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Sulfur diffusion in dacitic melt at various oxidation states: Implications for volcanic degassing

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Abstract

The diffusivity of S in a hydrous dacitic melt (4.5–6.0 wt.% H2O) has been investigated in the temperature (T) and pressure (P) range of 950 °C to 1100 °C and 200 to 250 MPa, respectively. Three series of experiments were conducted at relatively low oxygen fugacity (fO2) conditions [0.8 log units below fayalite-magnetite-quartz equilibrium (FMQ −0.8); referred to as “low fO2”] and high fO2 conditions (FMQ +2.5; referred to as “high fO2”) to determine if the diffusivity of S is affected by its oxidation state and speciation. Sulfur concentration profiles were measured by electron microprobe and the diffusion coefficient (D) was calculated by fitting these profiles. Sulfur diffusion is approximately one order of magnitude faster when S is dominantly present as sulfide species (low fO2) in comparison to the sulfate dominated experiments (high fO2). The following Arrhenian equations were obtained for high and low fO2 conditions at 200 MPa:

\[
\begin{align*}
\text{high } fO_2 & : \quad D = 10^{-5.92\pm0.86} \exp\left(-\frac{137.3 \pm 21.5 \text{ kJ/mol}}{RT}\right) \\
\text{low } fO_2 & : \quad D = 10^{-5.18\pm1.39} \exp\left(-\frac{125.7 \pm 34.4 \text{ kJ/mol}}{RT}\right)
\end{align*}
\]

where D is the average diffusion coefficient in m² s⁻¹, R is the gas constant in 8.3144 J mol⁻¹ K⁻¹ and T is the temperature in K. Our results demonstrate for the first time in natural melts that S diffusion is strongly sensitive to fO2. Our S diffusivities under low fO2 conditions are only slightly slower of those found for H2O, suggesting that S can be rather efficiently purged from reduced dacitic melts during volcanic eruptions. However, for more oxidized systems (e.g. subduction zones), S diffusion will be much slower and will hinder equilibrium syn-eruptive degassing during rapid decompression. Therefore, we conclude that the “excess S” measured during many explosive volcanic eruptions in arcs is dominantly derived from S-rich bubble accumulation in the eruptible portion of the magma reservoir.

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Keywords: Sulfur diffusion; Oxygen fugacity dependency; Sulfur excess; Volcanic degassing

1. INTRODUCTION

Volatiles play an important role in many igneous and magmatic-hydrothermal processes including magma formation, differentiation and transport up to the surface during volcanic eruptions (Hedenquist and Lowenstern, 1994; Huppert and Woods, 2002; Baker et al., 2005; Zellmer et al., 2015). After H2O and CO2, S is the next most important volatile species in both silicic and mafic magmas (Symonds et al., 1994; Carn et al., 2003; Shinohara, 2008). This has been testified by quantitative measurements of gaseous SO2 emissions from active volcanoes (Stoiber et al., 2000).
Detection and quantification of S outgassing by remote sensing is one of the tools used in the forecasting of volcanic eruptions (Galle et al., 2003). Furthermore, volcanic S emission has a significant impact on the Earth’s climate and, therefore, habitability of the planet (Angell, 1997; Grattan et al., 2003; Carn et al., 2015). For example, the 1991 eruption of Mt. Pinatubo released more than 17 Mt of SO₂ into the atmosphere with severe consequences for the environment (Gerlach et al., 1996). Additionally, S plays an important role in the formation of a variety of base and noble metal ore deposits (Gustafson and Hunt, 1975; Landtwing et al., 2010; Richards, 2011; Simon and Ripley, 2011).

One of the unresolved key questions in understanding the global S cycle is the sulfur excess problem (Keppler, 1999; Scaillet et al., 2003; Wallace, 2005; Shimohara, 2008; Edmonds et al., 2010; Wallace and Edmonds, 2011), which is based on the observation that the syn-eruptive S flux from the silicate melt to the gas phase, as estimated based on the comparison of silicate melt inclusion and quenched groundmass glass compositions, is often up to 10–100 times smaller than the total SO₂ released during eruptions (Andres et al., 1991; Shimohara, 2008). This discrepancy is most likely a consequence of varying S solubility and diffusivity in magmas during storage and ascent towards the surface. Early studies on S solubility were carried out in simple synthetic oxide melts (Holbrook and Joseph, 1936; Fincham and Richardson, 1954), whereas more recent studies examined SO₂ solubility in natural silicate melt compositions (Wallace and Carmichael, 1992; Scaillet and Pichavant, 2003; Clément et al., 2004; Scaillet and Pichavant, 2005; Moune et al., 2009; Baker and Moretti, 2011; Zajacz et al., 2012; Zajacz, 2015). As stated by Behrens and Stelling (2011), diffusion of volatile elements plays a key role during bubble nucleation and growth in magmas; most volatile diffusion studies in silicate melts focused on H₂O (Shaw, 1974; Zhang and Behrens, 2000; Freda et al., 2003) and CO₂ (Watson et al., 1982; Sierralta et al., 2002) while comparatively little work has been performed on S in natural silicate melts (for review see Zhang et al. (2010) and Behrens and Stelling (2011) and references therein).

This study focuses on diffusion of S in silicate melts, which can be considered as trace element diffusion, because the investigated concentrations are less than 1 wt.% (Zhang, 2010). Previous studies have shown that S diffusivity is a function of P, T and composition (including hydrous/anhydrous conditions); however, previously available data reveal large scatter compared to those on the diffusivity of other volatile species (Watson, 1994; Baker and Rutherford, 1996; Winther et al., 1998; Freda et al., 2005). One of the probable causes is the effect of the oxidation state of S on its diffusivity, which is not well established (Zhang et al., 2007). In magmatic silicate melts, S occurs in a variety of oxidation states ranging from S²⁻ (II) under reducing to SO₄²⁻ (+VI) under oxidizing conditions (Jugo et al., 2005; Wilke et al., 2008; Métrich et al., 2009; Wallace and Edmonds, 2011; Klimm et al., 2012a). In natural melts with a fO₂ of >FMQ +2, S is dominantly present as sulfate species. At values below FMQ, S is dominantly present in 2– oxidation state, mostly as FeS species (Fleet et al., 2005; Klimm and Botcharnikov, 2010; Klimm et al., 2012a). Between these two end-members, both species are present simultaneously (Nagashima and Katsura, 1973; Carroll and Rutherford, 1988; Jugo et al., 2005). Jugo et al. (2010) presented XANES measurements inferring that the transition between S⁶⁺ and S²⁻ is confined to a narrow interval of about 1 log unit corresponding to FMQ +0.5 to FMQ +1.5. For synthetic, alkali-rich, but Fe-poor samples, a shift of the transition to more reducing conditions (by around 1.5 log units) was observed (Klimm et al., 2012a). The contrasting S speciations result in a rather large range of possible (effective) ionic radii ranging from 1.84 Å for the reduced sulfide (Shannon, 1976) to 2.50 Å for the oxidized sulfate (SO₄²⁻) ions (Baker and Rutherford, 1996).

Although it can be expected that S diffusion is sensitive to S speciation and, therefore fO₂, experimental data obtained on natural melt compositions addressing this relationship are scarce. Data from studies using synthetic technical glasses point to a weak fO₂ dependency (Szurman et al., 2007; Stelling, 2009; Behrens and Stelling, 2011). The first study on melts approximating natural compositions was conducted by Watson (1994), who determined S diffusion in a variety of different compositions while keeping the fO₂ constant close to the iron - wustite solid buffer equilibrium (IW). Similar studies were conducted by Winther et al. (1998) and Freda et al. (2005) investigating S diffusion at constant fO₂ in albite and basalt melts. These studies did not allow evaluation of the effect of fO₂ on diffusion. In contrast, Baker and Rutherford (1996) studied the effect of fO₂ on S diffusivity by conducting a series of experiments in hydrous and anhydrous rhyolitic melts (at P between 0.1 and 200 MPa and T between 800 °C and 1100 °C). The fO₂ was varied between FMQ and very high values corresponding to air. Higher T and higher water contents led to increasing S diffusivity, but variable fO₂ did not result in any significant effect despite covering a large fO₂ range. Only under the most oxidizing conditions, a significant decrease of diffusivity (by one to two orders of magnitude) was observed. The authors were, however, not able to constrain different Arrhenius equations for low and high fO₂ conditions. The most recent S diffusion study was performed by Behrens and Stelling (2011), who determined a strong viscosity dependency of S diffusion in synthetic melts, but only small differences between sulfide and sulfate diffusivities (based on the interdiffusion experiments of Stelling (2009)).

