phases approaching ~30 µm or more in thickness can develop on altered basalts through which diffusion mechanics would continue to operate.

4.1.4 Effect of Reaction in the Substrate

The distribution of elements observed in both samples, summarized in Figure 9, indicates that Na, K, Fe, and Ca were mobilized during reaction and that the degree of alteration is compositionally dependent. In the alkali sample (VS-3A), the greater depth of alteration, 530–580 nm (Fig. 4), versus that seen in the tholeiite (VS-3B), 90–102 nm (Fig. 5), is consistent with the kinetic and charge-balancing mechanisms for Na described above (Cook et al., 1990; Cooper et al., 1996). They are applicable to K as well, though its diffusion rate is slightly slower. The near-complete depletion of Na and K from ~200 nm to the surface (Fig. 4) in the alkali basalt shows that they were free to migrate to the surface with little required to charge-balance Fe³⁺. This conclusion is further supported by the coincident mottled texture boundary seen in the image of the substrate (Fig. 5). It likely shows the presence of pre-experimental dendrites that grew larger and more enriched in Fe, Al, and Ca near the surface during alteration. Higher Na and K concentrations deeper in the substrate (Fig. 4 Zone 4) indicate Fe³⁺/Fe²⁺ was likely favorable for the oxidation of Fe and required Na and K for charge-balancing.

4.1.5 Comparison between CO₂-only and CO₂+SO₂ experimental atmospheres

Surface reaction products on samples from two-week runs (470°C and 700°C) in pure CO₂, at MH buffer and 90 bars pressure (Fig. 3), were compared with three-week specimens from the present study to isolate the effect of added SO₂ to the reactive atmosphere. Fe-oxides were observed on all sets of run products (Figs. 1 and 2); however, they were generally less abundant on the SO₂-bearing specimens. As predicted, sulfates were produced in the sulfur-bearing experiments. Siderite (FeCO₃) was also observed on the surfaces of CO₂ run products but was absent from the corresponding SO₂-bearing samples.

Abundances of alteration products on alkaline samples were significantly greater in the sulfur-bearing runs at both temperatures (Table 2). Here, it is proposed that this is the result of instantaneous reaction with Na cations at the surface of the alkali sample via SO₂ chemisorption, followed by diffusion of network modifying cations from the interior outward, compelled by both redox and chemical potential gradients created by the reactive gases (Fig. 9). Na has a greater diffusivity in glass than the other network-modifying cations, as detailed in the prior discussion of the effects of starting composition. Na was sufficient to stabilize Fe³⁺ in the glass matrix, freeing it to diffuse rapidly to the surface of the glass where it reacted with SO₂ to form thenardite.

Tholeiite-sulfur run products at 470°C were fewer, ~0.4%, compared with 2% on the CO₂ only specimen (Table 2). At 700°C, tholeiite reaction products were far greater (~30%) on the SO₂-bearing sample than the CO₂ sample (0.7%). As described in the discussion of the effects of starting composition, SO₂ was likewise adsorbed onto the tholeiite glass during reaction and reacted instantaneously with Ca and Na to form a surface layer of nano-scale sulfate phases (Figure 3b and d); however, the lower concentration of Na was largely consumed to stabilize oxidizing Fe. The nucleation of crystallites within the glass slowed cation diffusion to the surface. The higher temperature specimen, VS-1B, shows that the concentration of Ca may be sufficient to overcome these barriers to diffuse toward the surface of the glass over time.

Alkaline and tholeiite basalts appear to have similar reaction mechanics in a pure CO₂ atmosphere. The key difference is the absence of the chemical potential gradient imposed by SO₂. Without which, reaction via oxidation proceeds at a slower rate, as seen in the grain sizes and quantities of run products from the pure CO₂ runs (Figs. 3, 9), compared with SO₂-bearing run products (Figs. 1 and 2). It is notable that reaction product abundances were slightly greater in the lower temperature, pure CO₂ run. However, this is attributable to the production of siderite that is likely metastable at the run conditions (Koziol, 2004), but not stable at 700°C. If SO₂ is ephemeral at the Venus surface, then siderite may be a significant alteration phase on basalt surfaces.

The 580 nm and 102 nm deep alteration fronts observed in the present alkaline and tholeiitic specimens are far deeper than the 12 nm and 16 nm depths, respectively, reported by Teffeteller et al. (2022). Berger et al. (2019) presented a synthetic alkali glass that exhibited similar reaction phenomena to the alkali run in this study and an alteration depth greater than 200 nm. These results support the assertions that at Venus conditions, a blend of CO₂ and SO₂ gases, and possibly the Venus atmosphere, exerts a greater chemical potential gradient on basalt than either gas alone, and the initial reaction rate is rapid.

4.1.6 Alteration Rates and Venus' Surface Age Constraints

Alteration rates, as suggested by VIRTIS emissivity variations and based on the experimental oxidation of olivine crystals and glassy basaltic materials, have been used to estimate the ages of volcanic features on the Venus surface to between 2.5 Ma–250,000 years (Smrekar et al., 2010), or to $\leq$ a few hundred-thousand years (Teffetteller et al., 2021), or to perhaps even a few months to years old (Cutler et al., 2020; Filiberto et al., 2020), depending on the composition of the solid and the kinetic model used. Elevated 1 μm emissivity variations correlate with high total Fe^{2+} content in silicate materials (Smrekar et al., 2010; Stofan et al., 2016; Gilmore et al., 2017; D’Incecco et al., 2017; Dyar et al., 2020; Filiberto et al., 2020; Mueller et al., 2020; Helbert et al., 2021). Our results are consistent with prior studies showing alteration changes the glass structure at depth (e.g., Figs. 4 – 7) and creates divalent and univalent cation-depleted regions and Si-rich regions in the subsurface (Cook et al., 1990; Cooper et al., 1996; McCanta et al., 2014; Henley et al., 2015; King et al., 2018; Renggli and King, 2018; Berger et al., 2019; Renggli et al., 2018, 2019; Teffetteller et al., 2021, 2022). Surface alteration products and the subsurface chemical layers serve as an alteration rind that acts to obscure unaltered, FeO-rich glass beneath them, thereby reducing emissivity (Smrekar et al., 2010; Stofan et al., 2016; Dyar et al., 2020; Helbert et al., 2021). Alteration thickness in the subsurface of a silicate glass is predicted to be proportional to the square root of time (Cook et al., 1990; Cooper et al., 1996).

