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**Geochimica** et Cosmochimica Acta

Geochimica et Cosmochimica Acta 326 (2022) 1-16

www.elsevier.com/locate/gca

# Sulfide and sulfate saturation of dacitic melts as a function of oxygen fugacity

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Received 19 May 2021; accepted in revised form 28 March 2022; Available online 4 April 2022

#### Abstract

Sulfur is a key element in terrestrial magmatic processes yet its geochemical behavior remains one of the most difficult to model due to its heterovalent chemistry. The maximum amount of sulfur a silicate melt can dissolve before saturating with sulfide (e.g., pyrrhotite) or sulfate (e.g., anhydrite) changes with the redox state of the system and has important implications for the sulfur budget of a magmatic system. Several empirical models have been developed to predict the sulfur content of a silicate melt at either sulfide (under reducing conditions) or sulfate (under oxidizing conditions) saturation, but only one model existed that systematically assessed how the sulfur content of a basaltic melt changes as a function of oxygen fugacity  $(fO_2)$ across the transition from sulfide- to sulfate-dominated conditions. The applicability of that model to intermediate and felsic melts rests on the assumption that changes in melt composition do not affect how sulfide or sulfate dissolves in the melt. Here, we report new experimental data that constrain the sulfur concentration at sulfide saturation (SCSS) and the sulfur concentration at anhydrite saturation (SCAS) in a dacitic melt as a function of  $fO_2$ . The experiments were conducted using a H<sub>2</sub>Osaturated natural dacitic melt at 1000 °C, 300 MPa, and at log  $fO_2$  varying over four orders of magnitude encompassing the sulfide-sulfate transition (log  $fO_2 = \Delta FMQ - 0.7$ ,  $\Delta FMQ + 0$ ,  $\Delta FMQ + 0.5$ ,  $\Delta FMQ + 1$ ,  $\Delta FMQ + 1.48$ ,  $\Delta FMQ + 1.54$ ,  $\Delta FMQ$ +1.75,  $\Delta$ FMQ+2.08 and  $\Delta$ FMQ+3.3). New SCSS and SCAS data and modeling for dacitic melts reveals that the sulfidesulfate transition occurs at  $\Delta FMQ+1.81 \pm 0.56$ , defined by the following equations to predict the sulfur content of intermediate to evolved silicate melts as a function of  $fO_2$ :

$$\begin{split} &SCSS_{dacitic} = [S^{2-}] \left( 1 + 10^{(2.00\Delta FMQ - 3.05)} \right) \\ &SCAS_{dacitic} = [S^{6+}] \left( 1 + e^{(1.26 - 2.00\Delta FMQ)} \right) \end{split}$$

The results presented here demonstrate that the basaltic-derived SCSS-SCAS model is not appropriate for dacitic melts and that the sulfide-sulfate transition is shifted to higher  $fO_2$  in more evolved silicate melts. Implications include the stability of sulfides to higher fO2 in more evolved silicate melts and the potential for a narrower transition from a sulfide- to a sulfate-dominated melt than that predicted by thermodynamics.

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Keywords: SCSS; SCAS; Sulfide saturation; Sulfate saturation; Dacitic melts

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https://doi.org/10.1016/j.gca.2022.03.032 0016-7037/© 2022 Elsevier Ltd. All rights reserved.

# **1. INTRODUCTION**

Sulfur (S) is the third most important volatile component of evolved terrestrial magmatic systems behind H<sub>2</sub>O and Cl and participates in a myriad of processes. Sulfur content affects short term climate during S-rich volcanic eruptions (Faure, 1986; Self et al., 1996; Oppenheimer et al., 2011), is required to form metal sulfide ore deposits in magmatic and hydrothermal systems (Hedenquist and Lowenstern, 1994; Simon and Ripley, 2011; Richards, 2015), and is an essential ingredient in the biogeochemical cycle linked to the evolution of life on Earth (Canfield and Raiswell, 1999). As a heterovalent element, S exists in five main oxidation states in magmatic systems ( $S^{2-}$ ,  $S^{1-}$ ,  $S^0$ ,  $S^{4+}$ ,  $S^{6+}$ ; Fleet, 2005). Oxygen fugacity (fO<sub>2</sub>) controls the prevailing oxidation states of redox-sensitive elements and, by extension, dictates the behavior and mobility of S. The S content in silicate melts therefore depends on variables that control the oxidation state and solution mechanisms: namely fO2, temperature, pressure, and melt composition (Carroll and Rutherford, 1985; Carroll and Rutherford, 1987; Luhr, 1990; Carroll and Webster, 1994; Ducea et al., 1994; Burgisser et al., 2008; Moretti and Baker, 2008; Li and Ripley, 2009; Jugo et al., 2010; Webster and Botcharnikov, 2011: Baker and Moretti, 2011). Previous studies recognized that sulfide  $(S^{2-})$  and sulfate  $(S^{6+})$  are the primary oxidation states of S dissolved in a silicate melt and that the presence of sulfide or sulfate is directly related to the melt composition,  $fO_2$  and S content, whereas sulfite  $(S^{4+})$  and the S tri-ion  $(S_3^{-})$  are important in the aqueous fluid phase (Fincham and Richardson, 1954; Katsura and Nagashima, 1974; Carroll and Rutherford, 1988; Nilsson and Peach, 1993; Wallace and Carmichael, 1994; Métrich and Clocchiatti, 1996; Paris et al., 2001; Fleet et al., 2005; Jugo et al., 2005a, 2005b; Backnaes et al., 2008; Wilke et al., 2008; Li and Ripley, 2009; Métrich et al., 2009; Jugo et al., 2010; Klimm and Botcharnikov, 2010; Binder and Keppler, 2011; Wilke et al., 2011; Klimm et al., 2012; Fortin et al., 2015; Lesne et al., 2015; Pokrovski et al., 2015; Zajacz, 2015).

The transition from a sulfide-dominated to a sulfatedominated melt occurs over the relatively narrow range of  $fO_2$  from approximately  $\Delta FMQ+0.5$  to  $\Delta FMQ+2$ , where FMQ refers to the fayalite-magnetite-quartz mineral redox buffer (Fincham and Richardson, 1954; Carroll and Rutherford, 1988; Nilsson and Peach, 1993; Wallace and Carmichael, 1994; Jugo et al., 2005a, 2005b; Jugo et al., 2010). The  $fO_2$  range over which the dominant oxidation state of S transitions from sulfide to sulfate overlaps the range of redox states of magmatic systems in subduction zone environments (Carmichael, 1991; Ballhaus, 1993; Nilsson and Peach, 1993; Parkinson and Arculus, 1999). Considering that the  $fO_2$  of such magmas can change during their evolution owing to assimilation, fractionation, and degassing, constraining the relationship between  $fO_2$  and the stability of sulfide and sulfate in silicate melts is paramount to modeling the behavior of S in magmatic systems.