In this paper, S diffusion in dacitic melts under low and high fO₂ conditions was experimentally investigated in order (1) to fill the gap between determination of S diffusivities in basalt/andesite and highly evolved rhyolitic melt compositions, and (2) to constrain the potential effects of fO₂ on the S diffusion coefficient. The diffusivity of S was determined under hydrous conditions in the T range between 950 °C and 1100 °C under low (FMQ –0.8) and high fO₂ conditions (FMQ +2.5) corresponding to the sulfide and sulfate species dominated fields, respectively.
2. METHODS

2.1. Experimental apparatus

The synthesis of the starting materials and the diffusion experiments were performed in an externally heated hydrothermal, rapid-quench, cold-seal pressure vessel (CSPV) composed of molybdenum–hafnium carbide alloy (MHC) pressure vessels equipped with a water-cooled nut and a cold steel extension. The \( T \) gradient over the maximum capsule length of 29 mm was less than 10 \(^\circ\)C. Runs were performed with the vessel inclined by 5–10° with the hot end facing upwards to reduce convection of the Ar pressure medium and minimize the thermal gradients. Runs were terminated by rotating the vessel to a vertical position causing the capsule to drop to the cold steel extension (quenching rates on the order of 100 \(^\circ\)C s\(^{-1}\)). Oxygen fugacity was controlled using the double capsule technique employing different solid buffer assemblages (Fig. 1). Pressure was monitored by strain gauges and kept constant at 200 ± 2 or 250 ± 2 MPa.

One starting glass (#17) was produced in an end-loaded Boyd and England-type piston-cylinder apparatus at 500 MPa and 1000 \(^\circ\)C using a NaCl-Pyrex-MgO/BN assembly. The 5 mm diameter Au capsule (Table 1) was surrounded by MgO plugs and a BN sleeve. All parts were placed in a 36 mm long graphite furnace contained in a Pyrex sleeve and surrounded by a NaCl sleeve. The top of the capsule was separated from the B-type thermocouple (Pt\(_{94}\)Rh\(_{6}\) – Pt\(_{70}\)Rh\(_{30}\)) by a 0.6 mm ruby disk. The \( f_O_2 \) during the synthesis of this particular starting material is unknown, but the use of BN spacers around the capsules most probably led to a relatively reducing intrinsic \( f_O_2 \) of around FMQ (e.g. Kägi et al. (2005)).

![Fig. 1. Schematic drawing of the experimental setup for (a) high \( f_O_2 \) and (b) low \( f_O_2 \) experiments. The double capsule method was employed for both experimental series with the difference that for the high \( f_O_2 \) conditions the Re-ReO\(_2\) buffer, whereas for the low \( f_O_2 \) runs, the Co-CoO buffer was employed. A larger amount of H\(_2\)O had to be added to the buffer assemblage in the low \( f_O_2 \) setup resulting in longer capsules.](image-url)
### Table 1

| Run | $T$ (°C) | P (MPa) | $t$ (min) | $H_2O$ (wt.%) | Activity $H_2O$ | Avg. D | std.  
|-----|-----------|----------|-----------|---------------|---------------|--------|--------
| #17 | 1000      | 500      | 5 × 14    | 0.71          | 1.92          | 0.26   |
| #20 | 1000      | 250      | 4 × 23    | 0.12          | 1.91          | 0.24   |
| #21 | 1000      | 1200     | 4 × 29    | 0.37          | 1.90          | 0.23   |
| #22 | 1000      | 80       | 4 × 13    | 0.35          | 1.89          | 0.22   |
| #23 | 1000      | 100      | 4 × 15    | 0.38          | 1.88          | 0.21   |
| #24 | 1000      | 1200     | 4 × 12    | 0.58          | 1.87          | 0.20   |
| #25 | 1000      | 200      | 4 × 10    | 0.89          | 1.86          | 0.19   |
| #26 | 1000      | 300      | 4 × 8     | 0.98          | 1.85          | 0.18   |
| #27 | 1000      | 400      | 4 × 8     | 1.35          | 1.84          | 0.17   |
| #28 | 1000      | 500      | 4 × 8     | 1.93          | 1.83          | 0.16   |
| #29 | 1000      | 600      | 4 × 8     | 2.69          | 1.82          | 0.15   |
| #30 | 1000      | 700      | 4 × 8     | 7.13          | 1.81          | 0.14   |
| #31 | 1000      | 800      | 4 × 8     | 13.92         | 1.80          | 0.13   |
| #32 | 1000      | 900      | 4 × 8     | 26.88         | 1.79          | 0.12   |

2.2. Experimental setup

Throughout this study, the term “S-free” indicates that no additional S was added, whereas “S-bearing” infers that additional S was added. Each starting material pair (one S-free and one S-bearing) was produced at identical $fO_2$, $P$ and $T$ conditions and with the same $H_2O$ concentrations. Oxygen fugacity was constrained close to FMQ +2.5 by employing the Re-ReO$_2$ oxygen solid buffer to ensure that sulfate was the preferred stable S component in the high $fO_2$ runs. The low $fO_2$ runs were performed at a $fO_2$ corresponding to FMQ −0.8 by using the Co-CoO oxygen solid buffer (Table 1). The outer capsules contained about 100 mg of Re-ReO$_2$ or Co-CoO mixtures with a metal/metal-oxide ratio of 80/20 and some excess H$_2$O to maximize buffer life time under the rather oxidizing intrinsic conditions in the pressure vessel.

All capsules were weighed before and after welding, and to ensure their tightness, they were held at 110 °C for one hour to check for weight loss. Additionally, all capsules were immersed in acetone to detect potential leakages resulting in a weight gain. All experiments were terminated by rapid quench and after quenching, the recovered capsules were examined for visible damages and weighed to verify that the outer capsule remained intact during the experiment. Outer capsules were pierced and inspected to ensure that H$_2$O was still present. The preservation of the buffer assemblage was confirmed by inspection under a petrographic microscope. Subsequently, the inner capsules were extracted and weighed to ensure no weight loss/gain occurred.

2.2.1. Starting material synthesis

A dacitic pumice sample from the 1991 Mt. Pinatubo eruption was employed as anhydrous starting material (Table 2). It was fused in air at 1500 °C for 240 min to ensure the loss of all H$_2$O and S. The quenched and crystal-free glass was re-crushed and ground to a fine powder for the synthesis of anhydrite-buffered capsules (Table 1). The outer capsules contained about 100 mg of Re-ReO$_2$ or Co-CoO mixtures with a metal/metal-oxide ratio of 80/20 and some excess H$_2$O to maximize buffer life time under the rather oxidizing intrinsic conditions in the pressure vessel.

### Table 2

**Composition of anhydrous dacite starting material of the Mt. Pinatubo eruption of 1991.**

<table>
<thead>
<tr>
<th>wt.%</th>
<th>Anhydrous SM Avg. (46; 78)</th>
<th>Std.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>65.01</td>
<td>0.37</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.54</td>
<td>0.08</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>16.48</td>
<td>0.29</td>
</tr>
<tr>
<td>FeO</td>
<td>3.88</td>
<td>0.17</td>
</tr>
<tr>
<td>MnO</td>
<td>0.10</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>2.23</td>
<td>0.07</td>
</tr>
<tr>
<td>CaO</td>
<td>4.97</td>
<td>0.10</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>4.49</td>
<td>0.21</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.52</td>
<td>0.03</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.17</td>
<td>0.03</td>
</tr>
<tr>
<td>S (ppm)</td>
<td>36</td>
<td>15</td>
</tr>
<tr>
<td>Total</td>
<td>99.37</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Numbers in brackets denote total number of major elements and S measurements, respectively; Std. is the one-sigma standard deviation and Avg. stands for average.
powder that was used to fabricate six hydrous starting materials: one S-free and one S-bearing (250 MPa experiments) and two S-free and two S-bearing ones (200 MPa experiments; Tables 1 and 3). Synthesis runs were performed at 1000 °C to 1025 °C for 12–24 h. For synthesis of S-free hydrous starting materials, the anhydrous glass powder was loaded together with 4.5 and 6.0 wt.% pure H₂O, respectively, into 3–4 mm inner diameter Au and AuPd alloy capsules (Table 1). To produce the S-bearing hydrous starting materials, an aqueous H₂SO₄ solution was added to the capsules.

### Table 3

Composition of hydrous starting materials and run product glasses from diffusion experiments.

