SO$_2$ gas reactions with silicate glasses

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INTRODUCTION

Sulfur dioxide (SO$_{2(g)}$) is an important gas species in most common volcanic settings on Earth including subduction zones (Shinohara 2013). The relative abundances of SO$_{2(g)}$ may vary at a volcano over time with the highest rates of SO$_{2(g)}$ emissions occurring during eruptive degassing and lesser amounts emitted continuously during quiescent degassing, resulting in a large total amount of SO$_{2(g)}$ integrated over time of the order of 10 Mt/a (McCormick et al. 2013; Shinohara 2013; Henley and Hughes 2016). Much of the emitted SO$_{2(g)}$ is released at high temperatures. For instance, gas mixtures sampled at the highest temperature volcanic vents reach 1131 °C at Erta Ale volcano and these are the most likely to be representative of the volcanic gas phase (de Moor et al. 2013).

SO$_{2(g)}$ is the most abundant of the corrosive gases at volcanoes (Oppenheimer et al. 2014). In the 1970's, thermodynamic models were used to predict that SO$_{2(g)}$ reactions with silicates form sulfate and reduced sulfur (Gooding 1978; Burnham 1979). This was later shown experimentally through reactions of silicates and carbonates with SO$_{2(g)}$ (Fegley and Prinn 1989; Burnett et al. 1997). When SO$_{2(g)}$ reacts with silicates it covalently binds to the solid surface to build up a surface coating (Henley et al. 2015). In this manner, the SO$_{2(g)}$ reaction fundamentally differs from ionic reactions with some of the other species common in volcanic settings such as H$_2$O-rich fluids (e.g. Oelkers and Schott 2009) or carbon dioxide (DePaolo and Cole 2013). Other species common in volcanic gases such as fluorine and chlorine are also important (Delmelle et al. 2018, this volume, Henley and Seward 2018, this volume), but sulfur gases have particularly interesting properties because sulfur is a multivalent element. Several valence states are involved in SO$_{2(g)}$ reactions with aluminosilicate glasses (S^{-2}, S^{-1}, S^0, S^{4+} and S^{6+}). These different species add complexity to the reactions because they may affect the valence state of other multivalent cations in the solid (e.g., Fe$^{0/2+/3+}$, Ti$^{3+/4+}$, Cr$^{2+/3+}$, V$^{2+/3+/4+/5+}$, Eu$^{2+/3+}$).

Gaseous sulfur dioxide has been detected on a number of other planetary bodies. For example, on Jupiter's moon, Io, SO$_{2(g)}$ is emitted by large explosive eruptions and contributes to a transient S-rich atmosphere (Kumar 1985; Johnson and Burnett 1993; Burnett et al. 1997; Doute 2002). SO$_{2(g)}$ occurs as a minor volcanogenic gas species in the atmosphere of Venus, where it may play an important role in the alteration of the planet's surface (Zolotov 2018, this volume). On Mars, the regolith and dust are rich in oxidized sulfur (e.g., Berger et al. 2016) suggesting that past volcanic eruptions were rich in SO$_{2(g)}$ (King and McLennan 2010; Franz et al. 2017). Because SO$_{2(g)}$ dominantly forms in volcanic eruptions, it may be a good proxy for past or ongoing volcanic activity in planetary and exoplanet atmospheres (Hu et al. 2013; Misra et al. 2015). Reactions between gases, including SO$_{2(g)}$, and solids occurring in the solar system are discussed by Sossi et al. (2018, this volume) and Zolotov (2018, this volume).

In this chapter we discuss observations from gas-solid experiments where SO$_{2(g)}$ is reacted with aluminosilicate glasses. The understanding of SO$_{2(g)}$ reactions with glasses is important because of their ubiquity in volcanic systems (Ayris et al. 2013; Delmelle et al. 2018) and their

abundance on planetary surfaces due to impact processes (Schultz and Mustard, 2004). We discuss the chemistry, mineralogy and texture of the reaction products, as well as provide insights into reaction mechanisms.

GLASS PROPERTIES

Silicate glasses are an ideal substrate material to study gas-silicate reactions because they are amorphous, which avoids complications from mineral orientation effects. To provide context for $SO_{2(g)}$ reactions with glass, we refer the reader to King et al. (2018) for a review of the basic reactions between $SO_{2(g)}$ and silicate minerals.

Aluminosilicate glasses are dominated by Si^{4+} and Al^{3+} cations that are tetrahedrally-coordinated by O^{2-} anions and termed tetrahedral cations (T) (Mysen and Richet 2005). The T cations (in some cases including Ti^{4+} and Fe^{3+}) form a range of Si-O units (e.g., $[SiO_4]^{4-}$, $[Si_2O_7]^{6-}$, $[Si_6O_{18}]^{12-}$, $[Si_4O_{11}]^{6-}$, $[Si_2O_5]^{2-}$, $[SiO_2]$). These units are polymerized to form a network linked by a distribution of bond lengths and bond angles with a lack of long-range order. Monovalent and divalent cations (e.g., Na^+, K^+, Mg^{2+} and Ca^{2+}) have a role as network modifiers and/or charge compensators and do not contribute to the tetrahedral network (Mysen et al. 1982; Mysen and Richet 2005).

The structural arrangement of atoms in a silicate glass is of great importance for the physical properties, including structure and degree of polymerization, viscosity, glass transition temperature and diffusion rates (Dingwell 2006). The main variable affecting glass properties is the concentration of network-forming cations, the most abundant of which are Si^{4+} and Al^{3+}. Network-forming cations exhibit a low mobility and their self-diffusivities are a function of the melt's viscosity, and can be described by the Eyring equation (Dingwell 1990). Relative to network formers, network modifiers have diffusivities that are orders of magnitude higher (Dingwell 1990). More recently, the identification of charge compensating cations (e.g. Na, K, Ca) in simple glasses has shown that these elements may move in channels, which allows a more complex element mobility (Le Losq et al. 2017).

Temperature plays an important role in element mobility (Zhang 2010) and in glasses, the glass transition temperature is a key reference point. The glass transition is the temperature range below which the amorphous structure is locked in and becomes unrelaxed and the material behaves as a solid. As a consequence, configurational changes do not occur on a measurable scale below the glass transition temperature and the energetically most favorable state is not reached (Mysen and Richet 2005). The glass transition is a function of the relaxation of the network of Si-O units and hence of the lifetime of the bonds (e.g., Webb 1997). The temperature range from 600 to 850 °C, at which $SO_{2(g)}$ reactions with silicate glasses have been performed experimentally (Tables 1 and 2), is near the glass transitions of these systems (Martens et al. 1987; Knoche et al. 1992). Consequently, minor changes in the temperature conditions may affect the reaction rates and mechanisms considerably when the glass transition is crossed.

EXPERIMENTAL TECHNIQUES

Experiments reacting $SO_{2(g)}$ with silicate glasses have been performed with both open and closed systems. Early experiments were performed in closed systems, in respect to the glass, in sealed silica tubes where $SO_{2(g)}$ was produced via the decomposition of $K_2S_2O_8$. The decomposition of this compound forms $SO_{2(g)}$ and $O_{2(g)}$ (Johnson and Burnett 1993; Li et al. 2010) via Equation (1):
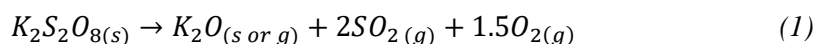
$$K_2S_2O_{8(s)} \rightarrow K_2O_{(s\ or\ g)} + 2SO_{2\ (g)} + 1.5O_{2(g)} \qquad (1)$$

In reaction 1, K_2O occurs as either a solid or gas species dependent on temperature and pressure (e.g., Muan and Osborn, 1965). As the sample is cooled, solid K_2O may be deposited in the tube and on the silicate sample. Removal of K_2O as a solid from the experimental system, will tend to favor the reaction:

$$2SO_{2\,(g)} + O_{2(g)} \rightarrow 2SO_{3(g)} \qquad (2)$$
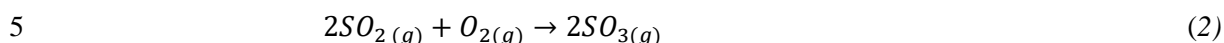
This reaction lowers the fugacity of $SO_{2(g)}$, creating an environment where $SO_{3(g)}$ is an important reactant and the reaction products are changed. Thus, to examine pure $SO_{2(g)}$, it is necessary to trap or remove the $O_{2(g)}$ if the gases are produced via Equation (1) (Burnett et al. 1997).

Monitoring of the $SO_{2(g)}/SO_{3(g)}$ in the gas phase is important because $SO_{3(g)}$-mineral reactions follow the general form:

$$SO_{3(g)} + MO\_silicate \rightarrow MSO_4 + silicate \qquad (3)$$
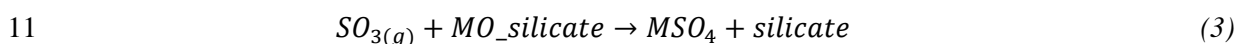
where M is a cation (e.g., Ca, Mg, Na, and Fe) and S remains in the 6+ state. In contrast, in $SO_{2(g)}$-mineral reactions, where S^{4+} in the gas phase disproportionates into 6+ and reduced sulfur (e.g., S^{2-}, a reduced sulfur radical, S^{-} or S^{0}), the reaction follows the form (modified after Burnham 1979):

$$2SO_{2\,(g)} + MO\_silicate \rightarrow MSO_4 + S_{reduced} + silicate(+oxide) \qquad (4)$$
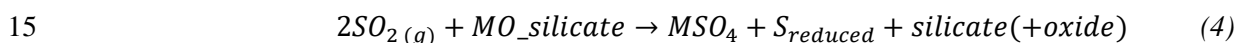
To avoid the issues associated with $K_2S_2O_8$ decomposition, recent experiments used commercial $SO_{2(g)}$ as the gas source (Tables 1 & 2; King et al. 2018, this volume). A Gibbs Free Energy minimization calculation reveals that $SO_{2(g)}$ is not pure at equilibrium conditions, even under the assumption that the gas source is pure. We used the software package HSC8 by Outotec, which is based on the JANAF database (Chase 1998). The most abundant trace gas species in equilibrium with $SO_{2(g)}$ are $SO_{3(g)}$, $SO_{(g)}$ and $S_{2(g)}$ (Fig. 1). All trace species have abundances of less than 10^{-5} mole fractions in the temperature range relevant to studies involving the reaction of $SO_{2(g)}$ (600-850 °C, see tables 1 and 2). The oxygen fugacity of this gas mixture is approximately at the magnetite-hematite buffer in the temperature range relevant to the experiments discussed here. It has been noted that the equilibration of the gas species in this system ($SO_{2(g)}$, $SO_{3(g)}$, $O_{2(g)}$) is relatively slow (Luthra and Worrell 1979). Therefore, actual abundances of trace gases may be even lower in these experiments because at the high flow rates of 20-50 cm^3 per minute, equilibrium speciation in the gas phase may not be attained. Changes in the composition of the gas during the reaction have not been determined in any experiment.