The sulfur content at sulfide saturation (SCSS) and the sulfur content at anhydrite saturation (SCAS) define the maximum concentration of sulfide and sulfate that can dissolve in a silicate melt before the melt saturates with Fe-sulfide or anhydrite, respectively (Baker and Moretti, 2011 and references therein). Many studies have investigated the SCSS and the SCAS in both synthetic and natural samples by performing experiments using melt compositions ranging from picritic to rhyolitic, temperatures from 700 °C to 1,800 °C, pressures from 1 bar to 9 GPa, and 12 orders of magnitude of log  $fO_2$  (-17.67 to -5.42 bars). Temperature, pressure, H<sub>2</sub>O, and FeO content of the silicate melt, along with the composition of the sulfide liquid have been found to exert the main controls on sulfide saturation, while temperature and the CaO, SiO2 and H2O contents of the silicate melt are the main factors controlling sulfate saturation (Luhr, 1990; Mavrogenes and O'Neill, 1999: Holzheid and Grove, 2002: O'Neill and Mavrogenes, 2002; Clemente et al., 2004; Liu et al., 2007; Moretti and Baker, 2008; Li and Ripley, 2005; 2009; Baker and Moretti, 2011; Beermann et al., 2011; Klimm et al., 2012; Fortin et al., 2015; Masotta and Keppler, 2015; Masotta et al., 2016; Matjuschkin et al., 2016; Smythe et al., 2017; Chowdhury and Dasgupta, 2019; Zajacz and Tsay, 2019; Nash et al., 2019). Mafic systems are the most well-studied, and the majority of studies on any silicate melt composition focused on anhydrous (dry) silicate melts under either very reducing or very oxidizing conditions. Therefore, there is a gap in literature data that investigates sulfide and sulfate saturation in silicate melts involving H<sub>2</sub>O-bearing intermediate to evolved silicate melts across the intermediate  $fO_2$  range that coincides with the sulfide-sulfate transition. The absence of these data limits our understanding of S behavior and mobility in subduction zone environments where intermediate silicate magmas are ubiquitous and associated with more explosive volcanic eruptions and porphyry-Cu mineralization.

To address this gap, we present new experimental data on sulfide and sulfate saturation in an H<sub>2</sub>O-saturated natural dacitic melt conducted at  $\Delta$ FMQ-0.7,  $\Delta$ FMQ+0,  $\Delta FMQ+0.5$ ,  $\Delta FMQ+1$ ,  $\Delta FMQ+1.48$ ,  $\Delta FMQ+1.54$ , ΔFMQ+1.75, ΔFMQ+2.08, and ΔFMQ+3.3 at 1000 °C and 300 MPa. The bulk composition and experimental conditions were selected to represent an intermediate silicate melt using a natural dacite from Quizapo (also known as Cerro Azul volcano), Chile, at mid- to upper-crustal levels in an arc magmatic system across the  $fO_2$  range of the sulfide-sulfate transition. In this study we demonstrate that the only existing model linking the S content of a basaltic silicate melt with  $fO_2$  overestimates SCSS values for dacitic melts for sulfide-only conditions and in the  $fO_2$  range where sulfide transitions to sulfate. We present a new SCSS-SCAS<sub>dacitic</sub> model based on the existing SCSS-SCAS<sub>basaltic</sub> model from Jugo (2009) and Jugo et al. (2010) that accurately predicts the S content of evolved silicate melts as a function of  $fO_2$ .

# 2. METHODS

#### 2.1. Starting materials

Starting materials included natural dacite from Quizapu Volcano (Chile; Ruprecht et al., 2012), Durango apatite

 $[Ca_{10}(PO_4)_6(F,Cl)_2]$ , pyrrhotite  $(Fe_{(1-x)}S)$ , elemental sulfur  $(S^0)$ , hematite (Fe<sub>2</sub>O<sub>3</sub>), and deionized H<sub>2</sub>O. An apatitedoped dacitic starting glass was prepared by mixing Quizapu dacite powder with 5 wt% powdered Durango apatite (grain size  $< 20 \ \mu m$ ), and then fused using a 1 atmosphere furnace for 78 minutes at 1500 °C in a platinum crucible. Apatite was added to investigate the incorporation of trace elements into apatite across a range of  $fO_2$ , which will be presented in a separate publication. The resulting silicate liquid was removed from the furnace and guenched to glass by submerging the crucible in a room temperature water bath (cooling rate  $\sim 100$  °C/sec). The absence of crystals was confirmed using scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA), which revealed a crystal-free glass with compositional homogeneity down to  $> 5.000 \times$  magnification and no loss of lighter elements during fusion (e.g., Na). Table 1 reports the initial Quizapu dacite, anhydrous apatite-doped starting glass, and initial Durango apatite compositions. The glass chips were ground in an agate mortar and divided into five aliquots.

In order to investigate the effect of initial S content on sulfide and sulfate saturation, five different bulk S contents were added to the fused starting glass depending on the  $fO_2$ of the experiment: 0.05, 0.19, 0.28, and 0.38 wt% S in an attempt to ensure that at each imposed  $fO_2$  there would be at least one sulfide- or sulfate-undersaturated experiment and at least one experiment that reached the SCSS or SCAS. The low S series (0.05 wt% S) was chosen to be less than the SCSS predicted by the model of Fortin et al. (2015) and was both sulfide- and sulfate-undersaturated at all imposed fO<sub>2</sub> conditions. The intermediate and high S series (0.19 and 0.28 wt% S, respectively) were designed to reach sulfide saturation in the more reducing experiments ( $\Delta$ FMQ-0.7 to  $\Delta$ FMQ+1) and approach or achieve sulfate saturation in the most oxidizing experiments ( $\Delta FMQ+1.75$ and  $\Delta$ FMQ+3.3). The 0.38 wt% S series was only included in the transition zone ( $\Delta FMQ$ +1.48,  $\Delta FMQ$ +1.54, and  $\Delta$ FMQ+2.08), where the SCSS and SCAS are predicted to be higher (Jugo 2009; Jugo et al. 2010). Reduced S as pyrrhotite from Chihuahua, Mexico (provided by Dr. George Harlow of the American Museum of Natural History) was added for experiments conducted under reducing conditions ( $\Delta$ FMQ-0.7,  $\Delta$ FMQ+0,  $\Delta$ FMQ+0.5,  $\Delta$ FMQ +1) in the amounts of 0.13 wt%, 0.50 wt%, and 0.75 wt% pyrrhotite corresponding to 0.05, 0.19, and 0.28 wt% initial bulk S. Elemental S was the source of S for the oxidizing experiments done at  $\Delta FMQ+1.48$ ,  $\Delta FMQ+1.54$ ,  $\Delta FMQ$ +1.75,  $\Delta$ FMQ+2.08, and  $\Delta$ FMQ+3.3, with the intent of adding a slightly more oxidized form of S to attain redox equilibrium faster. Additionally, since extra Fe was added to the reduced charges as pyrrhotite. Fe was added to the oxidized charges as hematite (Fe<sub>2</sub>O<sub>3</sub>) in the same proportion as that provided by pyrrhotite in the reduced experiments. Elemental S and hematite (hem) were added in the proportion 1 wt% S to 2.4 wt% hem. The apatite-doped starting glass + S materials were mechanically mixed under dry conditions using a mortar and pestle to ensure homogeneous distribution of S + Fe. In order to understand sulfide and sulfate saturation in a hydrous silicate melt that more