<table>
<thead>
<tr>
<th>Wt.%</th>
<th>High fO₂</th>
<th>Experimental runs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Starting material</td>
<td></td>
</tr>
<tr>
<td></td>
<td>#17</td>
<td>#20</td>
</tr>
<tr>
<td>SiO₂</td>
<td>61.14</td>
<td>0.27</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.48</td>
<td>0.01</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.55</td>
<td>0.11</td>
</tr>
<tr>
<td>FeO</td>
<td>3.39</td>
<td>0.11</td>
</tr>
<tr>
<td>MnO</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>2.06</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>4.64</td>
<td>0.07</td>
</tr>
<tr>
<td>Na₂O</td>
<td>4.11</td>
<td>0.14</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.46</td>
<td>0.02</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.16</td>
<td>0.02</td>
</tr>
<tr>
<td>S (ppm)</td>
<td>46</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>#38</td>
<td>#39</td>
</tr>
<tr>
<td>SiO₂</td>
<td>62.25</td>
<td>0.39</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.50</td>
<td>0.02</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.66</td>
<td>0.11</td>
</tr>
<tr>
<td>FeO</td>
<td>3.77</td>
<td>0.06</td>
</tr>
<tr>
<td>MnO</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>2.11</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>4.71</td>
<td>0.09</td>
</tr>
<tr>
<td>Na₂O</td>
<td>4.18</td>
<td>0.43</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.44</td>
<td>0.07</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.17</td>
<td>0.03</td>
</tr>
<tr>
<td>S (ppm)</td>
<td>46</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>#51</td>
<td>#57.2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>62.38</td>
<td>0.24</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.50</td>
<td>0.02</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.83</td>
<td>0.05</td>
</tr>
<tr>
<td>FeO</td>
<td>3.65</td>
<td>0.14</td>
</tr>
<tr>
<td>MnO</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>2.12</td>
<td>0.04</td>
</tr>
<tr>
<td>CaO</td>
<td>4.78</td>
<td>0.07</td>
</tr>
<tr>
<td>Na₂O</td>
<td>4.36</td>
<td>0.09</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.51</td>
<td>0.03</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.16</td>
<td>0.02</td>
</tr>
<tr>
<td>S (ppm)</td>
<td>26</td>
<td>6</td>
</tr>
</tbody>
</table>

Major element glass concentrations determined by EMPA and H₂O concentrations selectively by micro-Raman spectroscopy. Numbers in brackets denote number of measurements of major elements and of S measurements, respectively; Std. is the one-sigma standard deviation and Avg. stands for average.
(4.5 and 6.0 wt.%) was dissolved into the anhydrous glass powders to yield target S concentrations of 550 and 720 ppm for high and 206 ppm for the low \(fO_2\) conditions in the silicate glass. These S concentrations could be added safely without inducing anhydrite (high \(fO_2\)) or pyrrhotite (low \(fO_2\)) saturation based on previous studies (Carroll and Rutherford, 1985; Scaillet and Macdonald, 2006; Jugo, 2009; Zajacz et al., 2013; Masotta et al., 2016). The filled capsules were placed in 4–5 mm outer diameter capsule containing the redox buffer assemblages (Table 1). The resulting starting materials (consequently also the later diffusion experiments) were \(H_2O\)-undersaturated at 280 and 250 MPa (Moore et al., 1998; Holtz et al., 2001; Papale et al., 2006). Thus, we corrected the \(fO_2\) values for the effect of reduced water activity (Table 1). The quenched glassy hydrous starting materials were removed carefully from the inner capsules to avoid any contamination with the buffer material. The composition and homogeneity of the synthetized starting glasses were confirmed by Electron Probe Micro Analysis (EPMA) and they were subsequently reground to a fine powder.

2.2.2. Diffusion experiments

The starting material synthesis (S-bearing and S-free) were conducted under the same \(fO_2\) conditions as the subsequent diffusion experiments in order to have the same S species present. This eliminated any potential issues with hydrogen diffusion through the capsule being a rate limiting factor that could be caused if any change in S oxidation state was required during the diffusion experiment. The experimental conditions were chosen to simulate conditions prevailing in upper crustal magma reservoirs. The low \(fO_2\) experiments were conducted at 950, 1000 and 1050 °C, whereas the high \(fO_2\) runs were performed at 1000, 1050 and 1100 °C. The upper and lower \(T\) limits were selected based on the following arguments: (1) 950 °C is the required minimum \(T\) to avoid significant crystallization. (2) In order to keep the run \(T\) of both experimental series at the same maximum \(T\) and still obtain diffusion profiles with ideal width, it would have been necessary to lower the run duration of the low \(fO_2\) experiment at 1100 °C to around 10 min, which was considered critical (finite time is needed for the capsule to heat up). (3) Keeping the run \(T\) lower in the low \(fO_2\) experiments also allowed us to use AuPd alloy with no more than 10 wt.% Pd content minimizing the chance of any S loss to the capsule in the experimental charge.

In total, nine experiments were performed at different \(fO_2\), \(P\), \(T\) and run durations (Tables 1 and 3). They were conducted by employing the diffusion couple technique (Watson and Dohmen, 2010), where two otherwise identical glasses with contrasting concentrations of the element of interest are placed against each other in a single capsule. In our case, one half of the capsule was filled with the S-free and the other half with the S-bearing starting glass powders (Fig. 1). A fairly sharp and well-defined interface between the two glass powders was obtained by hammering the first glass powder into the capsule with a tight-fitting pin-gauge. The second material was placed and compacted on top of the first one. The general setup for the diffusion experiments was identical to the synthesis runs with the differences that (1) capsule sizes/diameters were generally smaller (Table 1) and (2) the capsules were kept in the cold end of the pressure vessel during heating until stable target \(T\) and \(P\) conditions were attained in order to avoid diffusion during heating. By tilting of the vessel into vertical position the capsule was injected into the hot zone and then brought back to near horizontal position (5–10°) for the duration of the experiment. After quenching and recovery, the inner capsule was mounted in acrylic hot mounting resin to expose a central longitudinal cross-section and polished with 1 μm diamond paste.

2.3. Analytical methods

Besides EPMA and micro-Raman spectroscopy, we also employed Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) in order to determine potential contaminations by the buffer material and to ensure tightness of the inner capsules. LA-ICP-MS setup and results are described in greater detail in the Appendix along with a description of the scanning electron microscope (SEM) methodology.

2.3.1. EPMA

Sulfur and major element concentrations were determined by EPMA. Measurements were conducted with a JEOL JXA-8200 electron microprobe equipped with five wave length dispersive spectrometers. The following standards were employed for major element analysis: rutile for Ti, pyrolusite for Mn, hematite for Fe, periclase for Mg,apatite for P, K-feldspar for K, albite for Na and Al and wollastonite for Si and Ca. An acceleration voltage of 15 kV, a beam current of 20 nA and a defocused electron beam with a spot size of 20 μm was employed. To minimize alkali loss counting time was set to 10 s and 5 s for Na and K and to 20 s and 10 s on peak and backgrounds, respectively, for all the other elements.

The standardization of S for the high \(fO_2\) samples was performed on barite. The beam current was set to 70 nA with a spot size of 20 μm and an acceleration voltage of 15 kV. In order to minimize the limit of detection (LOD) of the measurements, the counting time was increased to 180 s on the peak and 90 s on the backgrounds and, additionally, S was measured on two spectrometers simultaneously and the counts were added up. For the low \(fO_2\) samples, S was standardized on barite, but after measuring the standard, the peak position was readjusted to that determined on pyrrhotite and the run product glasses were analyzed subsequently (Zajacz et al., 2012). The LOD was calculated according to the equation given by Lifshin et al. (1998):

\[
LOD = \frac{3 \sqrt{N_b}}{N_b + N_p} * C
\]

where \(C\) the element concentration of S in ppm, \(N_p\) is the net intensity on the peak and \(N_b\) on the background. The LOD for the chosen setup for S analyses amounted to approximately 16 ppm. The 1-σ-error of the S concentration for each measurement is based on the obtained counting statistics and was calculated by the following equation:
\[
\sigma = \frac{\sqrt{N_p + N_b}}{N_p + N_b}
\]

where \(N_p\) is the net intensity on the peak and \(N_b\) on the background (Hahn-Weinheimer et al., 1984). To obtain a good spatial resolution and to be able to rule out potential effects of convection in the capsule, a measurement was made every 50 m and at least two parallel transects were taken per capsule. All measurement points were checked for the presence of bubbles or cracks potentially falsifying the results. If required, individual points were shifted orthogonally to the profile direction always keeping the along-profile-distance of 50 μm.

In order to constrain the S speciation, we determined the position of the SK\(\alpha\) peak by EPMA on all S-bearing samples and compared it to the peak positions measured on the barite and the pyrrhotite standards, representing the peak positions of \(S^{2-}\) and \(S^{2-}\), respectively (Carroll and Rutherford, 1988; Jugo et al., 2005). Measurement where performed on a PETJ crystal in the range of 171.7–172.5 mm with an acceleration voltage of 15 kV, a beam current of 100 nA and a defocused electron beam with a spot size of 40 μm. Measurement times were kept short in order to avoid potential peak shifts during longer acquisition times (Wallace and Carmichael, 1994; Jugo et al., 2005), therefore, a scanning step size of 20 μm was employed to cover the SK\(\alpha\) peak and the background with a dwell time of 20 s resulting in 800 s total measurement time.