Solid glass for experiments is best polished prior to reactions with $SO_{2(g)}$ so that the run products are easier to examine and to minimize artefacts. For example, gas-solid reactions are sensitive to the surface area, and so cracks and scratches may result in a higher degree of reaction. Furthermore, irregularities on the surface may act as nucleation points for sulfate formation on the surface (Fig. 2, Burnett et al. 1997). Additional details on experimental setups are given in Chapter 1 (King et al. 2018, this volume).

$SO_{2(g)}$ REACTIONS WITH FE-FREE SILICATE GLASSES

As indicated above, sulfur has many different valence states. This means that there can be considerable complexity in reactions between $SO_{2(g)}$ and multivalent cations, such as Fe, the most abundant multivalent element in most magmatic systems (Schreiber 1987). We therefore separate our discussion of experiments into either Fe-free or Fe-bearing glasses.

Mineralogy of phases formed on Fe-free glass substrates

Table 1 summarizes experiments on $SO_{2(g)}$ reacted with synthetic Fe-free glasses from both the literature and our laboratory. Compositions include glasses in the albite-anorthite-diopside (Ab-An-Di) system, Fe-free basalt, soda-lime (Na-Ca-silicate) glass, and albite-orthoclase glass.

Temperature conditions range from 600-850 °C and experimental durations vary considerably from 1 to1366 hours. The run products include Na-, Ca- and/or Mg-sulfates.

The observation and determination of the mineralogy of products formed in $SO_{2(g)}$ experiments is challenging due to small grain sizes (Dalby et al. 2018; Palm et al. 2018). Reaction products may have grain diameters of tens of nanometers, which are far below the resolution of conventional methods such as Raman spectroscopy or energy dispersive X-ray spectroscopy. When the reaction products are thinner than the analytical volume of the method used, the signal includes both the reaction product and the silicate substrate. Such reaction products require high resolution techniques such as transmission electron microscopy, atom probe microscopy, surface sensitive analysis (e.g., X-ray photoelectron spectroscopy) or thin film approaches such as grazing angle techniques or depth profiling (Dalby et al. 2018; Palm et al. 2018).

As the majority of reaction products from $SO_{2(g)}$-silicate reactions are sulfates, a brief overview of sulfate phase relations is necessary (see also King et al. 2018, this volume). At elevated temperatures, sulfates ultimately decompose into oxides and $SO_{3(g)}$ (Stern 2001). For example, $MgSO_4$ decomposes at temperatures above 900 °C and $CaSO_4$ above 1200 °C (Rowe et al. 1967; Du 2000). In addition to thermal decomposition some sulfates may also vaporize at high temperatures (e.g. $Na_2SO_{4(s)} = Na_2SO_{4(g)}$) (Stern and Weise 1966). At 600-800 °C, at which most $SO_{2(g)}$-reaction experiments have been performed (see table 1 and 2), some of the sulfates form limited solid solutions. The degree of solid solubility of Na_2SO_4 in $CaSO_4$ is poorly understood as experimental data is limited. In turn, Na_2SO_4 dissolves up to 35 mol.% of $CaSO_4$ and $Na_2Ca(SO_4)_2$ (glauberite) also forms (Freyer and Voigt 2003). Similarly, it also dissolves $MgSO_4$ although in a more limited temperature range. Na_2SO_4 and K_2SO_4 form a complete solid solution from 600 to 800 °C. $CaSO_4$ and $MgSO_4$ do not form solid solutions. Instead, the binary system includes the phase $CaMg_3(SO_4)_4$ (Rowe et al. 1967; Du 2000); this phase has not been reported in any $SO_{2(g)}$ experiment (Table 1). In these experimental studies the reporting of sulfates has generally identified only the pure end-member phases.

The interpretation of sulfate textures formed in $SO_{2(g)}$ reactions can be challenging due to the hydrophilic nature of the materials. Magnesium sulfate in particular readily hydrates, forming a large range of phases with various degrees of hydration (Wang et al. 2006). It is therefore crucial to protect experimental samples from water vapor after the reaction (e.g., in a desiccator or under controlled atmosphere). Even so, sulfates textures may evolve with time during sample storage and hydrate in air (Dalby et al. 2018, this volume).

Textures of sulfate coatings on Fe-free glass substrates

The textures of sulfates observed on Fe-free glasses vary strongly with the glass composition and experimental conditions. The sulfates form on the surfaces and are coating the glasses. In the oxidation community these types of reaction products are termed scales (Birks et al. 2006), but we use the term coating, which is consistent with the use in the geological literature. Sulfate surface coatings fall into two distinct categories of continuous and discontinuous coverage. Electron microscopy images of these textures are shown in Figures 2, 3, 4 and 5. Discontinuously distributed sulfates commonly display distinct crystal facets (Fig. 2 and 3). A secondary electron images of a sulfate texture with discontinuous coverage is shown from an experiment with albite glass (Fig. 3a, 600 °C, 1hour). This type of discontinuous coating occurs on albite glasses reacted with $SO_{2(g)}$ at 600-800 °C and experimental durations of 1 hour and 24 hours (table 1). Similarly well-defined sulfate crystals have been observed on soda-lime and obsidian glasses (Burnett et al. 1997). The mechanism of sulfate growth in the case of discontinuous coatings is relatively simple, because the glass surface remains exposed to the gas throughout the reaction as illustrated in Figure 3.

In experiments where the temperatures approach the thermal stability of the sulfates, the individual sulfate "islands" are poorly crystallized and can be polycrystalline and flakey in texture

(Johnson and Burnett 1993). Formed in sealed silica glass tubes, such sulfates may be the product of deposition from the gas phase or the quench product of a sulfate melt (Johnson and Burnett 1993). In experiments where these textures formed in a gas-furnace under a high $SO_{2(g)}$ flux, and at temperatures below the liquidus temperature of the sulfate, the formation as quench products is not possible and the textures are likely due to very high sulfate nucleation rates which exceed the rates of grain growth.

Continuously-distributed sulfate coatings occur on a range of Fe-free experiments, including Fe-free basalt and glasses in the Ab-An-Di ternary system. Anhydrite is commonly distributed in a single layer of equigranular columnar grains, such as on anorthite glass (Fig. 4a, 800 °C, 1h). For Fe-free basalts, the surface material consists of a mixture of $CaSO_4$ and $MgSO_4$. The back-scattered electron image (Fig. 4b) of Fe-free basalt glass (700 °C, 24h) shows areas of darker $MgSO_4$, partially hydrated after the experiment, and rhombohedral anhydrite grains. The textures of the continuous coatings have many similarities with coatings formed during the oxidation in a range of systems, such as aluminum oxide scales on metal alloys (Hsueh and Evans 1983; Evans et al. 1983; Tolpygo and Clarke 1998a, b; Chason et al. 2013). A comparison of the sulfate coatings with extensively studied oxide coatings is valuable as it allows an interpretation of the mechanism that form these coatings.

In experiments where continuous coatings form, the silicate glass is no longer directly exposed to the gas after the initial formation of the sulfate coating. Ongoing reaction requires a transport mechanism through the coating. Consequently, there are three possible growth pathways. First, if the reactive gas diffuses very fast through the sulfate, the reaction occurs at the interface between the sulfate and the silicate glass, below the coating. This type of mechanism commonly occurs during the oxidation of metals, where oxygen migrates through the oxide coating to the interface between the coating and the pristine metal (Evans et al. 1983). If a similar mechanism operates in $SO_{2(g)}$-substrate reactions we would expect a continuous outward displacement of the previously formed sulfate. Such an outward expansion would result in cracks in the coating around edges of the silicate glasses, which are not observed in any experiment. Second, if the cations diffuse rapidly through the coating, growth would occur at the surface interface between the sulfate and the gas. In this case growth would occur continuously across the surface and deformation of the coating would be avoided. This texture has not been observed in any experiments recorded in the literature. In a third possible mechanism, cations and the gas phase migrate at a comparable rate through the sulfate layer. In this case the reaction and growth occur within the sulfate coating, most easily at grain boundaries (Fig. 4c). This growth mechanism results in the accumulation of stress in the coating. The dissipation of this stress results in three different possible deformation textures (Fig. 5). First, because transport of cations and $SO_{2(g)}$ most easily occurs along grain boundaries (Fig. 4c), newly-formed sulfate would accumulate at grain boundaries preferentially (Fig. 5d). This epitactic overgrowth would continue to such an extent that it results in the formation of protrusions such as whiskers and hillocks. These features are indicated in Figure 5a for a reacted eutectic An-Di glass. The formation of whiskers and hillocks extending from coatings is also observed in thin film materials where strain is localized, and the growth of materials is focused outwards by diffusive transport. For example, tin whiskers are commonly observed growing out of intermetallic coatings (Sobiech et al. 2009; Chason et al. 2013). Second, where grains extend laterally and stress is not focused on a small area, individual sulfate crystals can be bent upwards at grain boundaries to form a chicken-wire texture (Fig. 5b and e) (Tolpygo and Clarke 1998b; Clarke 2003). Third, entire polycrystalline sulfate layers can wrinkle and buckle due to internal stress and expansion (Fig. 5c and f). This type of texture occurs when the rate of growth is very high (Clarke 2003). For example, such a coating is shown in Figure 5 with extensively deformed buckles. Within experimental durations, the volume between the buckled coatings and the substrate is not infilled with additional sulfate material, although this may occur over much longer durations. Similar deformation processes resulting in buckled coatings are observed in oxide coatings formed in gas-alloy reactions (Evans et al. 1983; Clarke 2003; Birks et al. 2006). The presence of diverse deformation textures formed by continuous sulfate coatings on glasses reacted with $SO_{2(g)}$ (Fig. 5)

1 strongly implies that these coatings indeed grow internally as illustrated in the schematic drawing
2 in Figure 4c. Independent of the mechanisms by which the sulfates grow, the reaction results in a
3 volume increase in the run products. In natural sub-volcanic systems this may result in the filling
4 of veins as the gas passes through and reacts with the surrounding rocks (Henley et al. 2017).

5 In summary, in the case of continuous sulfate coatings $SO_{2(g)}$ and cations need to migrate
6 into the sulfate coating, where new sulfate forms preferentially at grain boundaries (Fig. 4). This
7 process results in an increase of the coating volume and commonly causes deformation in the
8 coating. Deformation textures observed in experiments include whiskers, chicken-wire textures,
9 and buckling and wrinkling of the coating (Fig. 5). The degree of deformation increases with
10 increasing amount of sulfate formed.