97.27 100.49 100.92 Total Total 0.12 0.17 38.92 0.209 þd \* 0  $\overline{\mathbf{n}}$ 0.126 0.001 0.01 0.08 Starting compositions of natural Quizapu Volcano dacite, Durango apatite, and the apatite-doped dacite starting glass, measured by EPMA unless otherwise noted. U v 0.002 0.44 *0.025* 0.16U ſĽ, MnO 0.0043.76 0.091 0.08 0.09 ſт 0.06 0.006 P,0, 0.142.01 0.04š 17.83 0.036 К,О 3.28 3.47 0.01 م Na<sub>2</sub>O 0.001 0.035.05 5.15 0.02Ъe CaO 0.003 0.13 2.36 4.82 0.04Za MgO 38.31 0.033 0.86 0.79 0.01 Ca FeO<sup>tot</sup> 0.005 0.162.80 2.94 0.03 PZ 0.007 TiO, 0.560.540.470.01 ပိ Al,O<sub>3</sub> 15.39 0.007 15.5 0.06 0.41 La 66.41 65.52 0.002 0.19 SiO, 0.143 Starting glass: dacite + 5 wt% apatite Quizapu dacite VQ37D\* Material (wt% element) Material (wt% oxide) Durango apatite

see Ruprecht et al. (2012) for measurement errors for VQ37D All values in wt%. \* Determined via x-ray fluorescence by Ruprecht et al. (2012). in italics, Standard errors are shown

Reported compositions for Durango apatite and starting glass are the averages of 20 analyses each; probe conditions found in Supplementary Material.

Oxygen calculated by difference

closely represents an arc magma, all experiments were saturated with H<sub>2</sub>O by the addition of ~6.75 wt% pure H<sub>2</sub>O to the dry starting material. VolatileCalc 2.0 (Newman and Lowenstern, 2002) was used to estimate the amount of water required to reach H<sub>2</sub>O-saturation for a dacitic melt at 1000 °C and 300 MPa, which was ~6.75 wt%.

Starting materials were loaded in 12–15 mm long gold capsules (outer diameter 3.8 mm, wall thickness 0.12 mm) using the following procedure: ~2.7  $\mu$ L of deionized H<sub>2</sub>O was deposited at the bottom of the capsule using a metal syringe; the capsule weight confirmed the correct mass of water was added. Next, ~40 mg of pre-mixed apatite-doped glass + S was loaded and weighed before crimping the top of the capsule together and welding it shut. Sealed capsules were placed in a 110 °C oven for at least 1 hour and weighed upon removal to check for volatile loss due to capsule leakage. Capsules that showed any weight loss after heating were not used.

Table 2

Experimental details and run products.

#### 2.2. Experimental conditions

Experiments were conducted at Leibniz Universität in Hannover, Germany, in rapid-quench internally heated pressure vessels (IHPVs). A total of nine sets of experiments were conducted at nine different imposed oxidation states, ranging from reducing to oxidizing (see Table 2). Each set contained 1-4 individual capsules loaded with varying initial bulk S contents. All sets were run for 72 hours (±10 minutes) at 300 MPa and 1000 °C; Table 2 lists all experimental details. Temperature cycling facilitated the growth of larger apatite grains via Ostwald ripening following this procedure: temperature was programmed to be held constant at 1000 °C for the first 12 hours, then cycled at  $\pm 20$  °C for 55 hours (one full cycle = ramping up to 1020 °C for 30 minutes, then ramping down to 980 °C for 30 minutes; ramping rate was 5 °C per minute), and held constant at 1000 °C for the final five hours. Reported

logfO <sub>2</sub> <sup>a</sup>	Sample ID Source of S <sup>b</sup>		Initial bulk S content <sup>c</sup>	$pH_2$ initial <sup>d</sup>	SCSS/SCAS reached? <sup>e</sup>	Phase assemblage <sup>f</sup>					
ΔFMQ-0.70	QD7-1 QD7-2 QD7-3	0.13 wt% po 0.50 wt% po 0.75 wt% po	low intermediate high	11.9	no SCSS SCSS	gl - ap - v - spl gl - ap - v - spl - FeS gl - ap - v - spl - FeS					
ΔFMQ+0.00	QD4-1 QD4-4 QD4-6	0.13 wt% po 0.50 wt% po 0.75 wt% po	low intermediate high	5.39	no SCSS SCSS	gl - ap - v - spl gl - ap - v - spl - FeS gl - ap - v - spl - FeS					
ΔFMQ+0.50	QD3-1 QD3-3 QD3-5	0.13 wt% po 0.50 wt% po 0.75 wt% po	low intermediate high	3.03	no SCSS SCSS	gl - ap - v - spl gl - ap - v - spl - FeS gl - ap - v - spl - FeS					
ΔFMQ+1.00	QD1-1 QD1-3 QD1-4	0.13 wt% po 0.50 wt% po 0.75 wt% po	low intermediate high	1.82	no SCSS SCSS	gl - ap - spl - v gl - ap - spl - v - FeS gl - ap - spl - v - FeS					
ΔFMQ+1.48	QD8-1 QD8-2 QD8-3 QD8-4	0.05 wt% S <sup>0</sup> 0.19 wt% S <sup>0</sup> 0.28 wt% S <sup>0</sup> 0.38 wt% S <sup>0</sup>	low intermediate high 0.38 wt%	1.03	no no no SCSS	gl - ap - v - spl gl - ap - v - spl gl - ap - v - spl gl - ap - v - spl - FeS					
$\Delta FMQ+1.54$	QD10-1	$0.38 \text{ wt\% } \text{S}^{0}$	0.38 wt%	0.71	SCSS	gl - ap - v - spl - FeS					
ΔFMQ+1.75	QD6-1 QD6-3 QD6-4	$\begin{array}{c} 0.05 \ wt\% \ S^{0} \\ 0.19 \ wt\% \ S^{0} \\ 0.28 \ wt\% \ S^{0} \end{array}$	low intermediate high	0.81	no no no	gl - ap - v - spl gl - ap - v - spl gl - ap - v - spl					
ΔFMQ+2.08	QD9-1 QD9-2 QD9-3 QD9-4	0.05 wt% S <sup>0</sup> 0.19 wt% S <sup>0</sup> 0.28 wt% S <sup>0</sup> 0.38 wt% S <sup>0</sup>	low intermediate high 0.38 wt%	0.53	no no no no	gl - ap - v - spl gl - ap - v - spl gl - ap - v - spl gl - ap - v - spl					
ΔFMQ+3.30	QD2-2 QD2-4 QD2-5 QD-305	0.05 wt% S <sup>0</sup> 0.19 wt% S <sup>0</sup> 0.28 wt% S <sup>0</sup> 0.57 wt% S <sup>0</sup>	low intermediate high redox test*	0	no no SCAS SCAS	gl - ap - v - Fe-ox gl - ap - v - Fe-ox gl - ap - v - Fe-ox - anh gl - ap - v - Fe-ox - anh					