### 2.3.2. Micro-Raman spectroscopy

The \(H_2O\) contents of three representative recovered experimental glasses were quantified by micro-Raman spectroscopy. Raman scattering was excited using a 532 nm diode laser and measured with a Dilor Labram II confocal micro-Raman spectrometer. The laser beam was focused 5 μm below the sample surface with a spot size of 1–2 μm in confocal mode. Spectra were obtained in the 180–1500 and 2800–3900 cm\(^{-1}\) ranges to cover low and high frequency T-O stretching and vibration modes and the OH/\(H_2O\) stretching regions. Two to three spectra were acquired for each measurement point and four different spots were analyzed on each sample. The acquisition time was 120 s. The spectra were processed using OriginPro 9.1\(^{+}\) software employing a cubic baseline correction scheme similar to Di Muro et al. (2006) and Mercier et al. (2009). Quantification was obtained by acquiring Raman spectra of 20 synthetic glasses with known \(H_2O\) concentrations (Karl-Fisher titration, KFT) ranging in composition from olivine-tholeiite to rhyolite and \(H_2O\) contents from anhydrous to 10 wt.%. The relative peak ratios of the OH/\(H_2O\) peak(s) to either the low (LF; 470–510 cm\(^{-1}\)) or the high frequency (HF; 960–1120 cm\(^{-1}\)) silicate vibration modes was calibrated as a function of \(H_2O\) content and the LF/HF ratio (as a proxy for composition or polymerization of the silicate glass). Accuracy of the method is estimated at ±0.5 wt.% \(H_2O\).

Additionally, the S speciation was investigated by micro-Raman spectroscopy. In order to improve the counting statistics, we employed laser intensities of 10 mW on the sample and collected three spectra for 60 s on each analysis spot. In total, four different spots were analyzed in the run products of the diffusion experiments (two on the S-free and two on the S-bearing side of each capsule); for the starting material glasses two spots were acquired.

### 3. RESULTS

#### 3.1. Major element and \(H_2O\) concentrations

The results of the EPMA analyses are reported in Tables 2 and 3, and additionally, backscatter electron (BSE) images of the run products are depicted in the Appendix (Figs. A1 and A2). \(H_2O\) concentrations were estimated by the “difference method” (Devine et al., 1995) and additionally, three representative diffusion experiments (for each \(P\) and \(fO_2\) condition) were measured by micro-Raman spectroscopy to double check their \(H_2O\) content (Table 3). The comparison between these two methods reveals that the \(H_2O\) concentrations obtained by difference are systematically 8–12 relative % higher than the values obtained by Raman spectroscopy (Table 3). The anhydrous starting material yields an average total of 99.37 wt.% and a S concentration of 36 ± 15 ppm (Table 2) as a result of the devolatilization during the first heating phase at 1500 °C in air. For the hydrous starting glasses, the EPMA totals are consistent with the added amounts of 6.0 and 4.5 wt.% \(H_2O\), respectively, ranging between 93.08 and 95.38 wt.% (Table 3). The S-free hydrous starting materials reveal consistent results regarding their S concentrations with nearly the same low S values (46 ± 5, 31 ± 7 and 26 ± 6 ppm) as the anhydrous one (Table 3). The 250 MPa S-bearing hydrous starting material contains 555 ± 89 ppm S (Table 3), which corresponds to the targeted S amount of 550 ppm (Section 2.2). The 200 MPa S-bearing starting materials contain 533 ± 33 ppm (high \(fO_2\)) and 135 ± 22 ppm S (low \(fO_2\); Table 3), respectively. This infers a S loss of 26 and 34 relative % for high and low \(fO_2\) conditions, respectively, in comparison to the nominal values of 720 and 206 ppm S (Section 2.2). The potential reasons for the S loss are discussed in Section 4.2.

The totals of the six 200 and 250 MPa high \(fO_2\) experiments are consistent with each other and also with respect to their \(H_2O\) contents suggesting homogenous \(H_2O\) distribution (totals of 93.29–95.50 wt.%; Table 3). For low \(fO_2\) conditions, the high \(T\) experiment (1050 °C; #61) reveals a homogenous element distribution with a total of 94.92 wt.% (Table 3), whereas the experiment at 1000 °C (#59) yields a total of 95.35 wt.% with slightly higher standard deviations of nearly all element concentrations in comparison to other experiments (Table 3) due to the appearance of very tiny crystals (<1 μm). The low \(T\) experiment (950 °C; #60) has a total of 95.23 wt.% and the largest standard deviations (Table 3), which is consistent with the observation of larger (~1 μm) and more frequently occurring crystals. In both cases, their small size and dispersal arrangement identified them as quench crystals formed after diffusional re-equilibration, and therefore, they unlikely affected the S diffusion profiles. Their composition was determined semi-quantitatively by SEM due to their small size. They can be classified as pyroxene or amphibole (clear identification was prevented due to mixed measure-
ments incorporating the surrounding melt) and plagioclase. They are not homogeneously distributed in the capsule, but occur in small crystal-rich patches (Appendix Figs. A1 and A2). The S concentrations on the S-bearing and nominally S-free plateaus of the product glasses from the 250 MPa runs amount to 326 ± 92 ppm and 47 ± 17 ppm S, respectively (Appendix Figs. A3–A5). The 200 MPa, high \( f_{O_2} \) run product glasses yield 190 ± 42 ppm and 28 ± 3 ppm (Appendix Figs. A6–A8); whereas the low \( f_{O_2} \) experiments yield 79 ± 11 ppm and of 26 ± 4 ppm S on the S-bearing and nominally S-free plateaus, respectively (Appendix Figs. A9–A11). Consequently, the relative S loss from the S-bearing starting glasses amounts to 32–72 and 19–62 relative % for the 250 MPa and 200 MPa experiments, respectively.

### 3.2. Sulfur speciation

The qualitative characteristic X-ray scans obtained by electron microprobe positively confirmed that S is dominantly present in the run product glasses from the high \( f_{O_2} \) experiments in 6+ oxidation state (Carroll and Rutherford, 1988; Jugo et al., 2005; Klimm et al., 2012b). In these glasses, the S concentrations were sufficiently high to obtain well-defined SK\( \alpha \) peaks, which perfectly overlapped with the SK\( \alpha \) peak of the sulfate (barite) reference.

![Fig. 2. (a) SK\( \alpha \) peak profiles obtained on the S-bearing starting material glass (#20). (b) Original micro-Raman spectra of a run product glass of a diffusion couple experiment conducted at high \( f_{O_2} \) conditions. Black line (#23.2b) refers to the S-free and the red line (#23.2c) refers to the S-bearing side of the diffusion couple; the grey line located at 990 cm\(^{-1}\) marks the position of the narrow band assigned to SO\(_4^{2-}\) species. (c) SK\( \alpha \) peak profiles of the S-bearing starting material glasses produced at low \( f_{O_2} \) conditions (#57.2). (d) Original micro-Raman spectra of S-bearing staring material glass produced at low \( f_{O_2} \) conditions (#57.2a, b). In (a) and (c), the barite and pyrrhotite spectra are shown as reference for the peak positions characteristic of S\(^{6+}\) and S\(^{2-}\), respectively.](image-url)
material (Fig. 2a). The dominant presence of sulfate species in several oxidized run product glasses was additionally confirmed by Raman spectroscopy (not all samples reveal a peak due to low S concentrations). In this case, the presence of dissolved sulfate species is confirmed by the presence of a narrow band at \( \sim 1000 \text{ cm}^{-1} \) assigned to S-O stretching vibrations in sulfate groups (Bény et al., 1982; Lenoir et al., 2009; Klimm and Botcharnikov, 2010). This band occurs superimposed on the broad HF band typical of silicate glasses in the 800–1250 cm\(^{-1}\) region (Mysen et al., 1980; Seifert et al., 1982; Di Genova et al., 2016; Morizet et al., 2017). The comparison of the spectra of S-bearing and S-free glasses (with otherwise identical composition) reveals that the narrow band at \( \sim 1000 \text{ cm}^{-1} \) is only present in the S-bearing glasses consistent with its assignment to dissolved sulfate species (Fig. 2b).

In contrast, the S concentrations in the run product glasses from the low \( fO_2 \) experiments were too low to yield statistically significant SK\(_2\) peaks above the background noise on the EPMA. Previous studies already found that the determination of S speciation at such low concentration levels (<100 ppm) is very difficult or impossible (Matthews et al., 1999). Similarly, no sulfide peaks were observed in the Raman spectra for these glasses (Fig. 2c and d). Our low \( fO_2 \) experiments were conducted at \( fO_2 \) conditions around 1 log unit below the onset of sulfide to sulfate transition based on numerous previous experimental studies (Carroll and Rutherford, 1988; Jugo et al., 2005; Jugo et al., 2010), therefore, clearly supporting our conclusion that S was present dominantly in the 2- oxidation state in these experiments. All EPMA scans and representative Raman spectra are presented in the Appendix (Figs. A12 and A13).