Compositional changes in the Fe-free glass substrate

12 The mineralogical investigation of the coatings formed by reactions of $SO_{2(g)}$ with Fe-free
13 silicate glasses has shown that Ca-sulfates are the dominant reaction products. The observed
14 variation of sulfate phases formed as a function of temperature and relative to the glass transition
15 temperature underlines the importance of the role of the substrate composition on the overall
16 reaction mechanism and reaction rates. For example, Renggli et al. (in prep.) have shown that
17 sulfate reaction products have mole% Ca/(Ca+Mg) that generally exceed the mole% Ca/(Ca+ Mg)
18 in the reactant anorthite-diopside glasses ((Ca/(Ca+Mg))$_{diopside}$ = 0.5, (Ca/(Ca+Mg))$_{anorthte}$ = 1). In
19 the anorthite-diopside system at 600 °C the sulfate reaction products are relatively enriched in Ca
20 by 20-40%. At 800 °C, above the glass transition temperatures of all An-Di glasses except for the
21 anorthite endmember, this fractionation effect is much stronger and only minor or trace amounts
22 of Mg are detected in the sulfate reaction products. The mole% Ca/(Ca+Mg) at 800 °C is near 1 in
23 the sulfate formed on all anorthite-diopside glasses (Renggli et al. in prep.). This means that Ca
24 preferentially moves out of the glass to form the sulfates and Mg is relatively retained in the glass,
25 as discussed further below.

26 The reaction of $SO_{2(g)}$ with a silicate glass requires the mobilization of alkali or alkaline
27 earth metals to form sulfates at the reaction interface. As the relative abundances of Ca and Mg in
28 the sulfate reaction products vary both with temperature relative to the glass transition and also
29 with the composition of the unreacted glasses diffusional transport mechanisms appear to be
30 important rate controlling factors. The reaction at the surface causes chemical potential gradients
31 which drive mass fluxes. As Ca moves to the surface, additional chemical potential gradients result
32 in the interior of the silicate requiring charge compensation which causes compositional and
33 structural changes, in some cases resulting in crystallization. If the diffusion of Ca is a rate limiting
34 factor of the overall reaction, then the rate of sulfate formation must also change with experimental
35 duration. This change in the diffusivities of sulfate forming cations with experimental duration is
36 very poorly constrained and requires future experimental work.

37 The loss of charge-compensating cations and network-modifying cations from the glass to
38 the surface may require charge balancing. In systems without multivalent elements available to
39 change the valence state to accommodate a change in the electrochemical environment, charge
40 balancing may occur via four different mechanisms. First, anions can co-diffuse with the outward
41 fluxing cations. Second, charge compensation can occur via the counter diffusion of electron holes.
42 Third, charge compensation can occur via the counter diffusion of negatively-charged sulfur.
43 Fourth, Al^{3+} may adapt its coordination and partially become a network-modifier with five- and
44 six-fold coordination (Neuville et al. 2006; Le Losq et al. 2014). There is much work to be done to
45 demonstrate how these different charge balancing mechanisms behave in different materials.

46 Nucleation and growth of crystallites due to structural changes of the glass induce further
47 chemical potential gradients and affect the diffusivities of the diffusing cations. The interplay of
48 these processes during reactions of $SO_{2(g)}$ with the silicate surface can result in complex textures
49 that reflect the ongoing nature of the reactions and may result in phase assemblages which are out

of equilibrium, both in the surface coating and in the silicate. Crystallization in the substrate at the surface, in Fe-free glasses, has only been observed at or near the glass transition temperature. It has been documented in three experiments at 800 °C with diopside glass (T_g = 722 °C), $An_{15}Di_{85}$ glass (T_g = 729 °C) and $An_{48}Di_{52}$ glass (T_g = 760 °C), where diopside crystallized at the interface (Renggli et al. in prep.). When crystallization occurs at the reaction interface the overall reaction rate may be affected significantly and additional variables such as crystal structure, orientation and grain size distribution require consideration in the future (see King et al. 2018).

$SO_{2(g)}$ REACTIONS WITH FE-BEARING GLASSES

Mineralogy of phases formed on Fe-bearing glass substrates

The reaction products formed on Fe-bearing glasses include $CaSO_4$, $MgSO_4$, Na_2SO_4, $Na_2Ca(SO_4)_2$, K_2SO_4, $Al_2(SO_4)_3$, $FeSO_4$, hematite, magnetite and Ti-bearing oxides (Table 2). These phases have been determined by a range of direct and indirect methods including SEM, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM), nanoSIMS and leachate solution analysis (Johnson and Burnett 1993; Burnett et al. 1997; Li et al. 2011; Ayris et al. 2013). Examples of these analyses are described in more detail in Dalby et al. (2018, this volume) and Palm et al. (2018, this volume).

Early experiments between $SO_{2(g)}$ and Fe-bearing glasses provided variable of results, in part due to Equation (2) listed above. Johnson and Burnett (1993) used a 1:1 mixture of $SO_{2(g)}$ and $O_{2(g)}$ that likely formed $SO_{3(g)}$ (Equation (2)) compared to pure $SO_{2(g)}$ in a sealed silica tube used by Burnett et al. (1997). In the first case, the reaction products include a large range of different sulfates (Ca, Mg, Na, K, Fe and Al) in all three experiments, as summarized in Table 2.

The studies by Johnson and Burnett (1993) and Burnett et al. (1997) used the same glasses for their experiments, including a chondrule glass, obsidian and Kilauea basalt (Table 2). As described above, the presence of K-sulfate in some experiments by Johnson and Burnett (1993) is likely due to reaction with K from the starting $K_2S_2O_8$ used to produce the gas phase. Burnett et al (1997) were able to demonstrate the presence of reduced sulfur using photoelectron spectroscopy (XPS) on experimental products of disproportionation reactions with pure $SO_{2(g)}$, but the sulfide phases were not directly determined. The experiments using pure $SO_{2(g)}$ resulted in significantly smaller amounts of reaction products, with $CaSO_4$ on the chondrule glass, very small amounts of Fe-sulfate on the obsidian and no detected reaction products on the Kilauea basalt (Burnett et al. 1997).

Ayris et al. (2013) used a gas mixture which is closer to a naturally occurring mixture in explosive volcanic eruptions, consisting of a small quantity of $SO_{2(g)}$, air and $He_{(g)}$. They used glass substrates with tephrite, phonolite, dacite, and rhyolite compositions. In the 600-800 °C range, $CaSO_4$ is the only phase observed on the surface of any of the glasses (Ayris 2010; Ayris et al. 2013) (Table 2). At 300-600 °C, there was no detected reaction on the rhyolite glass yet the other glasses were coated with $CaSO_4$ and the tephrite glass also had minor amounts of Na_2SO_4. In the 0-300 °C range no reaction products were detected on any of the tested glass compositions after one hour.

On natural glasses, these authors found that the initial rates of reaction are very high, with sulfate detected by leachate analysis on the glass surfaces at 800 °C within 30 seconds. This high rate of $SO_{2(g)}$ uptake in the first minute is due to fast adsorption onto the surface. This is followed by lower reaction rates, which are controlled by diffusive transport of Ca^{2+} from the interior of the glass to the surface. Overall, the amount of reaction increases with the Ca-concentration in the glass (Ayris et al. 2013). The textures observed by Ayris et al. (2013) on glasses reacted at 800 °C for 1 hour show discontinuously distributed, faceted $CaSO_4$ crystals with diameters ranging from few hundred nanometers to 5 μm. The textures are comparable to those observed on soda-lime,

albite and diopside glass (see Fig. 2 and 3; Burnett et al. 1997). The texture in Figure 2 also underlines the importance of polishing the glass surface exposed to the reacting gas. The presence of a scratch results in an increasing degree of nucleation and formation of sulfate (Fig. 2; Burnett et al 1997).

Li et al. (2010) used the same experimental setup as Johnson and Burnett (1993), conducting experiments with crystalline basalts. At 600 °C they observed $CaSO_4$, whereas at 850 °C they observed an assemblage of $CaSO_4$, $MgSO_4$ and Fe_2O_3 (Li et al. 2010). Similar multi-phase assemblages were observed on basalt glasses reacted with $SO_{2(g)}$ (Table 2).

$CaSO_4$ and Na_2SO_4 and Fe_2O_3 were the major products with lesser $MgSO_4$, Fe_3O_4 and Fe-Ti-oxides, in the case of both tholeiitic basalt glasses at 700 °C for 1 hour and 24 hours, and alkali basalt glass at 800 °C for 1 hour (Table 2). These tholeiitic basaltic glasses included a series where the Fe^{3+}/Fe^{2+} was set at a range of values by pre-equilibrating the melt at different fO_2 conditions (Dufresne et al. 2015). The unreacted glasses had molar $Fe^{3+}/Fe^{2+} = 0.08$ (pre-equilibrated 1.5 log-units in fO_2 below the Ni-NiO buffer (NNO-1.5)) to 0.54 at one log-unit in fO_2 above the Ni-NiO buffer (NNO+1) (Dufresne et al. 2015).

The coating mineral assemblages depend on the Fe^{3+}/Fe^{2+} ratios in the unreacted glasses, the temperature and the experimental duration. Examples of the textures formed at 700 °C under a stream of $SO_{2(g)}$ for 24 hours are shown in Figure 6. In all three examples, $CaSO_4$ is the predominant sulfate phase in the coatings. The glass pre-equilibrated at NNO-1.5 is continuously coated with a mixture of Ca- and Mg-sulfate and very small sub-micron Fe-oxides. In the short experiment of 1 hour, the coating also included some Na_2SO_4. Glasses pre-equilibrated at NNO and NNO+1 show large $CaSO_4$ crystals with lengths of up to 100 µm (Fig. 6). The coating on the glass pre-equilibrated at NNO further includes dark areas of $MgSO_4$, smaller amounts of Na_2SO_4 and Fe_2O_3 in between the $CaSO_4$ crystals. At NNO+1 the coating includes a fine-grained mixture of Na_2SO_4 and micron-sized hematite crystals (Fig. 6c). Larger oxide crystals also occur, including some Fe-Ti-oxides on the $CaSO_4$ crystals and minor amounts of Al in some Fe-Ti-oxide grains (Fig. 6). Small grains of $MgSO_4$ were observed on the NNO+1 sample after 1 hour, whereas no $MgSO_4$ was detected after 24 hours.

In addition to Fe_2O_3 the more reduced magnetite (Fe_3O_4) mineral has been observed in the coatings of basalt glasses pre-equilibrated at the iron-wüstite redox buffer (Palm et al. 2018). The dominant sulfate phase in these experiments is $Na_2Ca(SO_4)_2$ (glauberite) with significant amounts of $CaSO_4$. The results from these experiments reacting basalt at 800 °C are described in detail as a case study in the chapter by Palm et al. (2018, this volume).