<sup>a</sup> log  $fO_2$  reported relative to the FMQ mineral redox buffer.

<sup>b</sup> po - natural pyrrhotite (Fe<sub>1-x</sub>S); S<sup>0</sup> - elemental sulfur.

<sup>c</sup> low = 0.005 wt%; intermediate = 0.19 wt%; high = 0.28 wt%; very high = 0.38 wt% initial bulk S concentrations.

<sup>d</sup> Partial pressure of hydrogen  $(pH_2)$  in bars added to the vessel before bringing the experiments up to run temperature and pressure. Calculated assuming a water activity of one inside the capsule as all experiments were H<sub>2</sub>O-saturated.

<sup>e</sup> Fe-sulfide indicates melt reached SCSS; anhydrite indicates melt reached SCAS. 'No' indicates melt was both sulfide- and sulfateundersaturated.

<sup>f</sup> gl - silicate glass; ap - apatite; v - volatile phase; FeS - Fe-sulfide melt; Fe-ox - Fe oxide; spl - spinel; anh - anhydrite.

\* Redox equilibrium test described in text.

temperatures are accurate to  $\pm 5$  °C and reported pressures to  $\pm 1$  MPa. The most oxidizing experiment was conducted at intrinsic  $fO_2$  conditions with a pressure medium composed of pure Ar gas, corresponding to  $\Delta$ FMQ+3.3 conditions (Schuessler et al., 2008).

For all runs except the most oxidizing, the  $fO_2$  in the IHPV was imposed by adding calculated amounts of H<sub>2</sub> gas before heating (see  $pH_2$  initial, Table 2) along with the Ar pressure medium and monitored throughout the duration of the experiment using a Shaw-membrane (Berndt et al., 2002). Noble metal capsules are permeable to H<sub>2</sub> at high pressure. Thus, considering the equilibrium reaction of water formation (H<sub>2</sub> +  $\frac{1}{2}$  O<sub>2</sub>  $\leftrightarrow$  H<sub>2</sub>O), increasing amounts of  $H_2$  in the pressure medium results in a decrease of  $fO_2$  in water-saturated samples. Since all experiments were volatile saturated, we assumed that  $a_{\rm H2O} = 1$ , which allowed us to calculate the necessary  $pH_2$  initial to achieve the target  $fO_2$  (Table 2). In our experiments, the run duration was too short to attain osmotic equilibrium between the Shaw membrane and the pressure vessel (the  $pH_2$  in the membrane was still increasing after 72 hours) so that the  $pH_2$  prevailing in the experimental sample at high temperature could not be measured accurately with the Shaw membrane. However, the expected  $pH_2$  was compared to the measured  $pH_2$  values at osmotic equilibrium by Berndt et al. (2002) in a series of tests performed on the same pressure vessel that was used for this study. The difference between both values was low or even negligible and transfers to an  $fO_2$  difference of less than 0.1 log unit (Berndt et al., 2002), which confirmed previous observations made by Scaillet et al. (1992) and is in agreement with more recent observations (Michaud et al., 2021). We acknowledge that the presence of additional volatile species in significant amounts would lower the  $a_{H2O}$ , which is an additional source of uncertainty in the calculated  $fO_2$  values. However, Zajacz et al. (2012; 2013) have shown that, for intermediate silicate melts, the S concentration in aqueous fluid in equilibrium with sulfide- and anhydritesaturated melts at similar pressures and temperatures is only on the order of 3-5 mol%. Those results, taken together with the small spread of expected values of the EPMA-derived water concentrations and the fact that the anhydrous starting glass total is very close to 100 wt%, point to the  $a_{\rm H2O}$  being very close to 1 for these experiments, which would not affect significantly the resulting  $fO_2$ . Taking into account that the  $a_{H2O}$  was slightly below 1 and that  $pH_2$  at high temperature was calculated from initial, we estimate that the uncertainty of  $fO_2$  is lower than  $\pm 0.25 \log$  units.

All capsules for each set of experimental conditions were run together to ensure that the final  $fO_2$  for each was identical. An isobaric rapid quench terminated each experiment and a small pressure increase of  $\sim 3-5$  bars related to the capsule drop from the hot end to the cold bottom of the vessel confirmed the success of this technique. The recovered capsules were then cleaned with ethanol and weighed to verify capsule integrity during the experiment; any capsules that showed weight loss after quenching were discarded. A total of 27 experimental run products were extracted, mounted in epoxy, and polished for analyses.

#### 2.3. Analytical methods

Electron probe micro-analysis (EPMA) was carried out at the University of Michigan on a CAMECA SX-100 to measure the major (Si, Al, Ca, Mg, Fe, Na, K) and minor element (Ti, P, Mn, Cl, S) concentrations in the quenched glasses. Two beam conditions were used for each spot, both with an accelerating voltage of 15 keV and beam size of 10 µm but with distinct beam currents. Silicon, Al, Ti, Ca, Mg, Fe, Mn, P, K, and Na were measured first using a beam current of 6 nA. followed by measurement of S and Cl using a beam current of 40 nA to achieve low detection limits for these latter elements (0.005 wt% for S and 0.014 wt% for Cl). Detailed EPMA conditions and settings are available in the Supplementary Material. Every attempt was made to perform analyses on crystal-free glass areas, and care was taken in monitoring for the contribution of other phases within the electron beam activation volume. Calcium and P were used as a proxy for apatite, and analyses with elevated concentrations of both CaO and P2O5 together with a decrease in Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, or Cl were discarded.