### 3.3. Diffusion coefficient calculation

At least two profiles were measured by EMPA for each capsule orthogonal to the interface between the S-free and the S-bearing side to determine average D values. The appearance of bubbles and cracks within the glasses led to some outlier data points in several profiles, which were discarded for the calculation of \( D \). The S concentration profiles were fitted to the following equation:

\[
C(x,t) = \frac{C_1 + C_2}{2} + \frac{C_1 - C_2}{2} \text{erf} \left( \frac{x - x_0}{2\sqrt{D}t} \right)
\]

where \( C(x,t) \) is the concentration along the diffusion profile at distance \( x \), \( t \) is the experimental run time, \( C_1 \) is the S concentration in the originally S-free and \( C_2 \) in the S-bearing side, \( x_0 \) is the position of the interface along the diffusion profile. This equation describes \( D \) as constant and uses Fick’s second law for a semi-infinite source consistent with the relatively short time scales used in the experiments (Crank, 1975). Best fits between the measured results and the modeled values were determined using the software “Igor”. The usage of a weighting function allows accounting for the standard deviations of every measured point along the profile. For the two plateaus, the standard deviation of the mean was calculated, whereas for the curved part of the profile, the relative errors of the intensities of the individual points were used (Eq. (2)). As outlined above, two of the low \( fO_2 \) runs contained some quench crystals, which did not significantly influence the S diffusion profiles, because (1) they formed after the diffusion profile was established and (2) even if a data point was measured in the crystal-rich patch, the S concentration was averaged out due to the use of defocused electron beam. The chosen beam size was large enough (20 \( \mu \text{m} \)) to smooth out the effect of the crystals, because the melt directly adjacent to the crystals is enriched in S whereas the crystals are virtually S-free.

### 3.4. Effects of temperature and oxygen fugacity on S diffusivity

To assess the effect of \( T \) and \( fO_2 \), only the two 200 MPa experiments are compared to each other as they were subjected to strictly the same experimental conditions. The 250 MPa experiments are discussed afterwards. The effect of \( T \) is consistent for both \( fO_2 \) regimes revealing an increase of the average S diffusivity with increasing \( T \) from 2.79 \( \times 10^{-12} \) to 7.13 \( \times 10^{-12} \text{ m}^2 \text{ s}^{-1} \) for the high \( fO_2 \) experiments (1000–1100 °C) and from 2.69 \( \times 10^{-11} \) to 7.12 \( \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \) for the low \( fO_2 \) experiments (950–1050 °C), respectively (Table 1). This \( T \) dependent behavior is in accordance with all previous studies on S diffusion (Watson, 1994; Baker and Rutherford, 1996; Winther et al., 1998; Freda et al., 2005). In addition to \( T \), \( S \) diffusivity reveals significant dependence on \( fO_2 \): the diffusivity is approximately 1.2 log units higher in the low than in the high \( fO_2 \) experiments at a given \( T \); e.g. at 1050 °C the low \( fO_2 \) experiments yield an average \( D \) of 7.12 \( \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \) as opposed to the high \( fO_2 \) that result an average \( D \) of 4.68 \( \times 10^{-12} \text{ m}^2 \text{ s}^{-1} \) (Fig. 3). The \( T \) dependent diffusivity for high and low \( fO_2 \) conditions for the 200 MPa experiments can be expressed by fitting Arrhenian equations to the results taking the relative errors of each diffusion profile into account (Appendix Figs. A6–A11). These error weighted fits result in the following expressions:

\[
\text{high } fO_2 : \quad D = 10^{-5.92 \pm 0.86} \times \exp \left( \frac{-137.3 \pm 21.5 \text{ kJ/mol}}{RT} \right)
\]

\[
\text{low } fO_2 : \quad D = 10^{-5.18 \pm 1.39} \times \exp \left( \frac{-125.7 \pm 34.4 \text{ kJ/mol}}{RT} \right)
\]

where \( D \) is the average diffusion coefficient in \( \text{m}^2 \text{ s}^{-1} \), \( R \) is the gas constant in 8.3144 J mol\(^{-1} \) K\(^{-1}\) and \( T \) is the temperature in K (Fig. 4).

It was not possible to constrain an Arrhenian equation for the 250 MPa experiments, because one experiment (#22) reveals a clearly lower diffusivity than the other experiments (Fig. 4). Possible causes for this outlier are (1) a unnoticed temperature fluctuation occurred during the experiment, (2) the capsule did not (completely) fall into the hot zone after rotation of the furnace or (3) the thermocouple dislocated during the rotation resulting in incorrect
The relative uncertainty on the D values derived from each individual profile range between 6–14% for the 250 MPa experiments and 11–20% and 15–42% for the high and low fO₂ experiments of the 200 MPa series, respectively (Appendix Figs. A3–A11). These uncertainties from each profile are calculated by using the uncertainty on D from the fit of each diffusion profile (weighted) which is based on the shape of the measured profiles dictated by the analytical error from the counting statistics (for the two plateaus the standard deviation of the mean and for the curved part the relative errors of the intensities). Additionally, the uncertainty of the activation energy
(Q in kJ mol\(^{-1}\)) and the pre-exponential factor are derived from the uncertainty of the individual diffusion coefficients in combination with the uncertainty for the Arrhenius line fits (Eqs. (4) and (5)). The resulting uncertainties for the pre-exponential factor are 14 and 27% and 16 and 27% for the activation energy for the high and low \(f_{O_2}\) experiments, respectively.

4. DISCUSSION

4.1. Redox control on S diffusivity

Our results demonstrate that decreasing \(f_{O_2}\) (from FMQ +2.5 to FMQ −0.8) enhances the diffusivity of S by around an order of magnitude in natural dacitic melts. A priori, this effect can be ascribed to redox-induced changes in (1) the structure of the melt, and/or (2) the speciation of the diffusing S species. Redox-induced structural modification of the melt is caused by partial re-speciation of the network-modifier Fe\(^{3+}\) to the network former Fe\(^{2+}\) (Virgo and Mysen, 1985; Dingwell and Virgo, 1987). Accordingly, a reduction and coeval increase of the Fe\(^{2+}\)/Fe\(^{tot}\) ratio, should depolymerize the silicate melt. At those conditions, a decrease of \(f_{O_2}\) would also change the diffusing S species from sulfate to sulfide. Because the diffusivity of a species is inversely proportional to size (Jambon and Carron, 1976; Ni et al., 2015) and field strength (\(Z^2/r\), Mungall (2002)), we anticipate that changing the S species must also affect the measured diffusivity.

To quantify the relative contribution of melt structure and S speciation effects on the overall diffusivity, we first estimated the structural contribution using the Eyring equation (Eyring, 1936) which has already been applied successfully in diffusion studies (Shimizu and Kushiro, 1984; Chakraborty, 1995; Lesher et al., 1996; Behrens and Hahn, 2009; Behrens and Stelling, 2011; Stelling et al., 2011). This equation is based on the assumption that the transition states of viscous flow and diffusion are the same (Chakraborty, 1995), and it relates diffusion and melt viscosity by:

\[
D = \frac{kT}{\eta} \tag{6}
\]

where \(D\) is the diffusion coefficient (m\(^2\) s\(^{-1}\)), \(k\) the Boltzmann constant (J K\(^{-1}\)), \(T\) the temperature (K), \(\lambda\) is the characteristic “jumping” Si-Si distance (m) between two neighbouring SiO\(_4\)-tetraedron (Henderson, 2005) – typically \(\lambda = 0.3\) nm (Behrens and Hahn, 2009; Stelling et al., 2011) – and \(\eta\) the viscosity (Pa s). To compute \(\eta\), we used the viscosity-composition model of Vetere et al. (2008) for andesites, which is based on the empirical Vogel-Fulcher-Tammann (VFT) equation (Vogel, 1921; Fulcher, 1925; Tammann and Hesse, 1926). The model of Vetere et al. (2008) not only considers \(T\) and the H\(_2\)O content, but also the Fe\(^{2+}\)/Fe\(^{tot}\) ratio when computing the viscosity. We are aware that our compositions are dacitic, but the Vetere et al. (2008) model allowed us to quantify the effect of changing Fe\(^{2+}\)/Fe\(^{tot}\) ratios due the change of \(f_{O_2}\) on melt viscosity. The Fe\(^{2+}\)/Fe\(^{tot}\) ratio was determined via the model of Kress and Carmichael (1991). Within this framework, we find that decreasing \(f_{O_2}\) from FMQ +2.5 to FMQ −0.8 leads to an increase of the Fe\(^{2+}\)/Fe\(^{tot}\) ratio from 0.58 to 0.88 at 1050°C and consequently, to a drop of the viscosity of the dacite by not more than 0.07 log units. Because the Eyring slope is minus one, the structural contribution may enhance the diffusivity of S by not more than +0.07 log units, which is within the error of the model (i.e. 0.17 log units) and, therefore, negligible. Since the increase in S diffusivity reached +1.2 log units in our experiments, we

Fig. 4. Arrhenius diagram of S diffusivity in hydrous dacitic melts under high and low \(f_{O_2}\) conditions at 200 MPa. The Arrhenius equations (green and black solid lines) are calculated from diffusion coefficients extracted from the S concentrations profiles (green and black symbols). The 250 MPa data points (red circles) follow the 200 MPa high \(f_{O_2}\) experiments except the data point at 1050°C. Sulfur diffusivity is more than an order of magnitude higher at low \(f_{O_2}\) conditions.
conclude that about 1.13 log units can be ascribed to S speciation effects.