In summary, phase assemblages of the coatings formed by the reaction of $SO_{2(g)}$ with Fe-bearing basalt glasses vary as a function of the composition and the Fe^{3+}/Fe_{total} of the glass prior to the reaction with $SO_{2(g)}$ (Table 2). The sulfates observed in the coatings are $CaSO_4$, $MgSO_4$, Na_2SO_4 and $Na_2Ca(SO_4)_2$. The oxides observed in the coatings are hematite, magnetite and Ti-bearing oxides. Future work will be required to determine the mechanisms which control the phases formed in $SO_{2(g)}$ reactions with Fe-bearing basalt glasses.

Textures of sulfate coatings on Fe-bearing glass substrates

All experiments produced by reacting $SO_{2(g)}$ with Fe-bearing glasses have discontinuous coatings (Fig. 6, Burnett et al. 1997; Ayris et al. 2013). After one hour at 700 °C the coatings cover up to 80% of the surface area of the glass. The coverage increases with time reaching more than 90% after 24 hours. The texture of the sulfate-coating on the tholeiitic basalt pre-equilibrated at NNO-1.5 reacted at 700 °C for 24 hours (Fig. 6a) is very similar to that on the Fe-free basalt reacted at the same temperature and for the same amount of time (Fig. 4b). Both figures show backscattered electron images with similar well-crystallized $CaSO_4$ grains with sub- and anhedral Mg-sulfates which partly hydrated after the experiments. Only a few gaps occur in the coatings, exposing the

substrate and they are usually surrounded by $CaSO_4$ crystals (Fig. 6a). The $CaSO_4$ have diameters of less than 2.5 μm.

The coatings on the more oxidized basalts (NNO and NNO+1) reacted at 700 °C for 1 hour and 24 hours share the feature of well crystallized large euhedral anhydrite grains. The large anhydrite grains usually show a distinct cleavage perpendicular to the longest axis of the grains. As anhydrite has the best cleavage in the (001)-plane (Tröger 2017), the longest axis of the grains in the coatings are the crystallographic c-axis of anhydrite (Fig. 6).

After one hour, Mg- and Na-sulfates form very fine-grained textures, with grain-sizes of few microns on the glasses pre-equilibrated at NNO and NNO+1. The Mg-sulfates form equant shaped grains, whereas the Na-sulfates have needle-shaped habits which are commonly twinned. The Na-sulfates usually occur as patches surrounding elongated $CaSO_4$ grains. The metal oxides are most frequently found lining the edges of these sulfate patches.

After 24 hours the $CaSO_4$ grains are up to five times larger compared to coatings on 1-hour experiments. Individual crystals of $CaSO_4$ are no longer isolated and there are gaps in-between crystals which are largely filled by other phases. On the glass pre-equilibrated at NNO, Mg-sulfate (where present) occurs in large patches which partially overgrow and surround the $CaSO_4$ grains. The Na_2SO_4 lines the edges of the $CaSO_4$ grains. In this coating, metal oxides reach grain sizes of more than 20 μm (Fig. 6b). In the coating formed on the most oxidized glass (NNO+1) Na_2SO_4 patches tend to overgrow the $CaSO_4$ grains (Fig. 6c). The metal oxides are either found as micron-sized needles in the Na_2SO_4 patches, or as large Fe-oxides (commonly Ti-bearing) between sulfates and on top of large $CaSO_4$ grains.

In comparison with the textures observed on Fe-free glasses, the coatings formed by reactions between $SO_{2(g)}$ and Fe-bearing glasses are significantly different. $CaSO_4$ is the dominant phase in most Fe-bearing and Fe-free systems, but the grain morphologies and sizes are very different. On Fe-bearing glasses, $CaSO_4$ forms large grains with diameters of up to tens of microns (Fig. 2, Fig. 6), whereas on Fe-free glasses $CaSO_4$ usually forms continuous coatings with small grain sizes of up to several microns (Fig. 4, Fig. 5). The large $CaSO_4$ grains in coatings on Fe-bearing glasses are, in some cases, associated with various other phases including sulfates and oxides (Fig. 6), whereas in other cases $CaSO_4$ remains the only phase detected in the coatings (Table 2, Ayris et al. 2013). This diversity of textures and assemblages shows that more work is needed to constrain the processes which control the textures and assemblages formed in reactions between $SO_{2(g)}$ and Fe-bearing aluminosilicate glasses.

Compositional changes in the Fe-bearing glass substrate

Reaction products are also found in the glass substrate in layers or dispersed near the interface with the gas and sulfate coating. For example, chondrule glass substrates produced a region rich in silica and a Na-Ca-Mg-Al silicate, possibly clinopyroxene, in the glass below the $CaSO_4$ coating (Johnson and Burnett 1993; Burnett et al. 1997). Ayris et al. (2013) used transmission electron microscopy energy-dispersive X-ray spectroscopy (TEM-EDS) to show that the reacted tephrite (Fig. 2) and phonolite glasses are depleted in Ca near the surface. This depletion supports the assumption that Ca diffusion in the glass is the rate controlling step in the sulfate forming reaction. The cross-section of the tephrite glass shows the nanometer scale nucleation of a silicate phase, identified as the clinopyroxene augite by X-ray diffraction (Ayris et al. 2013). Palm et al. (2018, this volume) also observed the crystallization of clinopyroxene in an alkaline basalt glass reacted with $SO_{2(g)}$ at 800 °C.

Reactions between tholeiitic basalt glasses and $SO_{2(g)}$ record considerable complexity in these non-equilibrium reactions. For example, a cross-section through the sulfate-rich coating on a tholeiitic basalt glass, pre-equilibrated at the NNO buffer is shown in Figure 7. The images are maps of major elements obtained by nanoscale secondary ion mass spectrometry (nano-SIMS, see Palm et al. 2018, this volume). The network-forming cations Si and Ti show small or negligible

concentration gradients across the interface from the coating into the glass. In some instances, SiO_2 needles form in the reacted glass substrate near the surface. Magnesium and Fe are strongly depleted within the outermost two microns of the glass and show an increase within 20 µm of the surface. The degree of nucleation of Mg- and Fe-rich phases varies considerably between the experiments although consistently crystallization occurs along a gradient of increasing crystal density towards the reaction surface (Fig. 7). The main sulfate-forming cation is Ca, as reflected by a high relative count rate in the surface layer. The glass substrate is accordingly depleted in Ca. Sodium shows a very different behavior because it partitions into the sulfate coating, but is also enriched in the near-surface silicate substrate (Fig. 7).

DISCUSSION

In this section, we discuss the reaction mechanisms and possible rate-limiting steps in gas-glass reactions. Since Ayris et al. (2013) found that reactions were most efficient above 600 ℃, we focus the discussion on experiments in the temperature range of 600-800 ℃. First, we discuss the observation from experiments with Fe-free aluminosilicate glasses. Second, we discuss Fe-bearing systems, in which redox reactions play an important role. For this reason, we will examine the variables $SO_{2(g)}$ and $O_{2(g)}$ and their effect on the reaction products in the coatings and the altered glass substrates.

In all experiments recorded in the literature, in which $SO_{2(g)}$ was reacted with Ca-, Mg- and Na-bearing aluminosilicate glasses, the sulfate reaction products are relatively enriched in Ca relative to the unreacted bulk glass composition, hence Ca migrates out of the glass more than Mg. This is the case for both Fe-bearing and Fe-free systems. As pointed out, the sulfates almost entirely consist of $CaSO_4$ on An-Di glasses reacted at 800 ℃, whereas at 600 ℃ some $MgSO_4$ is present. $CaSO_4$ has lower Gibbs free energies of formation than $MgSO_4$ from 25 ℃ to >1500 ℃, making it a more stable phase. At 600 ℃ calculated Gibbs free energies of formation are -1558.7 kJ/mol for $CaSO_4$ and -1372.3 kJ/mol for $MgSO_4$, and at 800 ℃ they are -1608.5 kJ/mol for $CaSO_4$ and -1418.1 kJ/mol for $MgSO_4$ (Chase 1998). The differences in the Gibbs free energies of formation are -186.4 kJ/mol at 600 ℃ and -190.4 kJ/mol at 800 ℃. These data show that $CaSO_4$ is thermodynamically more stable than $MgSO_4$, but the presence of $MgSO_4$ at 600 ℃, and not at 800 ℃, cannot be ascribed to the thermodynamic properties. Thermodynamic properties of the sulfates are discussed in more detail in King et al. (2018, this volume) and applied to reactions in planetary environments and on Venus in Zolotov (2018, this volume).

If the rate limiting factor is diffusion in the glass substrate, supplying cations to the surface for the formation of sulfate, we can expect that the cation with the larger diffusion coefficient is relatively more abundant in the sulfate reaction products. To our knowledge there is no data on the diffusivities of Ca and Mg in anorthite-diopside glasses, but in albite and jadeite glasses at 800 ℃ the tracer diffusivities of the cations follow the order of $D_{Na} > D_{Ca} > D_{Mg}$ (Roselieb and Jambon, 2002). The same relationship likely holds for the compositionally similar anorthite-diopside glasses and diffusivities in the glass follow $D_{Ca^{2+}}^{glass} > D_{Mg^{2+}}^{glass}$. The enrichment of Ca in the sulfate compared to Mg appears to depend on the temperature, relative to the glass transition, with a higher mobility for Ca than Mg (Renggli et al. in prep.). This suggests that the substrate properties control the supply of cations and the amount of reaction products formed. Further work is needed to unravel the relative mobilities of the sulfate forming cations as a function of temperature, composition and properties of the reactants.

We posit that network-modifying cations which are not charge-compensating are the most easily mobilized as a function of temperature or due to chemical potential gradients, as imposed by gradients in gas-solid and redox reactions. In the absence of systematic studies on the relative diffusivities of Ca and Mg in aluminosilicate glasses we draw on our experimental results. The high relative mobility of Ca indicates that it is less strongly bound in the glass aluminosilicate network than Mg, or that it is more readily mobilized by reaction with $SO_{2(g)}$. This distinction may

1 be explained by the difference in the ionic field strengths of the cations. The ionic field strength is
2 the ratio of the valence of the cation over the squared effective ionic radius for a given coordination
3 number. The calculated ionic field strengths for 6-fold oxygen coordinations are 3.86 for Mg and
4 2 for Ca (Shannon 1976), which suggests that Mg may form stronger bonds with non-bridging
5 oxygens, and is more likely to be retained in the glass to charge compensate Al^{3+} and Fe^{3+} cations.
6 This interpretation remains speculative and will require further experimental work on simple
7 glasses in the future.