# 2.4. Assessment of equilibrium

Equilibrium was assessed by measuring the compositional homogeneity of the run product glasses and performing an additional experiment to verify that the imposed  $fH_2$ of the vessel was equilibrated with that inside the capsule. Low standard errors for all elements measured in the silicate glasses (i.e., quenched dacitic melts) as reported in Table 3 evince that the melts were compositionally homogenous, given that the EPMA spot analyses were conducted across the entire exposed surface of each sample. The homogeneity of Fe and S are especially important in this test as these elements were mechanically mixed and added to the capsules, only mixing chemically upon attainment of run conditions where the starting dacitic glass powder existed as a dacitic liquid. One additional experiment (QD-305) that contained 1.5 wt% pyrrhotite as the source of 0.57 wt% S was performed under oxidizing conditions  $(\Delta FMQ+3.3)$  to test if the melt reached redox equilibrium within the run duration. Importantly, the test resulted in the same phase assemblage as experiment QD2-5 (Table 2) that started with 0.28 wt% elemental S at  $\Delta$ FMQ+3.3, indicating that 72 hours was sufficient to oxidize the reduced S and Fe initially present. This result is consistent with previous experiments involving S under the same temperature and pressure conditions employed here using the same experimental vessels that demonstrated that redox equilibrium was reached in <10 hours (Fiege et al., 2014).

#### 3. RESULTS

All run products contain silicate glass (i.e., quenched silicate melt), apatite, a spinel-group mineral, and a volatile phase. Fig. 1 shows representative back-scattered electron (BSE) images of run products and Table 2 reports the phases present in each experiment. The 0.19 and 0.28 wt%

Table 3		
Composition	of quenched	dacitic glasses.

Sample ID	n <sup>a</sup>	SiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub>		TiO <sub>2</sub>		FeO <sup>tot</sup>		MgO		CaO		Na <sub>2</sub> O		K <sub>2</sub> O		P <sub>2</sub> O <sub>5</sub>		MnO		S		Cl		Total <sup>b</sup>		$H_2O^c$		
QD7-1	23	62.94	0.11	15.85	0.05	0.49	0.01	2.20	0.03	0.78	0.01	2.57	0.02	4.60	0.03	3.26	0.01	0.36	0.01	0.070	0.005	0.0104	0.0005	0.069	0.001	93.20	0.16	6.80
QD7-2	31	62.59	0.10	15.76	0.04	0.48	0.01	2.35	0.01	0.79	0.00	2.64	0.01	4.57	0.03	3.29	0.01	0.38	0.01	0.070	0.005	0.0228	0.0004	0.069	0.001	93.03	0.10	6.97
QD7-3	39	62.20	0.10	15.79	0.04	0.50	0.01	2.35	0.01	0.79	0.01	2.61	0.01	4.56	0.03	3.26	0.01	0.38	0.01	0.080	0.005	0.0230	0.0005	0.068	0.001	92.63	0.12	7.37
QD4-1	12	63.64	0.10	15.99	0.07	0.50	0.01	2.57	0.02	0.82	0.01	2.65	0.02	4.75	0.05	3.28	0.02	0.38	0.01	0.058	0.007	0.0111	0.0006	0.068	0.001	94.72	0.16	5.28
QD4-4	14	62.87	0.12	15.91	0.05	0.51	0.01	2.66	0.02	0.82	0.01	2.62	0.02	4.66	0.03	3.30	0.01	0.37	0.01	0.075	0.009	0.0193	0.0004	0.068	0.001	93.90	0.13	6.10
QD4-6	14	63.04	0.13	15.93	0.07	0.51	0.01	2.68	0.02	0.81	0.01	2.65	0.02	4.69	0.04	3.22	0.02	0.36	0.01	0.075	0.006	0.0208	0.0003	0.070	0.001	94.07	0.19	5.93
QD3-1	13	63.35	0.12	16.03	0.06	0.51	0.01	2.70	0.02	0.81	0.01	2.67	0.02	4.69	0.04	3.32	0.03	0.37	0.02	0.070	0.006	0.0080	0.0008	0.069	0.001	94.61	0.15	5.39
QD3-3	15	63.18	0.11	15.94	0.04	0.51	0.01	2.73	0.02	0.80	0.01	2.64	0.02	4.76	0.04	3.29	0.01	0.37	0.01	0.080	0.007	0.0185	0.0007	0.067	0.001	94.41	0.14	5.59
QD3-5	15	63.04	0.10	16.00	0.04	0.50	0.01	2.79	0.02	0.81	0.00	2.62	0.02	4.67	0.04	3.27	0.02	0.37	0.01	0.080	0.006	0.0191	0.0003	0.068	0.001	94.27	0.15	5.73
QD1-2	18	63.53	0.14	15.89	0.06	0.50	0.01	2.81	0.01	0.80	0.01	2.65	0.02	4.61	0.04	3.31	0.01	0.38	0.02	0.080	0.004	0.0062	0.0011	0.068	0.001	94.62	0.18	5.38
QD1-3	17	63.26	0.21	15.74	0.05	0.48	0.01	2.96	0.01	0.81	0.01	2.64	0.02	4.67	0.04	3.26	0.01	0.39	0.01	0.080	0.006	0.0206	0.0008	0.067	0.001	94.39	0.24	5.61
QD1-4	18	62.82	0.21	15.74	0.06	0.49	0.01	3.03	0.02	0.80	0.01	2.65	0.02	4.57	0.04	3.26	0.02	0.40	0.01	0.080	0.004	0.0244	0.0005	0.068	0.001	93.95	0.28	6.05
QD8-1	12	63.83	0.09	15.65	0.08	0.51	0.02	2.98	0.01	0.81	0.01	2.77	0.02	4.53	0.10	3.25	0.01	0.47	0.02	0.082	0.005	bdl	-	0.072	0.002	94.95	0.18	5.05
QD8-2	8	63.43	0.51	15.51	0.29	0.52	0.06	3.18	0.09	0.79	0.03	2.74	0.11	4.49	0.15	3.22	0.07	0.48	0.04	0.072	0.021	bdl	-	0.083	0.023	94.50	0.61	5.50
QD8-3	10	63.28	0.18	15.58	0.06	0.49	0.01	3.29	0.03	0.81	0.01	2.79	0.02	4.39	0.08	3.25	0.01	0.47	0.01	0.088	0.012	bdl	-	0.074	0.002	94.51	0.25	5.49
QD8-4	13	62.95	0.07	15.32	0.04	0.50	0.01	3.54	0.02	0.80	0.01	2.74	0.02	4.36	0.09	3.20	0.02	0.52	0.01	0.071	0.006	0.0196	0.0025	0.071	0.001	94.09	0.12	5.91
QD10-1	11	62.78	0.11	15.46	0.07	0.51	0.02	3.50	0.03	0.80	0.00	2.73	0.03	4.38	0.11	3.20	0.02	0.46	0.02	0.074	0.007	0.0505	0.0037	0.071	0.001	94.08	0.15	5.92
QD6-1	27	62.52	0.11	15.71	0.03	0.48	0.01	2.86	0.01	0.80	0.00	2.69	0.01	4.57	0.02	3.26	0.01	0.43	0.01	0.090	0.004	0.0091	0.0004	0.068	0.001	93.47	0.12	6.53
QD6-3	28	62.56	0.10	15.72	0.04	0.50	0.01	3.16	0.01	0.79	0.00	2.73	0.02	4.56	0.02	3.25	0.01	0.47	0.01	0.070	0.005	0.0276	0.0010	0.068	0.001	93.94	0.13	6.06
QD6-4	28	62.13	0.11	15.60	0.03	0.50	0.01	3.33	0.02	0.80	0.01	2.73	0.02	4.52	0.02	3.26	0.01	0.48	0.01	0.080	0.004	0.0551	0.0024	0.068	0.001	93.56	0.13	6.44
QD9-1	10	63.57	0.14	15.71	0.05	0.50	0.01	2.97	0.02	0.79	0.01	2.77	0.03	4.46	0.07	3.25	0.02	0.47	0.03	0.078	0.009	0.0096	0.0014	0.079	0.008	94.67	0.20	5.33
QD9-2	12	63.22	0.14	15.52	0.05	0.52	0.01	3.22	0.02	0.79	0.00	2.71	0.02	4.48	0.05	3.18	0.01	0.48	0.01	0.075	0.005	0.0198	0.0014	0.068	0.001	94.31	0.15	5.69
QD9-3	14	63.27	0.12	15.64	0.06	0.49	0.01	3.39	0.02	0.78	0.01	2.76	0.03	4.46	0.04	3.23	0.02	0.48	0.02	0.075	0.007	0.0307	0.0024	0.069	0.001	94.71	0.15	5.29
QD9-4	15	62.47	0.13	15.33	0.06	0.50	0.01	3.52	0.02	0.79	0.01	2.84	0.02	4.38	0.03	3.17	0.01	0.52	0.01	0.087	0.007	0.1045	0.0059	0.070	0.001	93.89	0.17	6.11
QD2-2	18	63.78	0.23	15.76	0.09	0.50	0.01	2.93	0.02	0.79	0.01	2.74	0.01	4.42	0.05	3.28	0.02	0.45	0.01	0.090	0.005	0.0347	0.0005	0.066	0.001	94.87	0.34	5.13
QD2-4	24	63.27	0.15	15.67	0.05	0.49	0.01	3.21	0.01	0.78	0.01	2.74	0.02	4.51	0.03	3.25	0.01	0.49	0.01	0.080	0.004	0.0747	0.0029	0.065	0.001	94.69	0.22	5.31
QD2-5	24	63.26	0.17	15.64	0.05	0.48	0.01	3.31	0.01	0.77	0.00	2.71	0.01	4.55	0.03	3.22	0.02	0.58	0.01	0.080	0.004	0.1138	0.0005	0.067	0.001	94.89	0.23	5.11
QD-305	15	64.90	0.09	15.44	0.04	0.52	0.01	3.38	0.02	0.88	0.00	1.61	0.01	4.74	0.02	3.25	0.02	0.15	0.01	0.091	0.006	0.0847	0.0032	0.129	0.001	95.27	0.09	4.73