Thus, our experimental conditions led to marginal changes in the degree of melt polymerization and to a negligible contribution of melt structural changes to the overall change in S diffusivity. The observed variation in S diffusivity was dominantly due to redox-induced changes in the speciation of S. A decrease of $\text{JO}_2$ changes the diffusing S species from sulfate to sulfide and at the same time the radius decreases from 2.50 Å (Baker and Rutherford, 1996) to 1.84 Å for $\text{S}^{2-}$ (Shannon, 1976). Alternatively, S diffusion under oxidizing conditions could be viewed as diffusion of $\text{S}^{6+}$ cations, which would also be expected to be rather slow because of their very high charge (Mungall, 2002; Zhang et al., 2010). Either way, one would expect oxidized S to diffuse slower than reduced S, which is exactly what is observed in our experiments.

### 4.2. Discrepancy between nominal and effective S concentrations

The present study reveals a discrepancy between nominal and effective S concentrations of up to 34% for the starting material synthesis experiments and up to 71% for the diffusion experiments. Additionally, we observe that the 250 MPa experiments result in lower S losses than the 200 MPa ones (no S loss for the hydrous 250 MPa starting material #20). We find that runs that suffered partial S loss from the melt phase are characterized by the ubiquitous presence of bubbles (for the starting materials and diffusion experiments with the exception of run #20 where nearly no bubbles are observable). All runs were nominally $\text{H}_2\text{O}$-undersaturated and S concentrations were below expected anhydrite or sulfide saturation values. Therefore, the occurrence of bubbles is most likely related to the exsolution of an additional fluid-forming species such as $\text{N}_2$ contained in the air located in the interstices of the powdered starting material packed into the noble-metal containers. Li et al. (2015) demonstrated that $\text{N}_2$ is highly incompatible in oxidized basaltic melts with partitioning coefficients ($D_{\text{fluid/melt}}$) of up to about 10,000. Taking into account that additional open space at the top of the capsule is present in order to allow crimping of the capsule and assuming that the porosity of the packed starting material amounts to ca. 30–40%, we estimated that ~7.1–9.5 $\times$ 10$^{-6}$ mole $\text{N}_2$ would be enclosed in a capsule containing 1 g of starting material. According to Libourel et al. (2003), the solubility of $\text{N}_2$ in a basaltic melt at 1400 °C amounts to about 4.4 $\times$ 10$^{-6}$ and 5.5 $\times$ 10$^{-6}$ mole $\text{N}_2$ at 200 and 250 MPa, respectively. Considering that $\text{N}_2$ solubility strongly decreases with decreasing $T$ (e.g. Roskosz et al. (2006)), it is most probable that our experiments were $\text{N}_2$ saturated. As soon as the first bubbles are formed, S will likely partition into the fluid phase due to its high fluid/melt partition coefficient (Botcharnikov et al., 2004; Webster et al., 2009; Zajac et al., 2012). This infers that the presence of even small amounts of bubbles may have a large effect on the S concentration in the coexisting melt resulting in a significant depletion of the S concentration in the melt and, thus, in the run product glasses. Furthermore, during welding of the capsule additional Ar is injected into the capsule, which may partly or fully replace the air within the capsule. As outlined by Li et al. (2015) based on the data of White et al. (1989), Ar has an even higher fluid/melt partitioning coefficients than $\text{N}_2$ (12,500).

The smaller difference between nominal and effective S concentration in the glasses synthesized at 250 MPa is most likely due to the higher $P$ conditions resulting in higher $\text{N}_2$ solubility and potentially lower fluid/melt partition coefficients for S. This is consistent with the semi-quantitative observation of a somewhat lower volume fraction of bubbles in these experiments. The even larger discrepancy in the diffusion experiments in comparison to the starting materials is most likely due to a larger amount of bubbles in the experiments caused by a higher “free air to filled space” ratio at the top of the capsules increasing the amount of $\text{N}_2$ and/or Ar exceeding the saturation level. Fluid exsolution driven by $\text{N}_2$ oversaturation accompanied by S-extraction is consistent with increased depletion of S in the diffusion experiments that were conducted by packing of re-ground starting glass introducing again a comparable amount of air and/or Ar during preparation. Furthermore, we observed frequently that data points obtained along diffusion profiles resulted in elevated S concentrations when they were located on or close to an unexposed but shallow visible bubble which may have partially been included in the sample volume excited by the electron beam. This confirms that S depletion in the melt is most likely due to S fractionation into the bubbles. We stress that the relative depletion of the melt phase in S occurs at the very beginning of the experiment, when the glasses are remolten and bubbles form, and therefore, this S-loss should not disturb the later diffusion profiles. This assumption is based on the following observations: (1) bubbles are distributed relatively homogeneously in the quenched glasses (no “bubble pockets”; Appendix Figs. A1 and A2) and, (2) the diffusion profiles exhibit the theoretically expected shape suggesting that the process of S loss occurred at the very beginning of the experiment prior to the development of the diffusion profiles. Additionally, we systematically attempted to avoid the vicinity of bubbles during profile measurements (Section 2.3.2). Despite the fact, that the totals of our EPMA measurements fit well with the nominal amount of added $\text{H}_2\text{O}$, the uncertainty of the “difference method” is relatively large and together with the micro-Raman data, which point to slightly lower $\text{H}_2\text{O}$ concentrations than the nominal ones, it is most likely that the bubbles also contained some $\text{H}_2\text{O}$.

In summary, the process responsible for the S loss from the melt/glasses needs to be ubiquitous in both $\text{JO}_2$ environments which is inconsistent with S loss to the noble metal capsules because (1) it occurred on the same magnitude under low and high $\text{JO}_2$ conditions as well as when using pure Au capsules, and (2) S loss is time independent because we did not observe an increase of S loss in the starting material glasses in comparison with the diffusion experiments that lasted much shorter. In addition, the diffusion profiles exhibit the theoretically expected shapes and no pyrrhotite or anhydrite was observed in any of the run
products which is consistent with the selected S concentrations being below the expected pyrrhotite and anhydrite saturation values based on previous experimental studies (e.g. Carroll and Rutherford (1985) and Jugo (2009)).

4.3. Comparison with other S diffusion studies

A comparison with other S diffusion studies is not straightforward as all previous studies employed different experimental setups, melt compositions, H$_2$O concentrations and $T$ and $P$ conditions. In order to provide a comprehensive summary, all studies (including their specific parameters) are summarized in Table 4. At first glance, our results fit well into the overall picture that S diffusion depends on melt polymerization as the addition of network formers (mainly SiO$_2$) polymerizes the melt leading to slower diffusivity and the addition of H$_2$O depolymerizes it leading to faster diffusivity. These effects are well known for many diffusing species (Ni et al., 2015) and they were also supposed to be valid for S diffusion (Watson, 1994). In general, S diffusion is faster in hydrous than in anhydrous dacite (Watson, 1994) and S diffusion is faster in hydrous dacite than in more polymerized hydrous rhyolite (Baker and Rutherford, 1996) (Fig. 5 and Appendix Fig. A14). However, a closer inspection of our data reveals some significant discrepancies with published results. For instance, S diffuses faster in our experiments than in hydrous basalts (Freda et al., 2005) and andesites (Watson, 1994). We argue that extrapolating the Arrhenian equations to higher/lower $T$ of the different diffusion data is not warranted, as the linear relationships under anhydrous and hydrous conditions are not parallel to each other. This is apparent when comparing the data presented by Watson (1994), Baker and Rutherford (1996) and Freda et al. (2005) (Fig. 5): The difference between anhydrous and hydrous diffusion data diverge at lower $T$. In addition, diffusion data reveal different $T$ dependencies (slopes) for different compositions that are not fully consistent. In general, slopes increase from basalt to rhyolite with the notable exception of the hydrous andesite data of Watson (1994) that exhibit a rather flat $T$ dependence.