A hematite coating on Venus’ surface rocks has been suggested as the source of VIRTIS emissivity excursions at Idunn Mons and other volcanic landforms (Smrekar et al., 2010; Stofan et al., 2016; Gilmore et al., 2017; D’Incecco et al., 2017; Cutler et al., 2020; Filiberto et al., 2020; Mueller et al., 2020; Teffetteller et al., 2022). Instead, results here corroborate data from other SO_2 gas-solid experimental studies that propose sulfate alteration products and relatively minor magnetite likely coat basaltic rocks on the Venus surface (King et al., 2018; Palm et al., 2018; Renggli and King, 2018; Berger et al., 2019; Renggli et al., 2018, 2019). It has been proposed that the initial rapid surface reaction rate may be linear, which is followed by a parabolic reaction rate (Renggli et al., 2018). The reaction front depths and reaction product abundances may be consistent with that inference. However, it is not clear from the present run products how long the initial period lasts because experiments were not a time series.

Dyar et al. (2020) demonstrated that a coating of sulfate minerals would have a modest reducing effect on emissivity spectra that would require a sufficiently thick crust ($\sim 30 \mu\text{m}$) of secondary sulfate coatings to justify the thermal anomaly observed by VIRTIS spectrometers on Venus’ Idunn Mons. The results of the present study demonstrate that the rate to produce such a coating at Venus conditions could be very rapid and is strongly influenced by the composition of the primary basalt.

After 3 weeks of alteration at 470°C , tholeiitic specimens showed $\sim 100 \text{ nm}$ reaction depth and discontinuous grains and grain aggregates of anhydrite and Fe-oxides approaching $5\text{--}10 \mu\text{m}$ in diameter and covering $\sim 0.4\%$ of the surface. Glassy alkaline basalt developed a reaction depth of 580 nm and coatings of calcium carbonate and thenardite with grain sizes up to $>5 \mu\text{m}$ covering 40% of the surface. In comparison with the reaction front depths and product abundances from Teffetteller et al., (2021, 2022), basalt ages could be several orders of magnitude younger than their estimate.

Chemical weathering may proceed very quickly on either basalt composition on the Venus surface, which may produce sufficiently thick rinds of sulfate to reduce observable emissivity

within months to decades. The atmospheric concentration of SO₂ is ~150 ppm and reaction products and rates observed here are consistent with results reported by Berger et al. (2019) using 140 ppm and 320 ppm dry SO₂, under nearly identical *T*, *P*, and *f*O₂ conditions; however, reactions on Venus are dependent upon a near-surface SO₂ concentration that is currently unconstrained (Zolotov, 2018). Moreover, the results reported here assume that concentrations of atmospheric SO₂ are relatively constant at the near-surface. If so, the strong contrast of alteration rates could be used to crudely estimate primary rock compositions. Fluxes of SO₂ that dissipate over time, however, have been observed in Venus' atmosphere, similar to volcanic activity-related pulses documented on Earth (Esposito, 1984; Glaze, 1999; Marcq et al., 2012). If SO₂ concentrations are more transient at the surface as a result, then alteration rates would likely be variable, especially proximal to the source.

5 Summary

In the present work, glassy tholeiitic and alkaline basaltic specimens were reacted in SO₂-bearing CO₂ atmospheres at Venus surface conditions. Alteration depths and reaction product abundances showed that alkali basalt reacts more rapidly in a Venus-like atmosphere than a tholeiitic basalt. Grain sizes and abundances were consistent with a continual flux of Na, Ca, and Fe cations diffusing from the interior of the specimens to their surfaces. Moreover, the chemical and kinetic behavior of Na was recognized in the tholeiite glass as a charge compensator in Fe²⁺ to Fe³⁺ oxidation, and in the alkali glass as the prevalent diffusive cation when charge compensation was satisfied. This behavior was confirmed by observing the elemental distribution in the sample substrates.

When comparing our run products to those reacted in pure CO₂, we propose that diffusion kinetics were increased by the additional chemical potential gradient imposed by SO₂, as evidenced by more abundant, larger-grained reaction products, and greater depths of alteration into basalt glasses. Given the greater reaction rate produced in our experiments, we assert that the relative ages of basalt flows on Venus should be distinguishable based on their emissivity contrasts, caused by decreasing concentrations of FeO in reaction and the obscuring effects of an expanding alteration rind and mineral deposition layer. Furthermore, we observe that primary rock compositions of recently emplaced lavas may be crudely inferred by their contrasting rates of reaction in Venus' atmosphere. This distinction does not seem likely in a sulfur-free atmosphere.

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Open Research

Analytical data will be uploaded to EarthChem prior to publication.

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Table 1. EPMA analyses of experimental starting materials (Teffeteller, 2022).

Wt. % oxide	Synthetic tholeiitic basalt	Natural alkaline basalt
SiO₂	48.9	47.9
TiO₂	1.3	2.8
Al₂O₃	18.2	18.0
Cr₂O₃	0.5	0.0
FeO	10.1	9.6
MnO	0.2	0.1
MgO	8.3	3.3
CaO	10.2	7.7
Na₂O	2.1	6.0
K₂O	0.2	2.7

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Table 2. Samples, experimental parameters, and results. A hematite + magnetite + pyrite buffer assemblage was used in experiments in the present study.