8 **Role of the fugacities of $SO_{2(g)}$ and $O_{2(g)}$ on reactions with silicate glasses**

9   The reaction between $SO_{2(g)}$ and silicate glasses is thermodynamically expected to form
10 sulfates and sulfides due to the disproportionation of S^{4+} in the gas molecule to S^{6+} in the sulfate
11 and S^{2-} in a sulfide or gas phase (Equation (4)). However, the description of the experimental
12 reaction products from a range of different studies has shown that sulfides are rarely observed (only
13 with XPS), both in Fe-free and Fe-bearing systems. Fe occurs in hematite in experiments with
14 tholeiitic basalts (Fig. 6), thus a high oxygen fugacity seems to be a plausible mechanism,
15 prohibiting the formation of sulfides. If the reacting $SO_{2(g)}$ is in equilibrium, the speciation
16 calculation shown in Figure 1 can be used to establish the oxygen fugacity (fO_2) of the gas phase
17 ($\log fO_2 = -12.1$ at 700 °C), assuming that the gases mix in an ideal manner. This calculated value
18 is uncertain due to high gas flow rates (up to 50 standard cm^3 per minute) which likely ensures that
19 $SO_{2(g)}$ remains the dominant species and $\log fO_2$ may be lower. Second, the zone in the furnace at
20 which the experimental temperature of 700 °C is reached is small, so that equilibrium in the gas is
21 unlikely.

22   Understanding the fO_2 in Fe-bearing experiments is of importance because this variable
23 controls the stability of different Fe-oxide phases. The phase relationship in the system Fe-S-O is
24 commonly shown as a function of fO_2 and fS_2 (Hall 1986). Here instead we calculate the phase
25 relations using thermodynamic data (Chase 1998) to recast the relationship as a function of fSO_2
26 and $fO_{2(g)}$ (Fig. 8). It should be noted that the thermodynamic calculations assume activities of unity
27 in both the reactant and the product. This is not the case and results in uncertainties in applying the
28 experimental results to the calculated phase boundaries.

29   The Ni-NiO fO_2-buffer (NNO) is shown in Figure 8, at $\log fO_2 = -16.3$ (O'Neill and
30 Pownceby 1993). This is 4.7 orders of magnitude below the fO_2 of the calculated magnetite-
31 hematite buffer above which the oxides are placed in the coatings of the reacted tholeiitic basalt
32 glasses pre-equilibrated near NNO (Fig. 8). An even greater overall oxidation is required in the
33 reaction of $SO_{2(g)}$ with alkali basalt glasses pre-equilibrated at the iron-wüstite buffer, where both
34 magnetite and hematite were observed in the coatings (see Palm et al. 2018). Therefore, $SO_{2(g)}$
35 reactions with Fe-bearing silicate glasses are characterized by chemical potential gradients imposed
36 by the sulfate-forming reaction (Equation (4)) and by redox reactions (Fig. 8). This combination in
37 gradients creates a system which is highly out of equilibrium, forcing the reaction to be more
38 effective.

39   Burnett et al. (1997) were the only authors who reported the observation of Fe-sulfate, on
40 an obsidian sample reacted with $SO_{2(g)}$ at 850 °C, based on XPS spectra and optical microscopy.
41 In a reaction with pure $SO_{2(g)}$ Fe-sulfates are not predicted thermodynamically (Fig. 8). Overall,
42 the reaction with obsidian produced very small amounts of reaction product on the surface, likely
43 due to the low concentrations of Na_2O (3.80 wt.%), CaO (0.52 wt.%) and FeO (1.02 wt.%), and
44 the high concentrations of Al_2O_3 (12.32 wt.%) and SiO_2 (76.45 wt.%) (Burnett et al. 1997). As
45 traces of the same Fe-bearing phase were observed in an Fe-free experiment with an Ab-An-Di
46 glass, where the observation was interpreted as a contamination (Burnett et al. 1997), the same
47 contamination may also explain the observation on the obsidian sample.

48   Iron is the most abundant multyvalent cation in natural aluminosilicates. In glasses and
49 melts the redox state of iron affects its coordination state in the amorphous network and physical

1 properties including viscosity and liquidus temperatures (Farges et al. 2004; Wilke 2005). As
2 indicated above, $SO_{2(g)}$ reactions with Fe-bearing aluminosilicate glasses result in the formation of
3 Fe-oxides in the coatings and also affect the redox state of Fe in the glass substrates. With ongoing
4 reaction physical properties of the glasses affected by the redox state of iron are expected to change
5 accordingly. Therefore, it is important to investigate the mechanism of oxidation here.

6 The oxidation of Fe^{2+} in a silicate melt or glass may occur via several different kinetic
7 pathways. The pathway which reduces the chemical potential gradient of oxygen the fastest is the
8 dominant mechanism for Fe^{2+} oxidation. In hydrogen-bearing systems the diffusion rate of free H_2
9 is very high. The hydrogen is bound in the form OH-groups following the oxidation reaction of
10 ferrous to ferric iron (Gaillard et al. 2003). When studying reactions between gases and Fe-bearing
11 glasses it is therefore important to determine if hydrogen is present in the system, as it can
12 significantly affect redox reactions.

13 In a hydrogen-free system, three redox pathways are possible. First, molecular O_2 may
14 diffuse through the glass to increase the cation/oxygen ratio, or ionic O^{2-} and charge-compensating
15 electron holes can co-diffuse to decrease the chemical potential gradient (Magnien et al. 2008;
16 Wendlandt 1991). In both cases the cation/oxygen ratio changes in response to the redox gradient.
17 Second, divalent and monovalent cations move to the surface, balanced by the counter-diffusion
18 of electron holes (h˙) (Fig. 9b) (Magnien et al. 2008). It has been shown that molecular and ionic
19 oxygen diffusion is very slow in super-cooled melts and aluminosilicate glasses (Cook et al. 1990;
20 Cooper et al. 1996b, a; Magnien et al. 2008; Cochain et al. 2013). For example, there is negligible
21 uptake of atmospheric oxygen by oxidizing and reheating Kilauea basalt glasses at temperatures
22 below 1200 °C (Burkhard 2001). The third pathway dominates when the diffusivities (*D*) of
23 monovalent/divalent cations and electron holes are considerably faster than the diffusivities of
24 molecular and ionic oxygen, and if the system is hydrogen-free (subscripts denote diffusing
25 species):

26 $$D_{O_2}, D_{O^{2-}} \ll D_{M^+}, D_{M^{2+}} \ll D_{h^{\cdot}} \qquad (5)$$

27 In the case of oxidation of crystalline oxides, for which the same principle of cation
28 diffusion is valid, the diffusion of monovalent and divalent cations to the surface is charge-balanced
29 by the inward diffusion of cation vacancies, particularly along dislocations (Schmalzried 1983;
30 Ostyn et al. 1984; Schmalzried and Backhaus-Ricoult 1993). In crystalline materials electron holes
31 are the equivalent of Fe^{3+} cations occupying the sites of Fe^{2+} cations (Cooper et al. 1996a).

32 In aluminosilicate glasses with multivalent transition metals electron holes are mobile. For
33 example, Fe^{2+} easily releases an electron, or in other words takes up an electron hole. The material
34 behaves like a semiconductor for electron holes, as they can jump between transition metals almost
35 instantaneously (Cooper et al. 1996a; Cook and Cooper 2000). Due to this high mobility, electron
36 holes do not create an electrochemical potential gradient and their flux is not rate limiting. The
37 chemical potential gradient of oxygen from the surface to the interior results in the flux of
38 monovalent and divalent cations to the surface, expressed as:

39 $$j_{M^{2+}} = \frac{c_{M^{2+}} D_{M^{2+}}}{2RT} \cdot \frac{d\mu_{O_2}}{d\xi} \qquad (6)$$

40 where $j_{M^{2+}}$ is the flux of divalent cations to the surface, $c_{M^{2+}}$ is its concentration, $D_{M^{2+}}$ is the self-
41 diffusion coefficient, R is the gas constant, T is temperature in K and $\frac{d\mu_{O_2}}{d\xi}$ is the chemical potential
42 gradient of oxygen with ξ being the distance variable (Cooper et al. 1996a; Cook and Cooper 2000).
43 This relationship is fundamental for the oxidation mechanism, and shows the dependence of cation
44 diffusion on the chemical potential gradient of oxygen (Cooper et al. 1996a; Cook and Cooper
45 2000). As the major element abundance in the oxidizing surface layer is changed by the loss of
46 cations to the surface, the physical properties of the silicate change also. Consequently, the
47 diffusion coefficients are not constant with time (Schmalzried 1983).

1   A significant property of the reaction morphology of the oxidation of silicate glasses and
2 super-cooled melts is the nucleation of oxides between the surface and the oxidation front if
3 tetrahedrally coordinated Fe^{3+} is not sufficiently charge compensated (Fig. 9b; Cook et al. 1990;
4 Cooper et al. 1996b; Cook and Cooper 2000). If, for example, sufficient Na is available as a charge
5 compensator, nucleation of oxides in the glass is avoided. This is observed as an enrichment of Na
6 in the oxidized glass layer. In this case, the oxidation front coincides with a Na-front (Cook et al.
7 1990; Cook and Cooper 2000; Burkhard 2001). In the absence of sufficient charge compensating
8 alkalis the glass structure is no longer stable and oxides nucleate homogeneously (Cooper et al.
9 1996b, a; Cook and Cooper 2000). The nanoSIMS maps (Fig. 7) of a cross section through a
10 tholeiitic basaltic glass pre-equilibrated at the NNO oxide buffer and reacted for 24 hours at 700
11 °C show such an enrichment of Na near the surface in the glass substrate. The Na enrichment was
12 not sufficient to charge-balance the oxidizing and reacting glass, which resulted in the nucleation
13 of Fe-rich spherulites, surrounded by Mg-rich phases (Fig. 7).

14   The reaction mechanism of $SO_{2(g)}$ with Fe-bearing silicate glasses and supercooled melts
15 is comparable with that of oxidation. In both cases divalent cations diffuse to the surface due to a
16 chemical potential gradient (Fig. 9). In the case of the $SO_{2(g)}$ reaction (Figure 9a) gradients in fSO_2,
17 fS_2 and other gas species (see Fig. 1) occur in addition to a gradient in fO_2. In the absence of S-
18 bearing species diffusing divalent cations (Ca and Mg) form oxides near the surface (Cooper et al.
19 1996a; Cook and Cooper 2000). In the presence of $SO_{2(g)}$ the cations react to form sulfates and
20 oxides. Due to the high fSO_2 of the experimental gas (Fig. 1 and 8) it is likely that the cation
21 diffusion is predominantly due to the driving force of the reaction in equation (3) and only
22 secondarily due to the effect of oxidation as described by Cooper et al. (1996a). The relative
23 importance of these mechanisms remains to be determined experimentally.