The (extrapolated) difference in diffusivity between anhydrous (performed close to the IW buffer at 1000 MPa by Watson (1994)) and low $fO_2$ hydrous dacites (this study) amounts to approximately 4.0 log units. This difference is much larger than the reported increase between anhydrous and hydrous (7.0 wt.% H$_2$O) rhyolites by Baker and Rutherford (1996) of 1.5–2 orders of magnitude. The increase is also larger than that of Watson (1994) for andesite and that of Freda et al. (2005) for basalt (both studies were conducted at considerably higher $T$). Furthermore, Baker and Rutherford (1996) pointed out that they did not observe any dependence of S diffusion on $fO_2$ over a relatively large $fO_2$ range from FMQ to the manganosite-hausmannite equilibrium buffer (MNO). They suggested that sulfide was the dominating

Table 4
Summary of experimental conditions used in S diffusion studies in the literature.

<table>
<thead>
<tr>
<th></th>
<th>This study</th>
<th>Fre. et al., 2005</th>
<th>Win. et al., 1998</th>
<th>B. &amp; R., 1996</th>
<th>W. et al., 1994</th>
</tr>
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<tbody>
<tr>
<td>$T$ ($^\circ$C)</td>
<td>950–1100</td>
<td>1225–1450</td>
<td>1300–1500</td>
<td>800–1100</td>
<td>1100–1500</td>
</tr>
<tr>
<td>$P$ (MPa)</td>
<td>200–250</td>
<td>500–1000</td>
<td>1000</td>
<td>0–200</td>
<td>1000</td>
</tr>
<tr>
<td>$fO_2$</td>
<td>FMQ –1.0 to +2.5</td>
<td>FMQ –3</td>
<td>“oxidized”</td>
<td>FMQ to air</td>
<td>Close to IW</td>
</tr>
<tr>
<td>$H_2$O (wt.%)</td>
<td>4.5–6.0</td>
<td>0.0–3.5</td>
<td>0</td>
<td>0.0–7.3</td>
<td>0.0–5.5 for andesite</td>
</tr>
<tr>
<td>Compo.</td>
<td>Dacitic</td>
<td>Basaltic</td>
<td>Albitic</td>
<td>Rhyolitic</td>
<td>Andesite/dacitic</td>
</tr>
<tr>
<td>Technique</td>
<td>DC</td>
<td>DC</td>
<td>DC</td>
<td>Mineral dissol.</td>
<td>DC</td>
</tr>
<tr>
<td>Apparatus</td>
<td>CS</td>
<td>PC</td>
<td>PC</td>
<td>CS</td>
<td>PC</td>
</tr>
<tr>
<td>Comment</td>
<td>Natural</td>
<td>High FeO nat.</td>
<td>Fe-free synt.</td>
<td>Low FeO</td>
<td>Fe-free synt.</td>
</tr>
</tbody>
</table>

diffusing species and that only under very high $fO_2$ conditions (air), sulfate turned out to be dominant resulting in a sharp decrease of D by about 1.5–2.0 orders of magnitude. They proposed a single Arrhenius equation (anhydrous) for the entire $fO_2$ range investigated (without air) with a Q of 221 ± 80 kJ mol$^{-1}$. From the data of e.g. Carroll and Rutherford (1988) and Jugo et al. (2010) it is known that sulfate is the dominant S species at $>$FMQ +2. However, MNO (±FMQ +4.5) is clearly above this value questioning the inferred stability of sulfate at these high $fO_2$ conditions. A possible reason for this apparent discrepancy could be the experimental setup used by Baker and Rutherford (1996) who determined the diffusion by measuring the dissolution of anhydrite and pyrrhotite into a rhyolite melt.

Similarly, caution is required when comparing the data of this study with Watson (1994), because he constrained Arrhenian equations for synthetic, Fe-free dacite and synthetic, low-K andesite (anhydrous and hydrous), whereas in this study natural Fe-bearing melts were employed. Based on sulfide solubility (Carroll, 1994; Klimm et al., 2012a) and in situ spectroscopic studies (Fleet et al., 2005; Klimm and Botcharnikov, 2010; Wilke et al., 2011), it is evident that Fe plays a critical role in the dissolution of reduced S in silicate melts, and FeS is thought to be the dominant reduced S species in most natural silicate melts. On the other hand, in Fe-free melts, $S_2$ must complex with other cations (e.g. CaS or NaS), because free $S_2^-$ is not likely to exist as demonstrated by molecular dynamics simulations (Machacek et al., 2010). Therefore, we infer that the presence of Fe will have a significant effect on the diffusivity of S at low $fO_2$ conditions where S is dominantly present in 2− oxidation state. As discussed in Section 4.1, the presence of Fe and its oxidation state affects melt viscosity as well (Dingwell and Virgo, 1987; Dingwell, 1991; Lieske et al., 2003; Chevrel et al., 2013) and most likely also impacts S diffusivity. Probably even more important is the fact that the SiO$_2$ content of the dacite used by Watson (1994) is considerably higher (68.0 wt.%)) than our study (62.5 wt.%) exerting additional influence on S diffusion. Additionally, Watson (1994) used a piston cylinder apparatus at 1000 MPa, where the sample is in the hot zone during the heating phase potentially affecting the determination of diffusion in short experiments where “zero time” is difficult to establish. The activation energy of the anhydrous, reduced dacite is much lower (263 kJ mol$^{-1}$) than the one obtained in this study for hydrous low $fO_2$ conditions (125 ± 34 kJ mol$^{-1}$). In contrast, the hydrous andesites (115 kJ mol$^{-1}$) resulted in a much closer agreement with this study, which is probably the result of similar SiO$_2$ contents between the two studies (61.0 wt.% for Watson (1994) and 62.5 wt.% this study). A comparison with the study of Winther et al. (1998) is not warranted, as they investigated a simple, anhydrous, Fe-free albite system at relatively high $T$. They obtained a Q of 458 ± 51 kJ mol$^{-1}$, which is the highest value among all studies.

Freda et al. (2005) studied S diffusion in basaltic melts and obtained a Q of 131 ± 83 kJ mol$^{-1}$ for hydrous conditions (3.5 wt.% H$_2$O) that is, within uncertainty, consistent with our results. They employed graphite capsules generating rather reducing conditions at ±FMQ −3 and used an additional Pt capsule as outer capsule for the hydrated experiments. At a first glance, their S diffusivity values are relatively low compared to our data, which could be related to the fact that they used data obtained from two different basalt compositions (Etna and Stromboli) fitting them with a single Arrhenius equation. Plotting just the Etna diffusion coefficients results in a diffusivity increase of 0.3–0.5 orders of magnitude (possibly due to lower SiO$_2$ and higher FeO and H$_2$O contents). In addition, they used slightly lower H$_2$O contents (3.0–4.0 wt.%) than this study that may also partially explain the observed lower diffusivity. However, as pointed out by Freda et al. (2005), diffusivity is relatively insensitive to the exact H$_2$O concentration at values above 3.0–4.0 wt.%. This is also confirmed by comparing the 250 MPa (6.0 wt.% H$_2$O) and the 200 MPa experiments (4.5 wt.% H$_2$O) of this study revealing very similar diffusivities underlining an insensitive behavior as a function of H$_2$O at concentrations >4.5 wt.%. Additional small differences might arise from the contrasting experimental setups employed: Freda et al. (2005) used a piston cylinder at $P$ between 500 and 1000 MPa and carried out a single “zero time” experiment to evaluate if the heating rate had a significant effect on diffusivity. They concluded that a correction for the short interval between the glass transition and the run $T$ was not required, because the measured profile was just 160 µm long, but still there was a visible small shift implying that the inferred diffusivity might be somewhat lower than the real value considering the short duration of the experiments of 900 s (a correction would have resulted in even lower D values). In comparison, the usage of a rotating cold seal vessel apparatus as employed in this study allowed instantaneous heating of the sample (see Section 2.2).

As pointed out by Behrens and Stelling (2011) (see also in Section 4.1), viscosity plays an important role for diffusion of S in melts. Therefore, we compare our S diffusivity data to those reported in the literature as a function of estimated melt viscosity. For this purpose, we calculated the melt viscosities with different models, which are all based on the empirical Vogel-Fulcher-Tammann (VFT) equation (Vogel, 1921; Fulcher, 1925; Tammann and Hesse, 1926):

$$\log \eta = A + \frac{B}{T - T_0}$$

where $\eta$ is the viscosity (Pa s), $T$ is the temperature in K, and $A$, $B$ and $T_0$ adjustable parameters (pre-exponential factor, pseudo-activation energy and VFT-temperature, respectively (Giordano et al., 2008)). The viscosity of the dacites was calculated with the model of Whittington et al. (2009); the references for the other compositions are indicated in the figure caption (Appendix Fig. A14). As expected, diffusion is inversely proportional to viscosity and similar to Fig. 5, our S diffusion data for low $fO_2$ conditions plot above the literature data.