Sample	Composition	Run Conditions	Duration	Reaction Products	Surface Coverage
VS-1A	alkaline	700°C, 90 bars	14 days	Thenardite, glauberite, Fe-oxide	70%
VS-1B	tholeiite	700°C, 90 bars	14 days	CaSO ₄ , magnetite	30%
VS-3A	alkaline	470°C, 90 bars	22 days	Thenardite, CaCO ₃ , glauberite, Fe-oxide	40%
VS-3B	tholeiite	470°C, 90 bars	22 days	CaSO ₄ , magnetite	0.4%
VS-4A	alkaline	470°C, 90 bars	30 days	Thenardite, CaCO ₃ , Fe-oxide	20%
VS-4B	tholeiite	470°C, 90 bars	30 days	CaSO ₄ , Fe-oxide	0.3%
*VEN-4A	alkaline	700°C, 90 bars	15 days	Fe-oxide	0.2%
*VEN-4B	tholeiite	700°C, 90 bars	15 days	Fe-oxide, siderite	0.1%
*VEN-5A	alkline	470°C, 90 bars	15 days	Fe-oxide, siderite	3%
*VEN-5B	tholeiite	470°C, 90 bars	15 days	Fe-oxide, siderite	2%

*Samples from Teffeteller et al. (2022) using pure CO₂ atmosphere and magnetite + hematite buffer assemblage.

Alkali Basalt Experiments at 90 bars

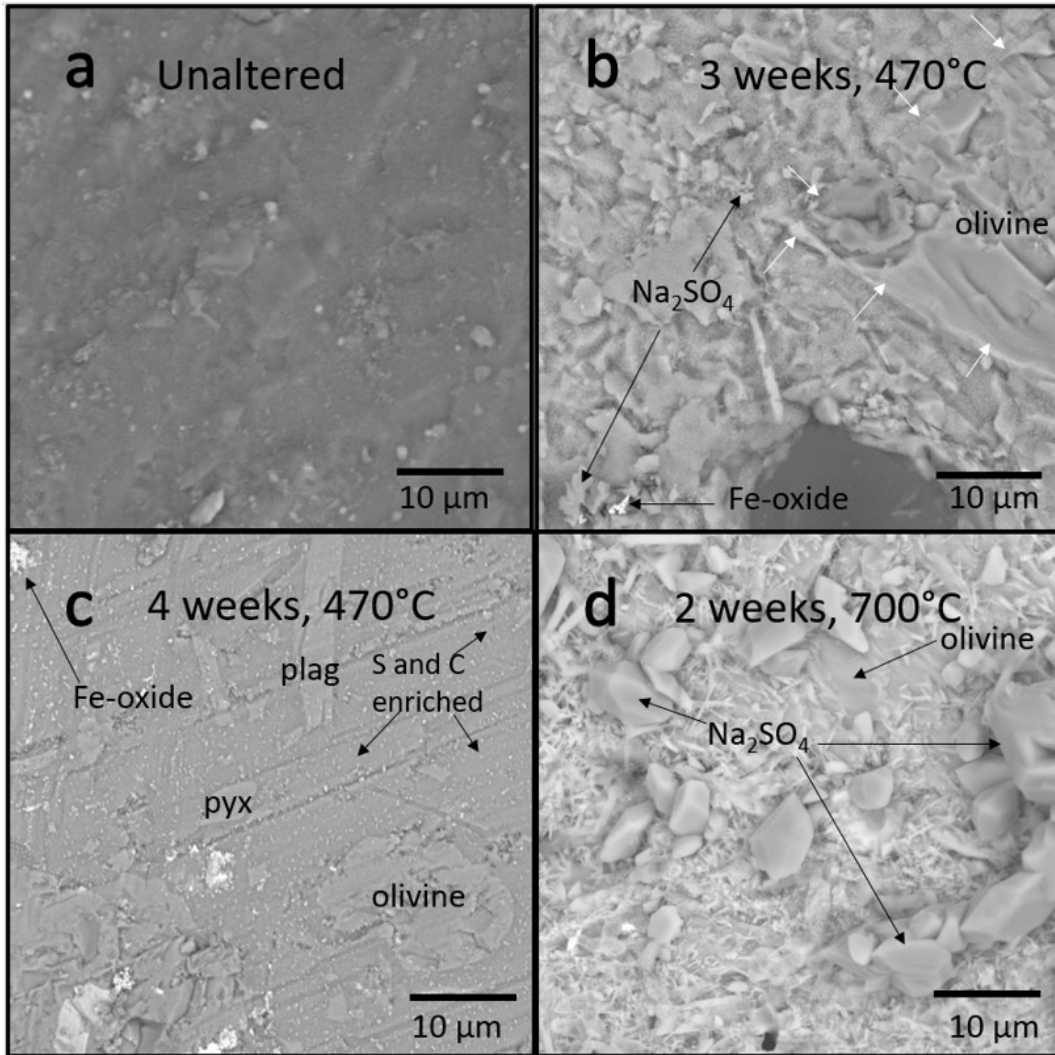


Figure 1. SEM BSE images of alkali samples. a) Unaltered; b) Alteration for 3 weeks at 470°C, 90 bars, showing thenardite and Fe-oxide alteration phases and olivine grain boundary (white arrows); c) 4 weeks at 470°C, 90 bars, showing nanoscale S- and C-enriched phases and Fe-oxide alteration products and microphenocrysts of plagioclase (plag), pyroxene (pyx), and olivine. Parallel lines are from sample preparation; d) 2 weeks at 700°C, 90 bars, exhibiting euhedral thenardite crystals up to several microns in size and a relatively bare surface of an olivine grain.