24 **Reaction rates**

25   The depletion of cations in the glass substrate, due to the formation of sulfates and oxides
26 on the surface, can result in the destabilization of the glass, resulting in the nucleation and
27 crystallization of oxide and silicate phases (Fig. 4 and 9). Crystal growth can impose additional
28 chemical potential gradients and affect the mobility of cations in the glass and their availability to
29 form surface coatings. Crystallization near the surface can also act as a barrier for further diffusion
30 of cations to the surface, and thus become reaction limiting.

31   The rate at which the reaction between $SO_{2(g)}$ or $O_{2(g)}$ with a glass occurs can be described
32 by three different rate laws, depending on which mechanism is rate-limiting. First, if the surface
33 reaction is rate limiting, then the law is linear and the rate is independent of time. This initial
34 chemisorption reaction (Henley et al. 2015) is not likely the rate controlling mechanism because
35 experimental work has shown that significant amounts of sulfate form almost instantaneously
36 within few minutes (Ayris et al. 2013). Second, if the reaction occurs at low temperature resulting
37 in a very thin oxide layer, it follows a logarithmic law, which is not the case in high-temperature
38 gas-solid reactions either. Third, if the reaction is diffusion controlled (Fig. 4 and 9) and the
39 transport mechanisms are rate limiting, the rate follows a parabolic law and is inversely
40 proportional to the square root of time (Birks et al. 2006):

41
$$\frac{d\xi}{dt} = \frac{k'}{\xi} \qquad (7)$$

42   Integrated:

43
$$\xi = \sqrt{2k't} \qquad (8)$$

44   where k' is the parabolic rate constant. The parabolic rate constant is an intrinsic property
45 dependent on the cation flux, composition, concentration gradient, thermodynamic driving force
46 and temperature and is derived experimentally (Pieraggi 1987; Cooper et al. 1996a; Monceau and
47 Pieraggi 1998; Birks et al. 2006).

The rates of sulfate formation have been determined by leaching the coatings in solution and measuring the concentration of the leached material as a function of the amounts of reacted solids. Ayris et al. (2013) measured the molar amount of sulfur as a function of the weight of reacted volcanic ash. After initial $SO_{2(g)}$ adsorption, the formation of $CaSO_4$ is limited by the diffusion of Ca from within the ash particles to the surface. Accordingly, they calculate a diffusion coefficient for Ca^{2+} ($D_{Ca^{2+}}^{glass}$) assuming constant diffusion rates and solving Fick's first law of diffusion for ideal spherical ash particles (Ayris et al. 2013). Diffusion rates are greatest in the tephrite glass ($D_{Ca^{2+}}^{tephrite\ gl.} = 6.5 \times 10^{-14}$), followed by phonolite glass ($D_{Ca^{2+}}^{phonolite\ gl.} = 1.8 \times 10^{-12}$), dacite glass ($D_{Ca^{2+}}^{dacite\ gl.} = 3.7 \times 10^{-13}$) and rhyolite glass ($D_{Ca^{2+}}^{rhyolite\ gl.} = 8.7 \times 10^{-13}$). These diffusion coefficients apply to the first minutes of the reaction after $SO_{2(g)}$ adsorbs onto Ca-O surface sites.

As the reaction proceeds, between $SO_{2(g)}$ and silicate glasses, significant amounts of sulfate can be formed. Consequently, the glasses become increasingly depleted in Ca, Mg or Na, depending on the system. As the network-forming cations (Si, Al) are not extracted by the reaction, the glass becomes increasingly Si- and Al-rich. This change in the chemical composition within the near-surface glass affects the rates at which the divalent and monovalent cations can diffuse and be extracted. For example, the rate of sulfate formation in reactions between $SO_{2(g)}$ and silicate glasses in the anorthite-diopside system is an order of magnitude higher within the first hour of reaction compared to the following 23 hours (Renggli et al. in prep.). As pointed out in the context of the oxidation of metal alloys (Schmalzried 1983), diffusion coefficients are not constant in these systems and evolve with time. Furthermore, $SO_{2(g)}$-silicate glass reactions frequently result in the nucleation of crystallites in the sub-surface glass. This has been observed in Fe-free and Fe-bearing glass of a various compositions as indicated in Figures 4, 7 and 9 (Ayris et al. 2013, Renggli et al. in prep.). It is for these reasons, that none of the rate laws, including parabolic rate laws, sufficiently describe the reaction rates of $SO_{2(g)}$ with silicate glasses. Future work needs to develop kinetic models that encapsulate the complexity of the reaction mechanisms.

Summary and outlook

In summary, reactions between $SO_{2(g)}$ and silicate glasses with diverse compositions have been observed to form significant amounts of sulfate over short time frames of few minutes to an hour at 600-800 °C (Ayris et al. 2013; Delmelle et al. 2018, this volume). In Ca-bearing systems, the reaction products primarily consist of $CaSO_4$ coatings on the glass surfaces and associated Ca-depleted glass substrates. In the presence of other di- and monovalent cations, in particular Na and Mg, Ca remains the main sulfate forming cation. Other sulfates, including $MgSO_4$, Na_2SO_4 and $Na_2Ca(SO_4)_2$ have been observed in some experiments, but they usually occur in lesser abundance than $CaSO_4$. Experimental studies with natural volcanic ash samples, synthetic Fe-free glasses and natural Fe-bearing glasses collectively suggest that the reaction rates and compositions of the reaction products are a function of the physical properties of the reacting glasses, and in particular the mobility of different cations in the glasses. In Al^{3+}- and Fe^{3+}-bearing systems some monovalent and divalent cations are preferentially retained in the glass to charge-balance the tetrahedrally coordinated Al^{3+} and Fe^{3+}. Calcium appears to be less strongly bound to the amorphous network than Mg and Na, and is more easily mobilized to form $CaSO_4$ coatings. The reactions are further complicated where Fe^{3+}_{tot} increases (Fe^{2+} is oxidized to Fe^{3+}) with time due to oxidation, gradually requiring more charge compensation.

The complexities underline the importance of future experimental investigations. In particular, reaction rates at different stages of the reaction remain under-determined. Another open question relates to what physicochemical properties and mechanisms control the mobility or retention of alkali and alkaline earth metals in the aluminosilicate glasses. Recently, Le Losq et al. (2017) have shown that percolation channels control the mobility of alkali metals in aluminosilicate glasses and melts. Similar structural properties may also control the mobility of alkaline earth metals in aluminosilicate glasses, and their transport to the surface to form sulfates as described in

this chapter. A better understanding of these structural properties is of fundamental importance for the interpretation of reactions between aluminosilicate glasses and reactive gas species such as $SO_{2(g)}$.

Experimental observations summarized in this chapter were all made at room temperature. However, a number of these observations may be affected by the cooling paths of the samples at the end of the experiments. For example, the nucleation of crystalline phases near the reacting surface may occur during quench. Furthermore, some salts formed in these experiments can go through phase transitions as they are cooled to lower temperatures (e.g. Na_2SO_4). Others such as $MgSO_4$ are prone to hydration or may recrystallize at room temperatures. These mechanisms may result in textural, mineralogical and chemical changes between experiment and analysis. Experiments investigating gas-solid reactions *in situ* are therefore essential to better constrain these secondary processes.

In systems which contain multivalent elements, in particular Fe, the oxygen fugacity is an important variable. It varies in the glasses during the reactions, but also in the gas phase and in the resulting coatings. Future interpretations would benefit from fO_2 monitoring during experiments and the understanding of the reactions will improve with the determination of Fe^{3+}/Fe^{2+} and S^{6+}/S^{2-} across the reaction interface after the experiments, for example with XANES, which additionally provides information about the coordination of Fe in the glasses (Wilke et al. 2007 and 2011).

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FIGURE CAPTIONS

Figure 1. Equilibrium speciation of $SO_{2(g)}$ at 1 bar and temperatures from 500 to 1300 °C. The speciation was calculated using a Gibbs free energy minimization approach based on the JANAF database (Chase 1998) using the program HSC8 from Outotec. $SO_{2(g)}$ dissociates to $SO_{3(g)}$, $SO_{(g)}$, $O_{2(g)}$ and sulfur allotropes, the most prominent of which are $S_{2(g)}$ and $S_{3(g)}$. The mole fraction of $O_{2(g)}$ is equivalent to its oxygen fugacity (fO_2) under the condition of ideal gas behavior.

Figure 2. Scanning electron microscopy images of surface coatings (view from top) formed in reactions between $SO_{2(g)}$ and glasses. a) Well crystallized platy $CaSO_4$ crystals formed on a tephrite glass reacted for 1 hour at 800 °C with gas mixture of 1% $SO_{2(g)}$, air and He gas (Figure provided by Paul Ayris, Ayris et al. 2013). b) Discontinuously distributed Na_2SO_4 grains on a soda-lime glass reacted with $SO_{2(g)}$ for 21 days at 600 °C. The large crystals cover a scratch in the unreacted glass surface, which resulted in a higher surface area and an associated higher degree of reaction (Used by permission of the American Geophysical Union, from Burnett et al. 1997, *Journal of Geophysical Research*, Vol. 102, Fig. 5, p. 19378).

Figure 3. Discontinuous sulfate coating on glass surfaces reacted with $SO_{2(g)}$. a) SEM image (view from top) of the discontinuous Na_2SO_4 coating on an albite glass surface reacted with $SO_{2(g)}$ at 600 °C for 1 hour. The sulfate grains show facets. Individual crystals are commonly connected to one

1 or more surrounding grains forming small clusters. b) A schematic cross-section showing how in
2 the case of discontinuous coatings parts of the silicate glass surface remain exposed to the gas phase
3 allowing the reaction to proceed. In this type of reaction the diffusion of cations in the glass to the
4 surface is the rate controlling mechanism (Renggli et al. in prep.).

5 **Figure 4.** Continuous sulfate coatings observed on the surfaces of some Fe-free glasses. a) SEM
6 image of the anhydrite coating on an anorthite glass surface reacted with $SO_{2(g)}$ at 800 °C for 1
7 hour. b) Backscattered electron image of the coating on an Fe-free basalt glass reacted with $SO_{2(g)}$
8 at 700 °C for 24 hours. The brighter euhedral grains are anhydrite, whereas the darker material is
9 $MgSO_4$ which was partially hydrated in air after the experiment. c) Schematic drawing of the
10 reaction forming continuous coatings. After initial coating the glass is no longer directly exposed
11 to the gas, such that an additional mechanism is required to transport the gas and/or the cations
12 through the coating for ongoing sulfate formation. When growth occurs within the coating the
13 grains accumulate stress which can result in the deformation of the coating (see Fig. 5). The
14 outward diffusion of cations results in a depletion in the glass which can cause destabilization, and
15 in some nucleation and crystallization near the surface.