All values in wt%. 1 $\sigma$  standard errors reported in italics. <sup>a</sup> Number of analyses. <sup>b</sup> Totals calculated with S as SO<sub>3</sub>. <sup>c</sup> H<sub>2</sub>O estimated by difference method.

bdl - below detection limit.



Fig. 1. Representative BSE images of run products. All experiments contained quenched dacitic glass (dark gray groundmass), apatite, a spinel-group mineral, and volatile phase (dark circles). Imposed  $fO_2$  of experiment shown in upper right corner. (a) QD2-5 is sulfate-saturated and contains anhydrite. (b) QD6-4 is both sulfide- and sulfate-undersaturated and does not contain Fe-S melt or anhydrite. (c) QD3-4 is sulfide-saturated and contains an immiscible Fe-sulfide present as bright rounded blebs. (d) Spinel crystal from QD4-4. This experiment is also sulfide-saturated. (e) An area of crystal- and bubble-free glass in QD2-5.

S charges from runs conducted at  $\Delta$ FMQ-0.7,  $\Delta$ FMQ+0,  $\Delta$ FMQ+0.5, and  $\Delta$ FMQ+1 also contain an Fe-sulfide phase, evidence that sulfide saturation was attained. The runs at  $\Delta$ FMQ+1.48 and  $\Delta$ FMQ+1.54 did not attain sulfide-saturation until 0.38 wt% S was added. The 0.28 wt% S charge at  $\Delta$ FMQ+3.3 is the only experiment that reached sulfate-saturation as indicated by the presence of anhydrite crystals (Fig. 1a). Apatite, with the general formula Ca<sub>9.6</sub>(PO<sub>4</sub>)<sub>5.9</sub>(F<sub>0.98</sub>,Cl<sub>0.08</sub>,OH<sub>0.92</sub>), exists as euhedral crystals from 3 µm up to 35 µm in diameter and as acicular crystals (~1 µm wide by 10 s of µm long). The euhedral apatite grew by Ostwald ripening at the expense of smaller grains during temperature cycling, evidenced by 4–10 µm