Tholeiite Basalt Experiments at 90 bars

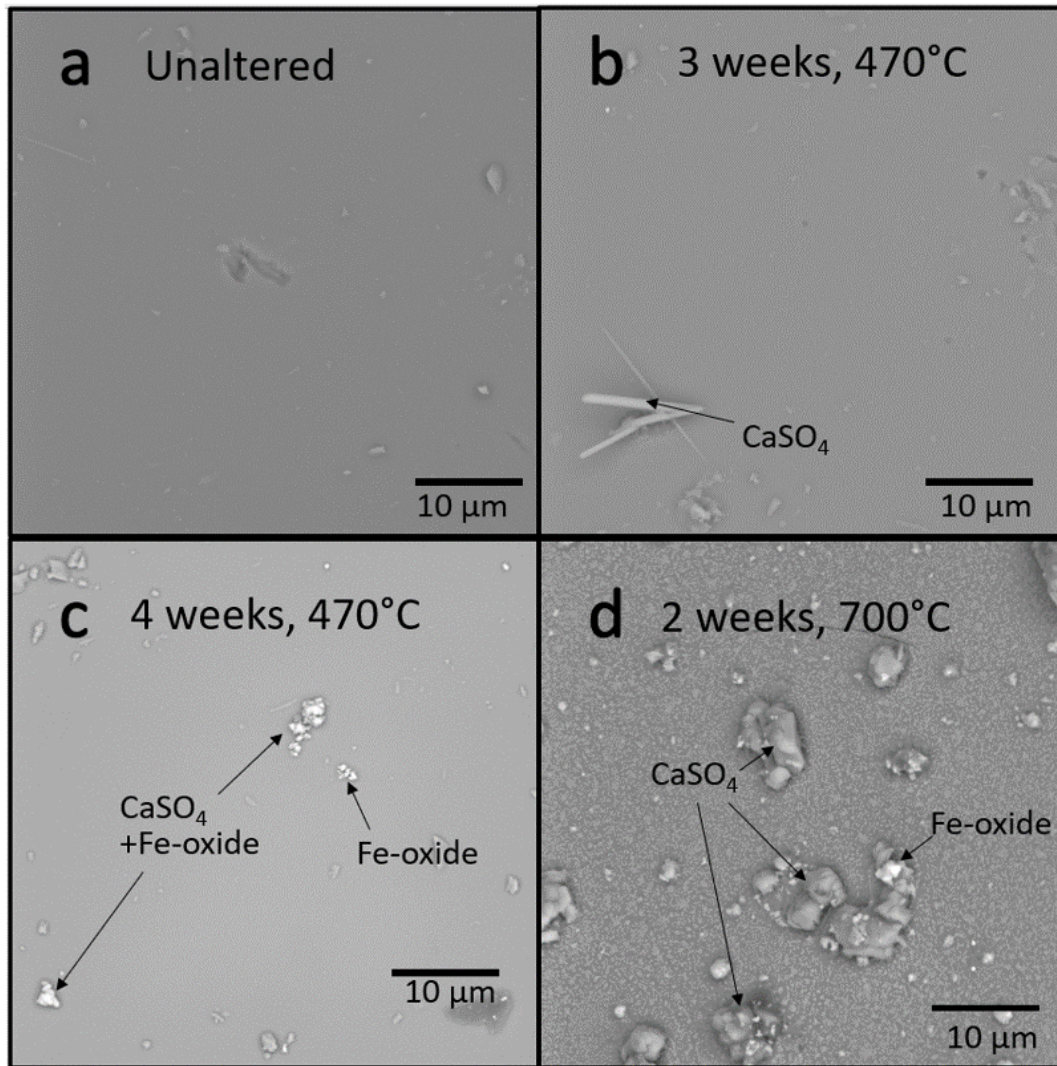


Figure 2. SEM BSE images of tholeiite samples. a) Unaltered; b) Alteration for 3 weeks at 470°C, 90 bars, showing a prevalent vitreous surface with nanophase- and ~10 µm acicular anhydrite and Fe-oxide alteration phases; c) 4 weeks at 470°C, 90 bars, showing nanoscale anhydrite and Fe-oxide alteration products in heterophase masses and discrete Fe-oxide grains on a glassy surface; d) 2 weeks at 700°C, 90 bars, exhibiting a nearly continuous and evenly distributed dusting of nano-scale anhydrite grains with clusters of subhedral thenardite crystals up to several microns in size in heterophase masses with minor Fe-oxides.