16 **Figure 5.** Images a, b and c show SEM images of deformed continuous anhydrite coatings on Fe-
17 free glasses. The coatings shown in a and c were formed on the eutectic An_{36}-Di_{64} glass reacted at
18 800 °C for 24 hours. Image b shows the coating of anhydrite on an $Ab_{73}An_{27}$ glass reacted at 700 °C
19 for 24 hours. The drawings d, e and f schematically represent how the respective textures imaged
20 in a, b and c developed. All of the textures are the result of stress accumulation within the coating
21 due to internal sulfate growth as shown in Figure 4. In the first case, whiskers can be formed by
22 epitactic overgrowth at grain boundaries and triple junctions (a and d). In the second case, laterally
23 expanding crystals in the coating have bent upwards at grain boundaries resulting in the imaged
24 "chicken-wire" texture (b and e). A third texture type forms as thick polycrystalline sulfate layers
25 continue to grow they detach from the glass surface and wrinkle and buckle (c and f).

26 **Figure 6.** Back-scattered electron images of coatings formed on Fe-bearing basaltic glasses which
27 were pre-equilibrated at different fO_2. The textures and assemblages vary considerably as a
28 function of the pre-equilibration. The observed phases are labelled as: gl.: substrate glass; Ca:
29 $CaSO_4$; Mg: $MgSO_4$; Na: Na_2SO_4; hem: Fe_2O_3; FeTi-ox: Fe-Ti-oxide. All three textures are not
30 continuous and in some areas parts of the glass substrate can be observed (gl.). a) Tholeiitic basalt
31 (NNO-1.5, 700 °C, 24h) is coated with $CaSO_4$ (forming brighter crystals, Ca), hydrated $MgSO_4$ (in
32 darker greys, Mg), and sub-micron sized Fe-oxides (hem and FeTi-ox). b) Tholeiitic basalt (NNO,
33 700 °C, 24h), coated with large columnar $CaSO_4$ (Ca), hydrated $MgSO_4$ (darker grey in the lower
34 left corner of the image, Mg), Na_2SO_4 (Na) in between $CaSO_4$ and mixed into the $MgSO_4$, and
35 Fe_2O_3 (bright white, hem). Some Fe-oxides contain significant amounts of Ti (FeTi-ox). c)
36 Tholeiitic basalt (NNO+1, 700 °C, 24h) coated with large columnar $CaSO_4$ (Ca), fine-grained
37 Na_2SO_4 (Na) mixed with sub-microns sized Fe-oxides, and larger Fe-oxides (hem) including some
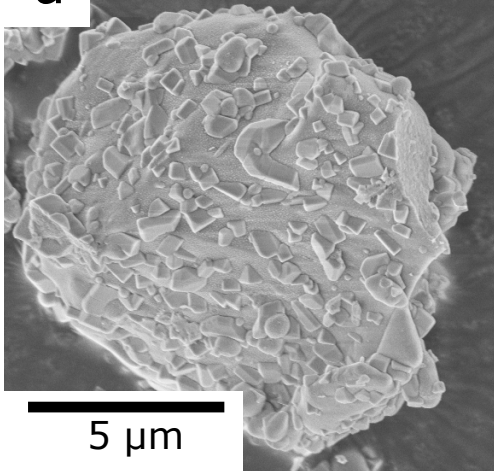38 Fe-Ti-oxides (FeTi-ox). No $MgSO_4$ occurs in this coating.

39 **Figure 7.** NanoSIMS maps of major elements in a cross-section of a tholeiitic basalt (NNO, 700 °C,
40 24h). The dashed line shows the location of the interface between the basaltic glass to the right and
41 the sulfate coating to the left. a) Si: The network-forming cation remains in the glass and is possibly
42 slightly enriched just beneath the surface, whereas it is not detected in the coating. b) Ti: Ti is not
43 detected in the coating material in this cross-section, even though Ti-bearing Fe-oxides were
44 observed in the coating. c) Mg: Mg is predominantly retained in the glass substrate. Mg-rich zones
45 occur as rings surrounding more depleted Fe-rich nuclei. d) Fe: Fe forms spherulites which are
46 relatively depleted in Ti, Mg and Ca, but slightly enriched in Na. The number of spherulites
47 increases toward the original surface of the glass (dashed line). This cross-section has not sampled
48 a Fe-oxide grain in the coating. e) Na: Na is a major component of the coatings and is also enriched
49 in the substrate towards the surface. f) Ca: Ca is depleted in the glass substrate with decreasing
50 concentrations towards the surface and enriched in the coating.

1 **Figure 8.** Phase relationships in the system Fe-S-O as a function of fSO_2 and fO_2 calculated from
2 the equilibrium constants of equations 5 to 13 at 700 °C and 1 bar. Fe-phases observed in coatings
3 of $SO_{2(g)}$ experiments are Fe_2O_3 in most cases and assemblages including both Fe_2O_3 and Fe_3O_4
4 (Palm et al. 2018) as indicated by the box at $\log fSO_2$ near 0. The figure also shows the $\log fO_2$ of
5 the NNO redox buffer relative to which some of the reacted basalt glasses were pre-equilibrated.
6 The geometric relationship of the phase boundaries remains constant with temperature. At 700 °C
7 and 1 bar the fugacities of minor gas species in equilibrium with $SO_{2(g)}$ (see Fig. 1) are $\log fO_2$=-
8 12.1, $\log fS_2$=-7, $\log fS_3$=-11.4, $\log fSO_3$=-5.7, $\log fSO$=-6.1 and $\log fS_2O$=-6.5. The calculations were
9 made using the package HSC8 by Outotec based on the JANAF database (Chase 1998).

10 **Figure 9.** Schematic drawings of the reaction between gases and Fe-bearing silicate glasses at 700
11 °C and 1 bar. a) $SO_{2(g)}$ reaction results in the formation of sulfate and oxide coatings. The oxidation
12 of Fe in the glass occurs via the inward diffusion of electron holes and the outward diffusion of
13 alkali and alkaline earth cations, forming the sulfates. The glass subsurface is relatively enriched
14 in Si and Al (network-forming cations) due to the diffusive loss of other cations. The change in the
15 chemical composition of the glass results in the crystal nucleation near the glass surface. b) $O_{2(g)}$
16 reaction with Fe-bearing silicate glasses requires the outward diffusion of alkaline earths and
17 inward diffusion of electron holes. Na diffuses into the oxidizing surface layer to stabilize
18 tetrahedrally coordinated ferric iron. Insufficient charge balancing of ferric iron can result in the
19 destabilization of the glass and the nucleation of oxides and silicates (Cook et al. 1990; Cooper et
20 al. 1996b, a; Cook and Cooper 2000; Burkhard 2001).