melt regions surrounding euhedral grains. The spinelgroup mineral in all charges is present as microlite crystals ( $\sim 1 \times 1 \mu m$ ) with cubic habit, the composition of which was semi-quantitatively determined using energy dispersive spectroscopy (EDS). In all experiments except those conducted at  $\Delta FMQ+3.3$  the EDS spectra consisted of Fe + Al + Cr + O peaks, while in the experiments at  $\Delta FMQ$ +3.3 the EDS spectra contained only Fe + O peaks. Therefore, 'spinel' is used to refer to the oxide mineral in all experiments except those at  $\Delta FMQ$  3.3, where 'Fe-oxide' is used, to distinguish the qualitative change in oxide mineralogy. Fe-sulfide, if present, exists as rounded to elongated blebs from 1  $\mu m$  to 50  $\mu m$  in diameter, indicating it existed as a Fe- and S-rich immiscible liquid at run conditions. Anhydrite, if present, exists as euhedral to sub-rounded grains 1 µm to 8 µm in length. A volatile phase is present in all run products trapped fully in glass and is vapor-dominated with a thin rim of liquid as determined using a petrographic microscope, indicating H<sub>2</sub>O-saturation was achieved. The apatite and volatile phase are homogeneously distributed throughout the dacitic glass in the reduced experiments ( $\Delta$ FMQ-0.7,  $\Delta$ FMQ+0,  $\Delta$ FMQ+0.5,  $\Delta$ FMQ+1) and are mostly homogeneously distributed in the oxidized charges ( $\Delta$ FMQ+1.48,  $\Delta$ FMQ+1.54,  $\Delta$ FMQ+1.75,  $\Delta$ FMQ+2.08 and  $\Delta$ FMQ+3.3), although several experiments at these higher *f*O<sub>2</sub> conditions have areas of crystal- and/or bubble-free glass, as seen in Fig. 1e, especially at higher initial bulk S contents.

Table 3 reports the composition of silicate glass from each experiment. The dacitic glasses are homogeneous with respect to the elements analyzed, evidenced by the low standard errors. The average S content of the glass varies as a function of  $fO_2$  and initial bulk S content. As  $fO_2$  increases, there is an overall increase in the S content of the silicate melt for all initial bulk S series. Under reducing conditions, the maximum S content of the melt decreases slightly from 0.0230 wt% at  $\Delta$ FMQ-0.7 to 0.0191 wt% at  $\Delta$ FMQ+0 and increases to 0.0244 wt% S at  $\Delta$ FMQ+1. The sulfide-saturated experiment at  $\Delta$ FMQ+1.48 contains 0.0196 wt%, and the S content of the melt increased rapidly at  $\Delta$ FMQ+1.54 to 0.0505 wt% S. At  $\Delta$ FMQ+1.75 and  $\Delta$ FMQ+2.08 the highest S content increases to 0.0551 and 0.1045 wt%, respectively, however, these two experiments remain both sulfide- and sulfate-undersaturated. Sulfate saturation was reached at  $\Delta$ FMQ+3.3 in only the high bulk S charge and the highest measured S content in the melt is observed in this experiment (0.1138 wt%).

The low initial bulk S series (0.005 wt% S) is always sulfide- and sulfate-undersaturated. The S content of the silicate melt for this series decreases from ~0.0110 wt% at  $\Delta$ FMQ-0.7 and  $\Delta$ FMQ+0 to below the detection limit of 0.0050 wt% S at  $\Delta$ FMQ+1.48 before increasing again to 0.0091 wt% at  $\Delta$ FMQ+1.75, 0.0096 wt% at  $\Delta$ FMQ+2.08, and 0.0347 wt% at  $\Delta$ FMQ+3.3. Our results demonstrate that the minimum S content in a dacitic melt is located at  $\Delta$ FMQ+1.5 (Fig. 2), which is consistent with previous studies (e.g., Clemente et al., 2004; Baker and Moretti, 2011; Matjuschkin et al. 2016). The SCSS does not decrease in this region, and we note that this minimum occurs immediately before the SCSS increases by a factor of two over just 0.06 log units of  $fO_2$  (Fig. 2).



Fig. 2. Sulfur content in dacitic silicate melt as a function of  $fO_2$  relative to FMQ. Filled circles indicate sulfide-saturated runs that contain Fe-S melt and filled triangles indicate sulfate-saturated runs that contain anhydrite. The X symbol indicates runs that are both sulfide- and sulfate-undersaturated. Errors for the  $fO_2$  are  $\pm$  0.25 log units and shown for all points. Unless shown, the standard errors for the S content are smaller than the symbol size. Thin black horizontal line shows the EPMA detection limit of S (DL = 0.005 wt%). Both solid curves represent a sulfide and sulfate saturation surface for dacitic silicate melts as  $fO_2$  varies; points that plot on or above this line are predicted to be sulfide- or sulfate-saturated and points that plot below the line are predicted to be undersaturated. Gray solid line shows the results of the combined SCSS-SCAS Jugo (2009) and Jugo et al. (2010) model using Eqs. (1) and (2) and over-predicts the SCSS at  $\Delta$ FMQ+1,  $\Delta$ FMQ+1.48, and  $\Delta$ FMQ+1.54. The black solid line is a new fit of the gray curve obtained using the Jugo (2009) and Jugo et al. (2010) models as a starting point and described in Eqs. (3) and (4) to improve the SCSS-SCAS model in the sulfide-sulfate transition zone, based only on experiments performed in this study. Vertical black dashed lines and gray box show the standard error calculated by performing a bootstrap on the change point model ( $\pm$ 0.56 log units  $fO_2$  centered at  $\Delta$ FMQ+1.81) described in the text and Supplementary Material. The sulfide-sulfate transition zone of the original gray curve occurs over  $\sim$ 2 log units  $fO_2$ , while the sulfide-sulfate transition occurs over 1.12 log units  $fO_2$  using the new model.

### 4. DISCUSSION

# 4.1. SCSS and SCAS models

Several studies have empirically modeled either the SCSS (Mavrogenes and O'Neill, 1999; Holzheid and Grove, 2002; O'Neill and Mavrogenes, 2002; Li and Ripley, 2005; 2009; Liu et al., 2007; Fortin et al., 2015; Smythe et al., 2017) or the SCAS (Li and Ripley, 2009; Baker and Moretti, 2011; Masotta and Keppler, 2015; Chowdhury and Dasgupta, 2019; Zajacz and Tsay, 2019) in a variety of silicate melt compositions over a range of experimental conditions. Currently, only one model exists to predict the S content of silicate melts as a function of  $fO_2$ , essentially combining the SCSS and the SCAS (Jugo, 2009; Jugo et al., 2010). Jugo et al. (2005a; 2005b) performed experiments at 1300 °C and 1 GPa over a range of  $fO_2$  using a basaltic melt. Jugo (2009) first described the empirical SCSS-SCAS model, and the SCSS portion of the model was updated in Jugo et al. (2010) using synchrotron X-ray absorption near edge structure (XANES) spectroscopy at the S K-edge to measure the proportion of sulfide to sulfate species in the melt. The model developed by those authors is based on experimental results obtained exclusively in basaltic glasses showing that the change from a sulfide to a sulfate saturated melt occurs over ~2 orders of magnitude  $fO_2$  (from  $\Delta FMQ+0$  to  $\Delta FMQ+2$ ) and a maximum S content is attained when the basaltic melt is simultaneously saturated with both sulfide and sulfate at  $\sim \Delta FMQ+1.5$ . The basaltic SCSS-SCAS model is defined by Eqs. (1) (Jugo et al., 2010) and (2) (Jugo, 2009) given below:

$$SCSS_{basaltic} = [S^{2-}](1 + 10^{(2.0\Delta FMQ - 2.1)})$$
(1)

$$SCAS_{basaltic} = [S^{6+}](1 + e^{(2.89 - 2.23\Delta FMQ)})$$
 (2)