Basalt-CO₂ Experiments at 90 bars, 2 Weeks

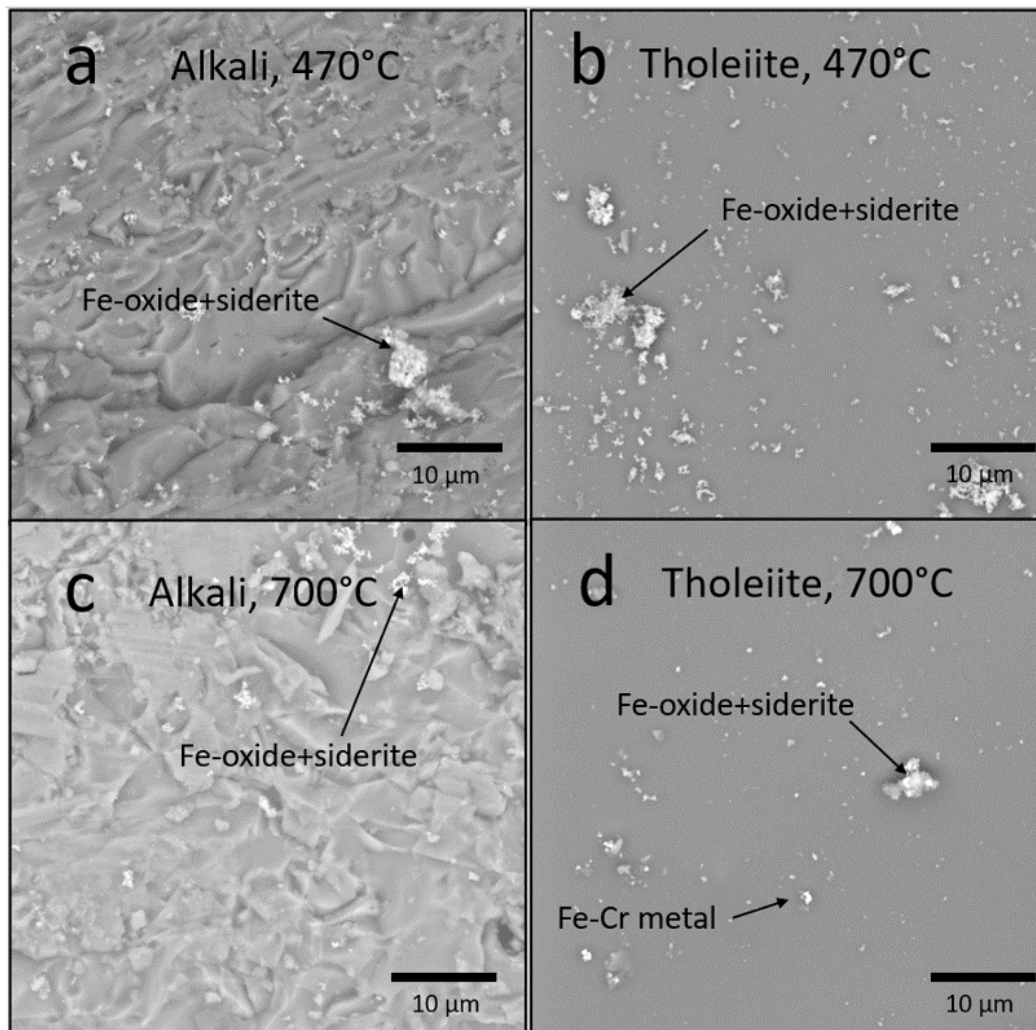


Figure 3. SEM BSE microphotographs of samples reacted for two weeks in pure CO₂ at 90 bars. a) (VEN-5A) Alkali 470°C; b) (VEN-5B) Tholeiite 470°C; c) (VEN-4A) Alkali 700°C; d) (VEN-4B) Tholeiite 700°C. On each sample, Fe-oxide and siderite (FeCO₃) phases are present together in clusters of <1 µm grains, which makes them indistinct from one another.

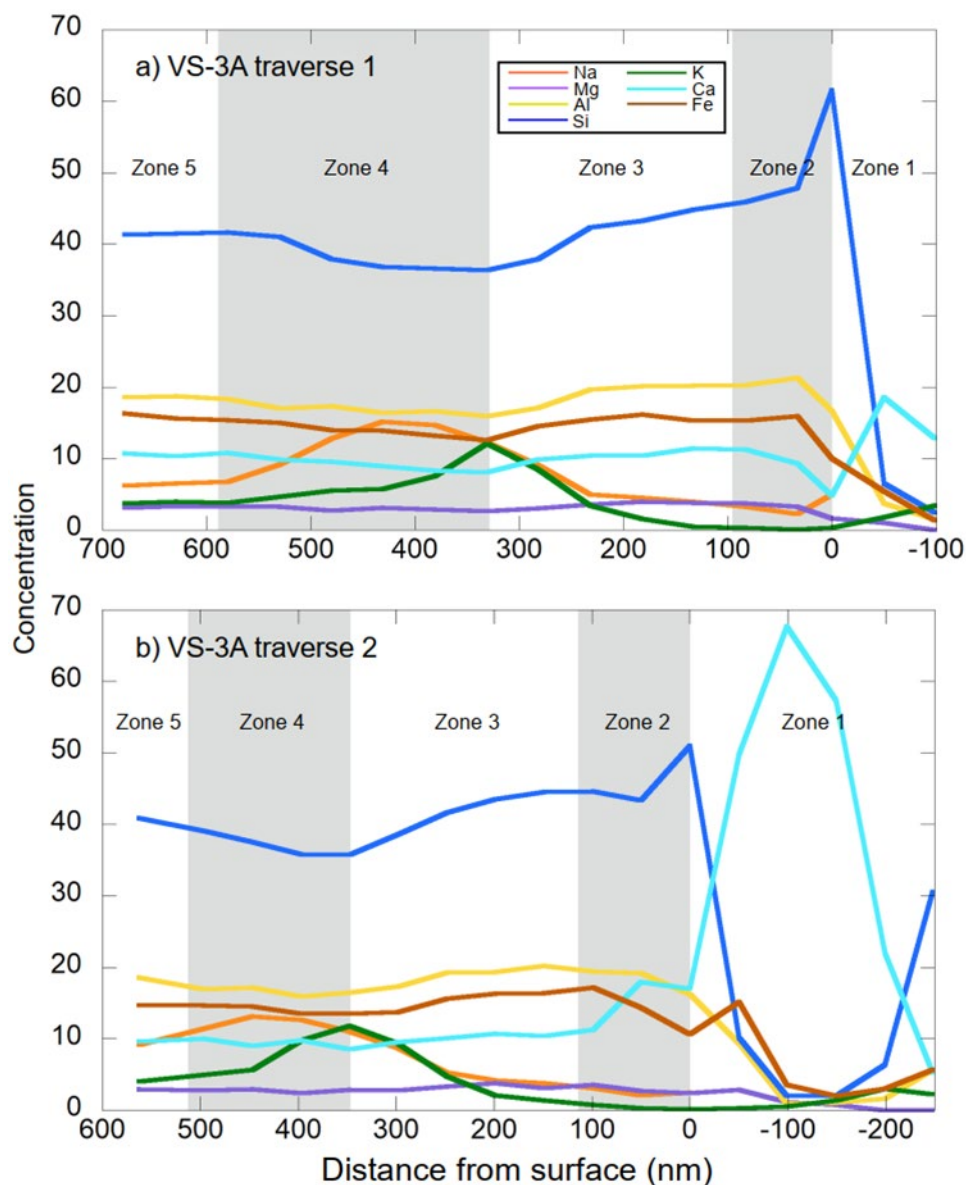


Figure 4. Plot of compositional data in wt. % oxide within the sample body of VS-3A, collected using TEM EDX. Zones demarc correlated changes in cation concentrations. Na concentrations are not plotted in Zone 1, as NaK α is also GaL α .