Our relative uncertainties on the pre-exponential factor (14 and 27%) and the activation energy (16 and 27%) are similar to those in other studies, except for Watson (1994), who did not present any errors (they solely state that their Arrhenian equations have an uncertainty of...
around 10% for the activation energy and a much higher one for the pre-exponential factor). The uncertainty reported by Baker and Rutherford (1996) for the activation energy is somewhat larger than in this study (221 ± 80 kJ mol⁻¹). It is, however, not clear how the uncertainties on single profiles were computed as they utilized the standard deviations of several profiles to compute the Arrhenian equation. Freda et al. (2005) presented errors of 26% and 63% for the activation energies in anhydrous and hydrous systems, respectively (226 ± 58 kJ mol⁻¹ and 131 ± 83 kJ mol⁻¹). They used a Monte Carlo simulation to calculate errors of individual measurements and obtained a value of 20%, which is comparable to the results from our curved part of the profiles where the relative errors of the measured signal intensities were used. No error on the pre-exponential factor is given by Baker and Rutherford (1996) and Freda et al. (2005). The study of Winther et al. (1998) reveals a large uncertainty of 266% (14.7 ± 39.1 m² s⁻¹) on the pre-exponential factor resulting from large scatter of their data, whereas their activation energy has a rather small uncertainty of 11% (458 ± 51 kJ mol⁻¹).

In summary, the overall trends that increasing water contents and T result in increasing diffusivity for given compositions are evident, but the relative magnitudes of these effects are variable and interpolation of the D values to different T or compositions way outside of the experimental conditions is not recommended. Most importantly, significantly increased S diffusivity below the sulfide to sulfate transition has been shown for the first time in this study.

4.4. Geological implications

Volatile diffusion plays a key role for bubble growth during ascent of magmas in volcanic conduits (Sparks, 1978; Navon et al., 1998; Lensky et al., 2004). Hence, determining S diffusion (particularly in comparison to H₂O) is key to access potential reasons for the “excess S” degassing observed during many volcanic eruptions (e.g. Shinohara, 2008). Excess S in volcanic eruptions is defined by the following equation:

Excess S = \( \frac{\text{S released to the atmosphere}}{\text{S determined by petrological estimates}} \)  \( (8) \)

Bubble growth under supersaturated conditions occurs by the ascent of the viscous melt and the diffusion of volatiles into the bubbles (Navon et al., 1998; Lensky et al., 2004; Mancini et al., 2016). H₂O (as well as CO₂) is the most important volatile species in ascending and cooling magmas that drives volatile exsolution and, thus, bubble formation. In a closed system, the exsolution of a volatile phase (including S) can occur by two different processes: (1) decompression-induced decrease of the solubility of volatiles in the melt phase (first boiling), (2) the increase of volatile concentrations in the melt due to the crystallization of minerals devoid of volatile species in their crystal lattice (second boiling) (Bumham, 1967; Shinohara, 2008). Sulfur can also enter the silicate melt and magmatic volatile phase prior to eruption due to the breakdown of S-bearing minerals (Whitney and Stormer, 1983; Luhr et al., 1984; Bernard et al., 1991).

In order to evaluate if the observed “excess S” in volcanic eruptions is controlled by contrasting diffusivities of H₂O and S species in the silicate liquid, a comparison of the diffusion data of the two volatile species is required. The diffusivity of H₂O is a function of the dissolved H₂O concentration and is in general higher compared to those of most other species in silicate melts (Shaw, 1974; Zhang and Ni, 2010). Several studies demonstrated that H₂O diffusivity is not a linear function of H₂O concentration at <3 wt.% dissolved H₂O (Zhang et al., 1991; Zhang and Behrens, 2000). In contrast to S, H₂O diffusivity becomes lower in more depolymerized melts. Furthermore, diffusivity of H₂O is more strongly dependent on the concentration of dissolved H₂O in less polymerized melts at low T (Behrens et al., 2004; Liu et al., 2004). As the present study focuses on magmatic processes, we will only compare diffusion coefficients obtained in hydrous basalt (Zhang and Stolper, 1991), rhyolite (Ni and Zhang, 2008) and dacite melts (Ni et al., 2009) at similar P and T conditions. Sulfur diffusivity ranges over three orders of magnitude, whereas H₂O diffusivity varies within a relatively narrow range of <0.5 log units at the identical T, P and H₂O conditions. This suggests that melt polymerization affects the diffusion of S more than that of H₂O. A direct comparison of S and H₂O diffusion reveals that S diffusion is lower than that of H₂O (Fig. 6). The largest difference is apparent for rhyolites. For basalts, the difference is about one order of magnitude, but the variability of H₂O concentrations (3.5 wt.% H₂O at 1000 MPa of Freda et al. (2005) compared to 0.2 wt.% H₂O at 1000 MPa of Zhang and Stolper (1991)) renders a direct comparison difficult. It can be expected that

![Fig. 6. Comparison of S and H₂O diffusivities in hydrous silicate melts. The purple field is based on the H₂O diffusion of rhyolite (7.0 wt.% H₂O) from Ni and Zhang (2008), dacite (4.5 wt.% H₂O) from Ni et al. (2009) and basalt (0.2 wt.% H₂O) from Zhang and Stolper (1991). Data for S in rhyolite (7.0 wt.% H₂O) are from Baker and Rutherford (1996), for basalt (3.5 wt.% H₂O) from Freda et al. (2005) and for dacite high fO₂ (4.5 wt.% H₂O) and S dacite low fO₂ (4.5 wt.% H₂O) are from this study.](image-url)
H₂O diffusivity and, therefore the difference, would increase at higher H₂O concentrations. For dacitic melts, the diffusivity of oxidized S is more than one order of magnitude lower compared to that of H₂O, whereas the diffusivity of reduced S is only 0.2 orders of magnitude smaller than that of H₂O.

Using previously published S and H₂O diffusion data, Su et al. (2016) presented a numerical model for the intake of S by growing bubbles, either due to first or second boiling. On the basis of the much lower diffusion of S in comparison to H₂O in previous studies, Su et al. (2016) concluded that S cannot reach equilibrium partitioning between the gas and melt phases for decompression rates that are typical of explosive eruptions (10⁵–10⁶ Pa s⁻¹) for Plinian to sub-Plinian eruptions; Toramaru (2006). Hence, S remains largely in the melt during ascent and first boiling in the conduit cannot easily explain the excess S issue. Thus, second boiling in the reservoir (a much slower process) is required to account for the observed enrichment of S during syn-eruptive degassing. Our comparison of diffusion data (Fig. 6) reveals that the difference in diffusivity between H₂O and S may not be as large as previously indicated Arrhenian equations for low and high fO₂ crustal magma reservoirs. We were able to define two divisions (FMQ +2.5) at P-T conditions typical of shallow crustal magma reservoirs. We were able to define two distinct Arrhenian equations for low and high fO₂ conditions and showed that S diffusivity is about one order of magnitude higher under low fO₂ conditions. The increased diffusivity is due to changes of the intrinsic (diffusing species size) and extrinsic properties (degree of melt polymerization). We infer that the larger effective ionic radii is most likely the dominant driving force slowing down the movement of the sulfate ion relative to the sulfate species. Comparison with previous studies is not straightforward, but confirms that S diffusion in dacitic melts is (1) faster under hydrous than anhydrous conditions and (2) faster than in rhyolitic melts at similar T, and (3) comparable to those found in basalts at higher T. Furthermore, S diffusivity is insensitive to H₂O concentrations >4.5 wt.% and independent of S concentrations. In general, interpolation of S diffusivity simultaneously as a function of melt composition and T is not advised and to obtain a better understanding on the compositional dependence of S diffusion, the need for future experiments is clearly warranted. Compared to H₂O diffusion, S diffusion in dacitic melts under high and low fO₂ conditions is generally slower, but only by a factor of 2 at low fO₂ conditions. The strong control of fO₂ on S diffusion plays also an important role for the “excess S” problem, and suggests that oxidized, volatile-rich arc magmas typically build their excess S mostly in bubbles within magma reservoirs prior to eruption.

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APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.gca.2018.01.026.

REFERENCES


Bernard A., Demaiffe D., Mattielli N. and Punongbayan R. S. (1991) Anhydrite-bearing pumices from Mount Pinatubo:


Mineral. Mag.