a

5 µm

b

30 µm

a) Albite, 600 ºC, 1h

5 µm

b) growth of single crystals

$S_{2(g)}$ $SO_{2(g)}$

Na_2SO_4

cations
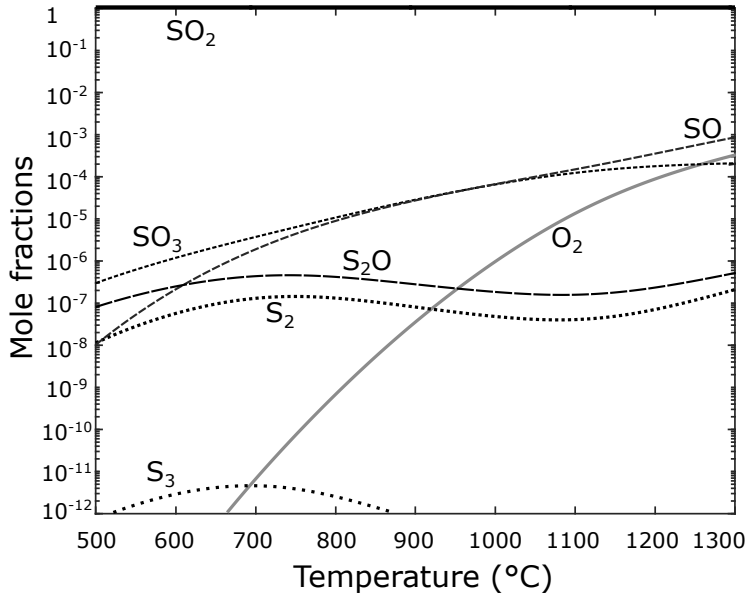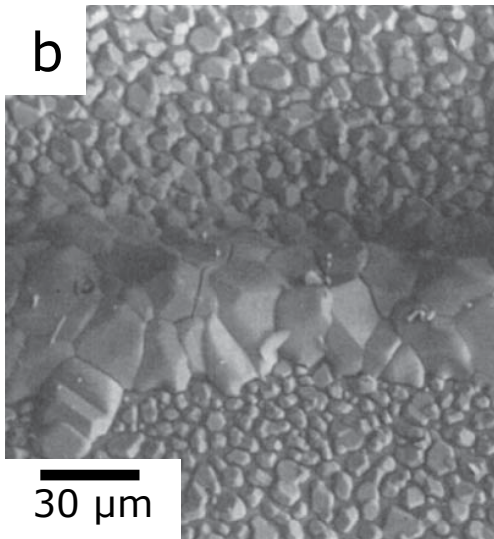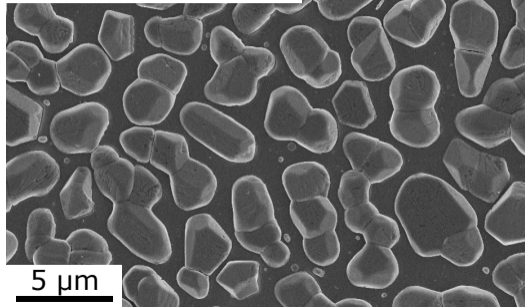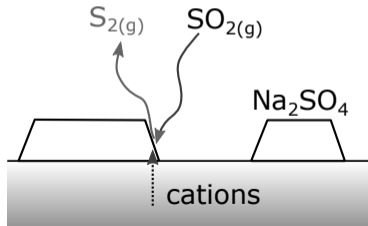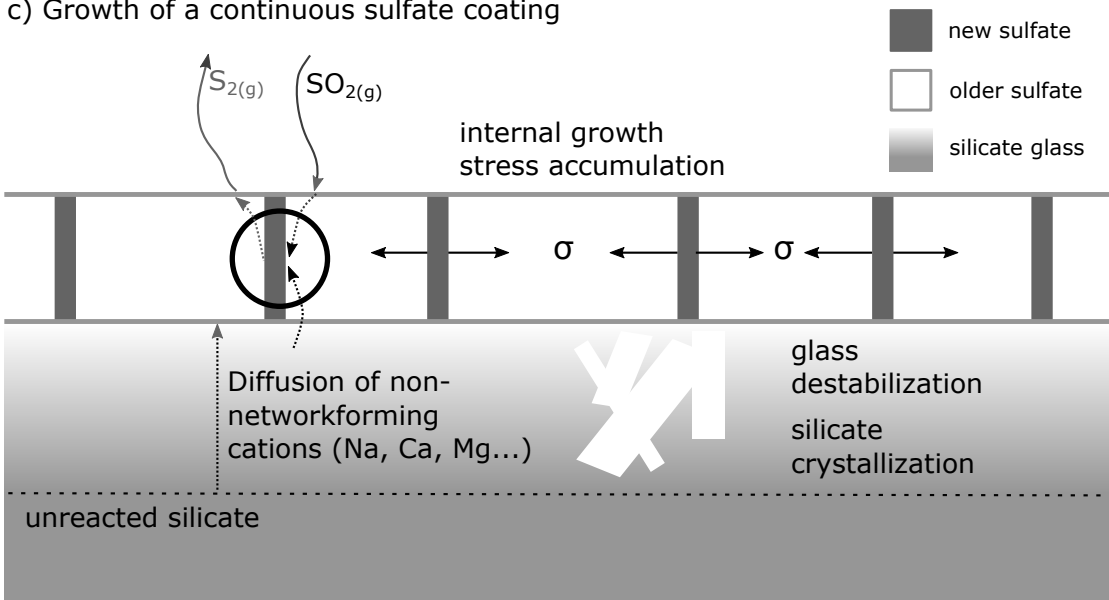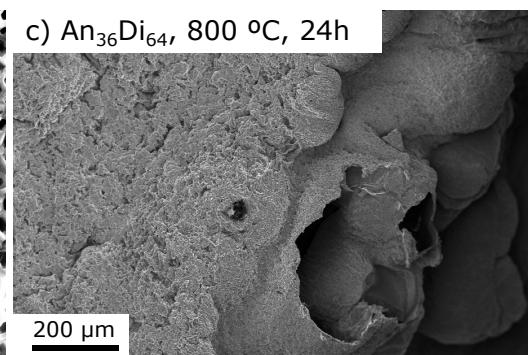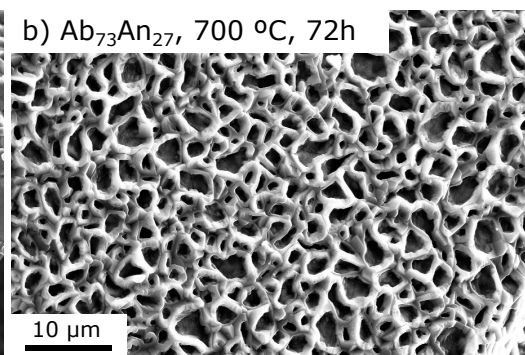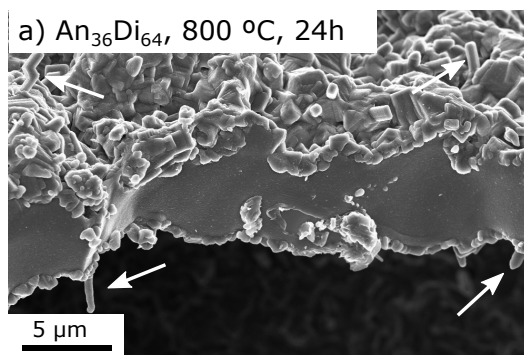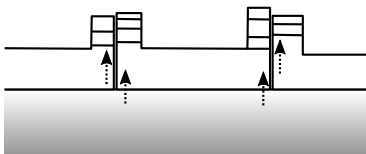
a) Anorthite, 800 ºC, 1h
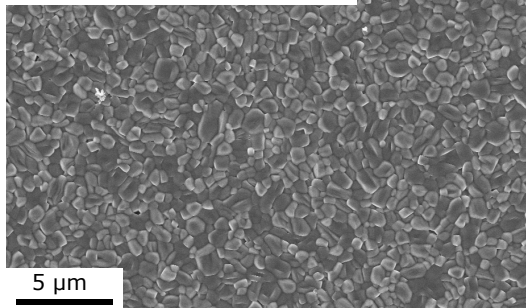
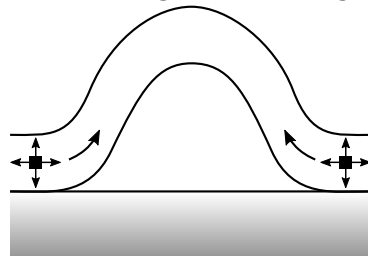b) Fe-free basalt, 700 ºC, 24h
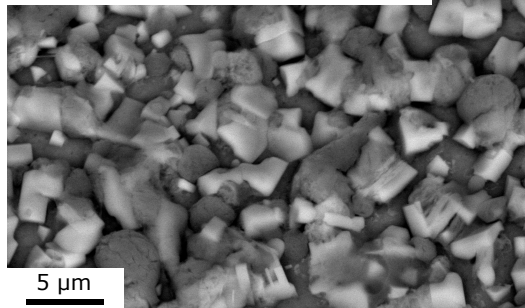
c) Growth of a continuous sulfate coating

new sulfate

older sulfate

silicate glass

$S_{2(g)}$

$SO_{2(g)}$

internal growth
stress accumulation

σ

σ

Diffusion of non-
networkforming
cations (Na, Ca, Mg...)

glass
destabilization

silicate
crystallization

unreacted silicate

a) An$_{36}$Di$_{64}$, 800 ºC, 24h b) Ab$_{73}$An$_{27}$, 700 ºC, 72h c) An$_{36}$Di$_{64}$, 800 ºC, 24h

5 µm 10 µm 200 µm

d) epitactic overgrowth at grain boundaries

e) lateral growth of single crystals
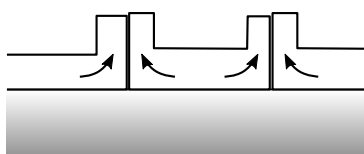
f) polycrystalline layer, wrinkling and buckling
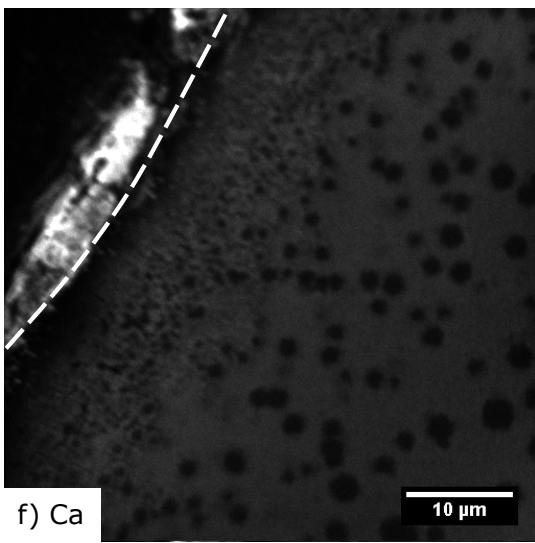
a) Tholeiitic basalt, NNO-1.5 700 ºC, 24h

Mg

gl.

Ca

hem

5 µm

b) Tholeiitic basalt, NNO, 700 ºC, 24h
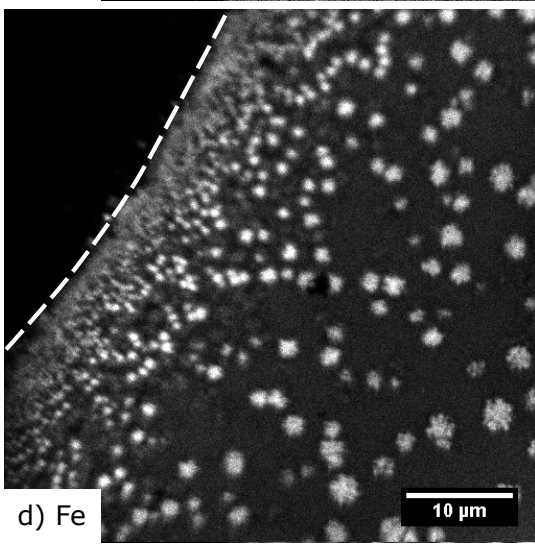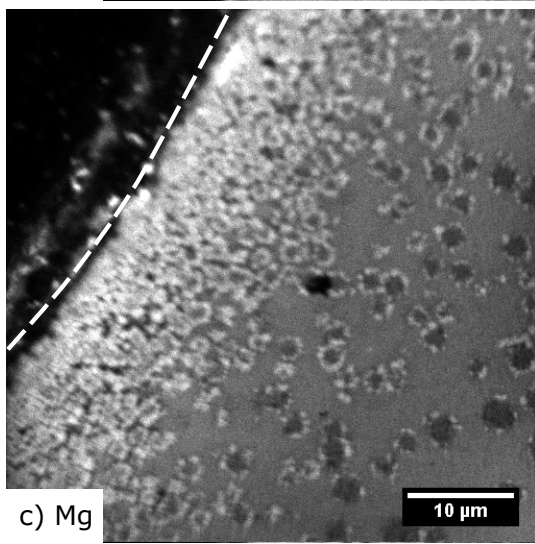
gl.

hem

FeTi-ox

Na

Mg

Ca

25 µm

c) Tholeiitic basalt, NNO+1, 700 ºC, 24h

gl.

Na

FeTi-ox

Ca

hem

25 µm

a) Si   10 μm

b) Ti   10 μm

c) Mg   10 μm

d) Fe   10 μm

e) Na   10 μm

f) Ca   10 μm

700 °C, 1bar

FeSO$_4$

Fe$_2$O$_3$

coatings

NNO

Fe$_3$O$_4$

Fe$_{1-x}$O

Fe

Fe$_{1-x}$S

FeS$_2$

log$f$O$_2$

log$f$SO$_2$

a) SO$_2$-reaction, Fe-bearing glass

SO$_{2(g)}$

± Na$_2$SO$_4$
± MgSO$_4$

Fe-oxides

CaSO$_4$

Si-rich layer

Mg-rich layer

Ca
Mg
Na

crystal
nucleation

Fe

*electron
holes*

oxidation front

unreacted silicate

b) O$_2$-reaction, Fe-bearing glass

O$_{2(g)}$

MgO

CaO

Ca- & Mg-
depleted
Na-enriched
oxidized

oxide
nucleation

*Ca
Mg*

*electron
holes*

oxidation front

Na

unreacted silicate