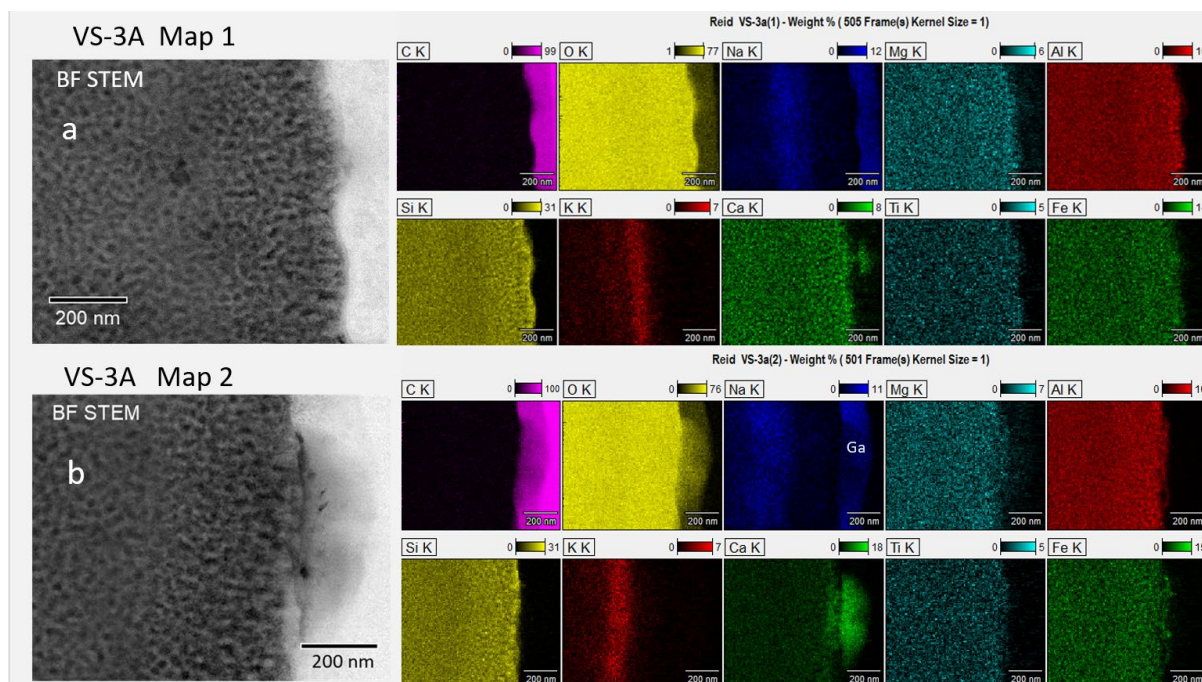


Figure 5. a) and b) show the substrates of VS-3A from which each traverse was taken. TEM
 brightfield images (left) show dendrites (grainy textures) in the substrates that are coarser from
 ~250-300 nm deep to the surface and TEM EDX maps (right) showing elemental abundances.
 The scale bars above each color image show relative abundance for each element using color
 intensity and show regions of enrichment beneath the sample surface. The region showing
 depleted Na and K correlates to the coarse dendrite region. a) A Ca-rich phase is seen on the
 sample surface from the first map. b) Goethite coated by amorphous CaCO₃ is seen on the
 surface in the second map. NaKα is also GaLα.

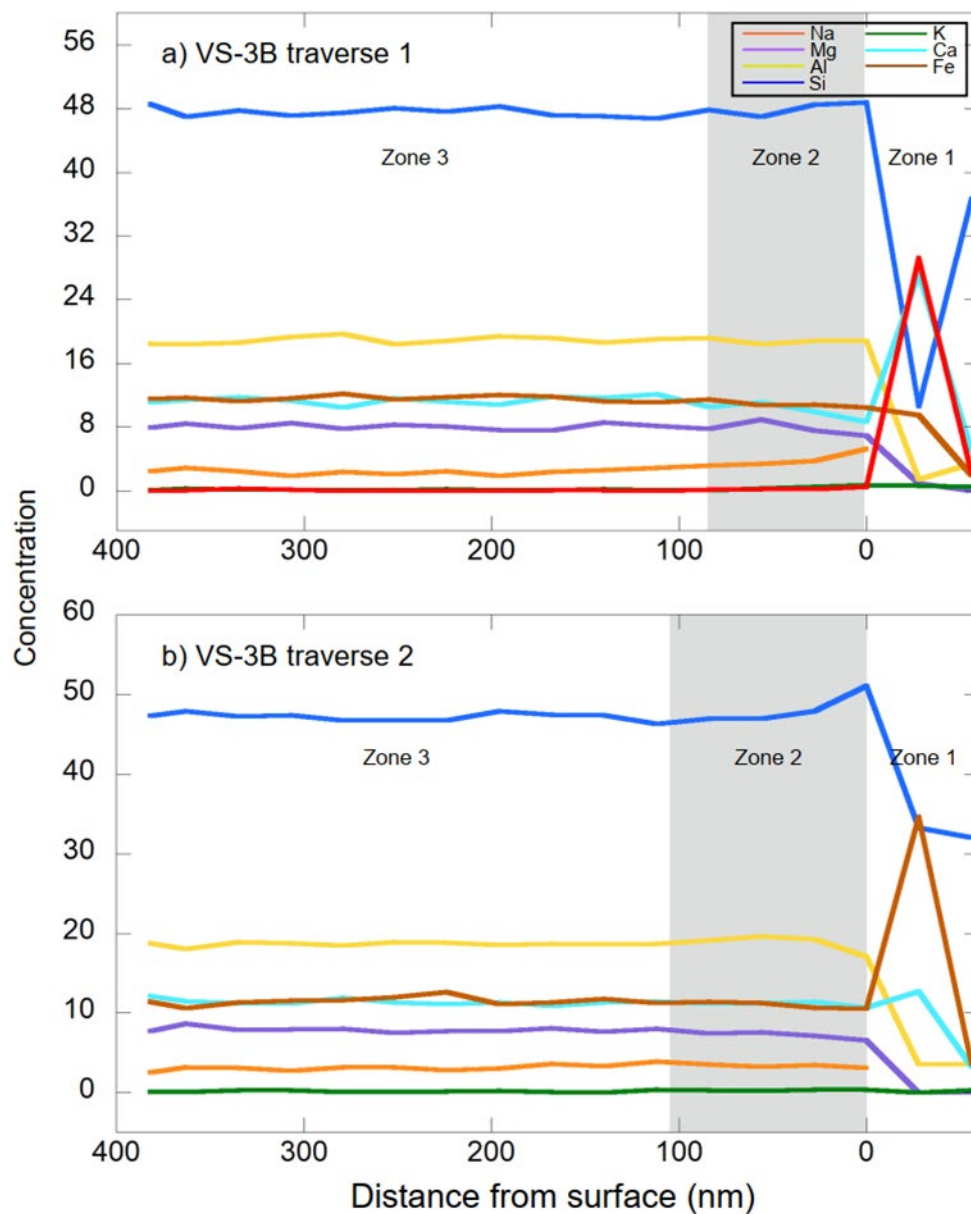


Figure 6. Plot of compositional data in wt. % oxide within the sample body of VS-3B, collected using TEM EDX. Zones demark correlated changes in cation concentrations. Na concentrations are not plotted in Zone 1, as NaK α is also GaL α .

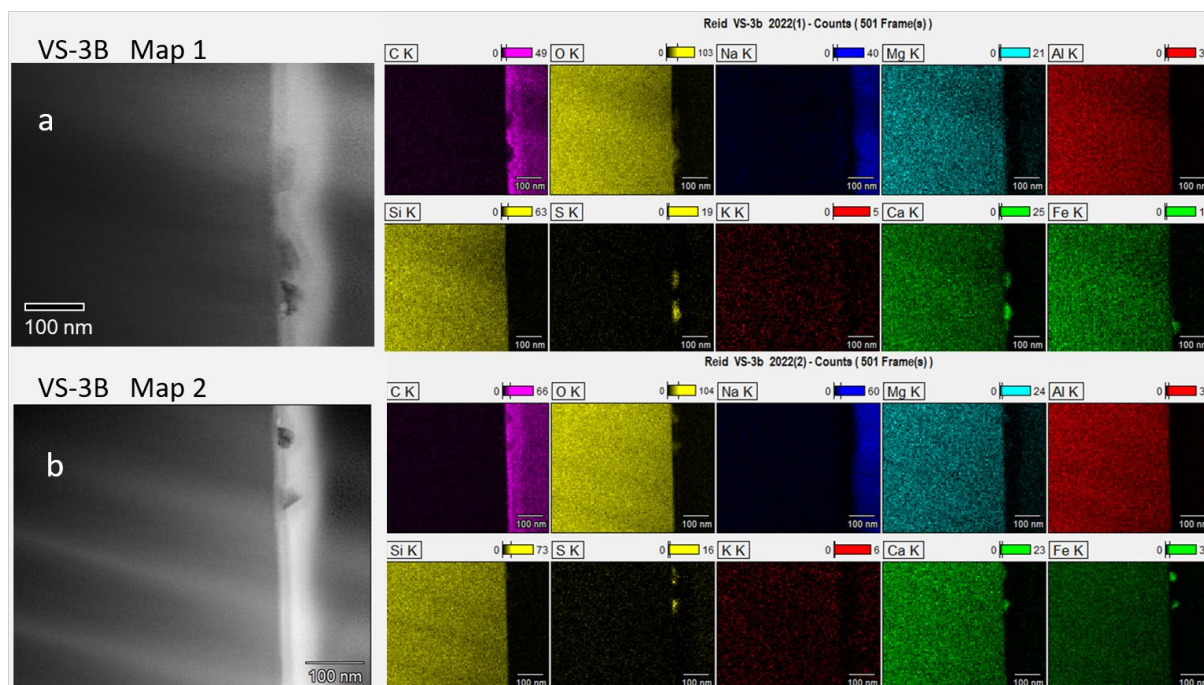


Figure 7. a) and b) show the substrates of VS-3B from which each traverse was taken. Two TEM brightfield images (left) with TEM EDX maps (right) showing elemental abundances. The scale bars above each color image show relative abundance for each element using color intensity. Fe-oxide and CaSO_4 phases are seen on the sample surface. Note that the $\text{NaK}\alpha$ is also GaLa .

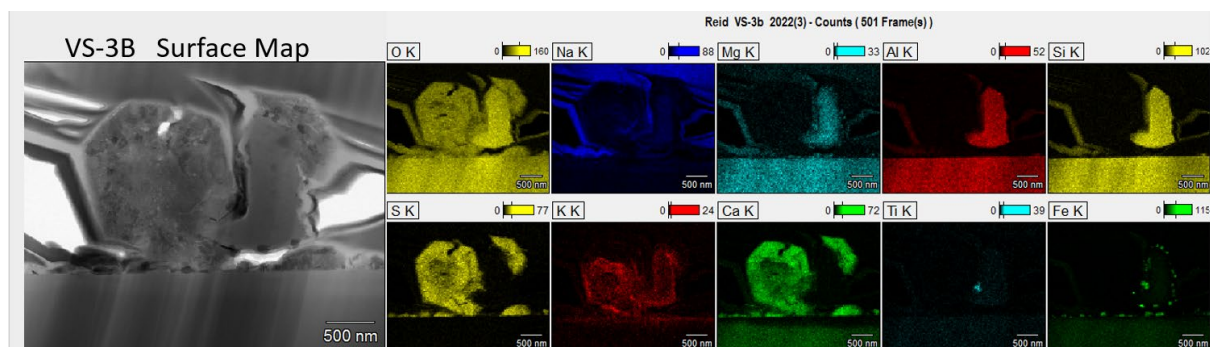


Figure 8. The grayscale image (left) is a basal cross-section of an acicular calcium sulfate crystal. To the right of the crystal is a spur of reacted glass that is covered by another crystal of calcium sulfate. To the right of the image are TEM EDX elemental maps of sample VS-3B. The scale bars above each image show relative abundance for each element using color intensity. Reaction products show enrichments in Ca, S, K, and Fe. Note that NaK α is also GaL α .

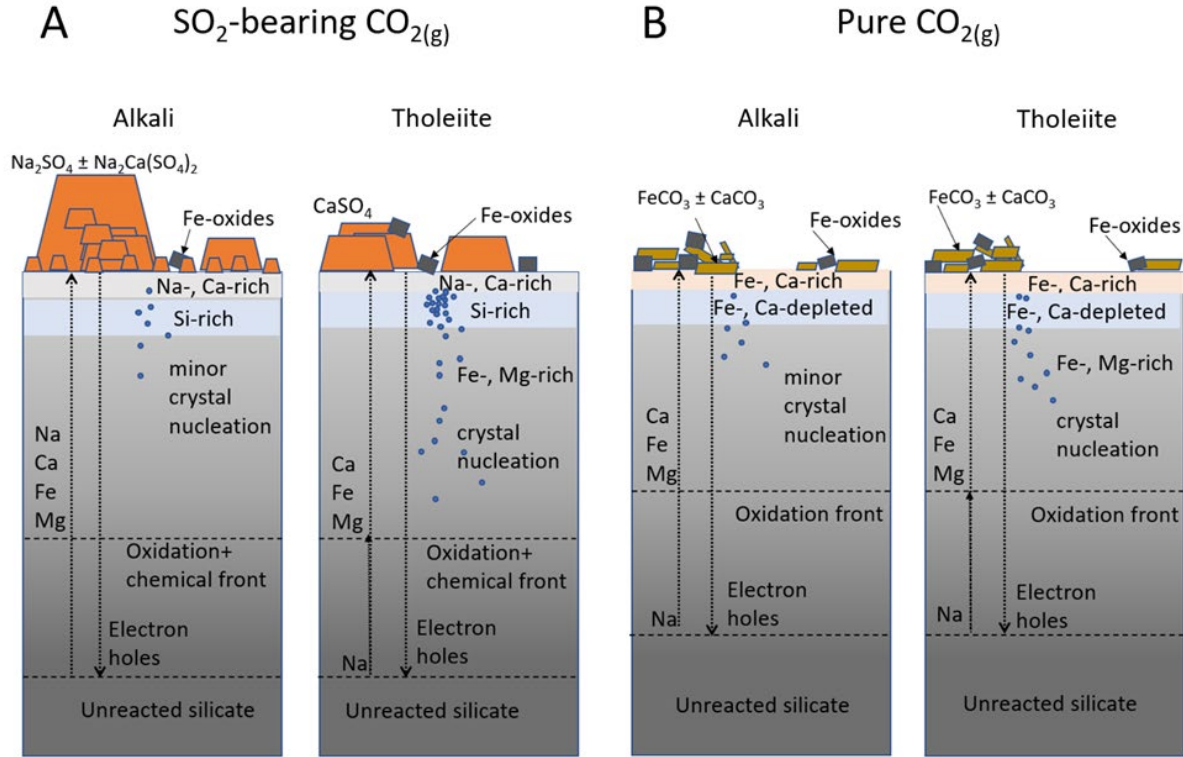


Figure 9. Schematic depicting basalt glass reactions in gases at 470°C, 90 bars pressure for 2 weeks at $MHfO_2$. A) Alkali and tholeiite basalts react with an SO_2 -bearing atmosphere which exerts both oxidation and chemical potentials, creating reaction fronts in the solids. Surface Na and Ca react immediately with adsorbed SO_2 . Na, Ca, Fe, and Mg cations diffuse through the glass toward the free surface in response to the redox and chemical gradients. Cation diffusion is countered by an inward flux electron holes which oxidize Fe^{2+} to Fe^{3+} in the subsurface, where Fe^{3+} is charge compensated by Na. If the concentration of Na is sufficient to stabilize Fe^{3+} (i.e., the alkaline composition), Na outpaces other diffusing cations to the surface where it enriches the near surface region and then reacts with SO_2 at the surface-atmosphere interface to form Na_2SO_4 . In the tholeiite composition, the concentration of Na is inadequate to stabilize all of the oxidizing Fe in the subsurface, which nucleates as Na-rich pyroxenes and Fe-oxide spherulites. Near-surface Fe is oxidized to form magnetite $\pm$ hematite, while near-surface Ca reacts with atmospheric SO_2 to form anhydrite (Modified from Renggli and King, 2018 and interpreted from Renggli et al., 2019b; Cook et al., 1990; Cooper et al., 1996). B) In a pure CO_2 atmosphere (interpreted from data from Teffeteller et al., 2022), reaction phenomena are similar; however, the chemical driver of diffusive cation migration is solely an oxidation potential. The role of Na in the glass is maintained; however, it is either not reacted at the surface, or phase(s) are amorphous or too small to be observed. Other network modifying cations, Ca, Fe, and Mg, migrate toward and enrich a zone near the surface. Just beneath this layer, the glass is depleted in Ca, Fe, and Mg. At the surface, Fe^{2+} partially oxidizes to Fe^{3+} and reacts with CO_2 to form magnetite ($3FeO + CO_2 \rightarrow Fe_3O_4 + CO$; Zolotov, 2018) which reacts further with CO_2 to produce siderite ($Fe_3O_4 + 3CO_2 \rightarrow FeCO_3 + \frac{1}{2} O_2$) or is additionally oxidized to form hematite ($Fe_3O_4 + CO_2 \rightarrow FeCO_3 + Fe_2O_3$) (Koziol, 2004). Additionally, Ca at the surface and migrating from the interior reacts with atmospheric CO_2 to form nano-scale or amorphous $CaCO_3$ (calcite) (Dyar et al., 2020).