The model inputs are  $[S^{2-}]$  and  $[S^{6+}]$ , which are the S contents of the silicate melt that is saturated with sulfide or sulfate, respectively (Eq. (1) is Eq. 12 in Jugo et al. (2010); Eq. (2) is Eq. (8) in Jugo (2009)). This model has no compositional parameter, therefore, the application of this model to more evolved melt compositions assumes that melt composition does not affect how sulfide or sulfate dissolves in the melt. However, experiments on andesitic (Botcharnikov et al., 2011) and dacitic (Jégo et al., 2016) melts demonstrate that the sulfide-sulfate transition occurs at a slightly higher  $fO_2$  than for basaltic melts, which is also predicted with modeling (Moretti and Baker, 2008; Baker and Moretti, 2011). The differences in melt polymerization and chemistry that impact the position of the sulfide-sulfate transition might also affect the SCSS and SCAS. In Fig. 2. we show the extent to which the combined SCAS model of Jugo (2009) and the SCSS model of Jugo et al. (2010) predicts the measured S contents of dacitic melt examined in this study (gray curve in Fig. 2). Fig. 2 demonstrates that the basalt-derived SCSS-SCAS model does not fit with data for a dacitic system in the sulfide-sulfate transition zone ( $\sim\Delta$ FMQ+0.7 to  $\Delta$ FMQ+2), overpredicting the SCSS

from  $\Delta$ FMQ+1 to  $\Delta$ FMQ+1.5 by a factor of 2–3 at  $\Delta$ FMQ+1.5. Using the SCSS and the SCAS in dacitic melts determined in the current study, we fitted a new SCSS and SCAS model using nonlinear least squares with nls from the stats package in R version 4.1.2 (R Core Team, 2021). Eqs. (3) and (4) describe the two models.

$$SCSS_{dacitic} = [S^{2-}](1 + 10^{(2.00\Delta FMQ - 3.05)})$$
(3)

$$SCAS_{dacitic} = [S^{6+}](1 + e^{(1.26 - 2.00\Delta FMQ)})$$
(4)

Importantly, the model is derived only from the experiments conducted in this study. Sulfide- and sulfateundersaturated experiments are reported here for completeness, even though they were not used in deriving Eqs. (3) and (4). For fitting purposes, we assumed that the SCAS would be reached for the QD9 series at  $\Delta FMQ+2.08$  at 0.1125 wt% S, which is a similar melt S content to the anhydrite-saturated experiment at  $\Delta FMQ+3.3$  (QD2-5;  $\sim 0.1138$  wt% S) and is above the upper bound on the uncertainty of the measured S content of QD9-4, which was anhydrite-undersaturated. Due to the relatively large uncertainty in  $fO_2$  and the paucity of data points within the transition region, we fixed the slope parameter of both models to the value predicted theoretically (a = 2, Table S3 in the Supplementary Material). Next, we fitted a change point model to estimate the  $fO_2$  where the sulfide-sulfate transition occurs. To obtain an estimate of the change point, we fitted a Bayesian change point model using the Gibbs sampler JAGS (v 4.3.0) in R (v 4.1.2). The model likelihood is given as SCSS or SCAS ~  $N(\mu_i, \sigma^2)$  where  $\mu_i$  is the average SCSS before (i = 0) or SCAS after (i = 1) the change point. We specified weakly informative uniform priors on the change point, each of the  $\mu_i$ 's, and model variance  $\sigma^2$ . Of the joint posterior distribution of the model parameters, interest centered on the distribution of the change point, or the  $fO_2$  value and credible range over which the sulfide-sulfate transition occurs. We obtained the mean and standard deviation of the change point from this distribution. We estimate that the change point happens between experiments QD10-1and QD9-4, or between  $\Delta FMQ+1.54$  and  $\Delta FMQ+2.08$ . We take the midpoint between these experiments as an estimate of the  $fO_2$  of the sulfide-sulfate transition ( $\Delta FMQ+1.81$ ). Table S3 in the Supplement reports the model estimates for the nls and change point models. Finally, we assessed the uncertainty in  $fO_2$  at the sulfide-sulfate transition by performing a bootstrap of size n = 1,000 of the change point model. The bootstrap procedure consisted of resampling the data with replacement to produce a population of  $fO_2$  values, refitting the Bayesian change point model, and saving the estimated change point for each bootstrap iteration. We then computed the bootstrap standard error of the change point over the n iterations, which was  $\pm 0.56$  log units fO<sub>2</sub>. The R script and data used to run the three models are included in the Supplementary Material.

The application of Eqs. (3) and (4) along with the change point model to fit the SCSS and SCAS data in

Fig. 2 (black solid line) indicate that the transition from a sulfide- to sulfate-saturated dacitic melt occurs at  $\Delta$ FMQ+1.81  $\pm$  0.56, or over 1.12 log units fO<sub>2</sub>. In the absence of a detailed error estimate for the basalticderived SCSS-SCAS model (gray solid line in Fig. 2), we use the fO2 at which the SCSS<sub>basaltic</sub> and SCAS<sub>basaltic</sub> curves depart 5% relative from the SCSS and SCAS plateaus to estimate that the sulfide-sulfate transition occurs from approximately  $\Delta FMQ+0.6$  to  $\Delta FMQ+2.5$ , or nearly 2 log units of  $fO_2$ . The comparison demonstrates that the new dacitic-derived SCSS-SCAS model predicts that the sulfide-sulfate transition is narrower  $(1.12 \log units fO_2)$ than that predicted using the basaltic-derived SCSS-SCAS model when applied to dacitic melts of this study. This observation indicates that the compositional differences between dacitic and basaltic silicate melts may impact the solubility of sulfide and sulfate by affecting the activity coefficients of reduced and oxidized S species.

The transition from a sulfide- to sulfate-dominated silicate melt at  $\Delta FMQ$ +1.81  $\pm$  0.56 is defined by the following redox reactions:

$$S^{2-} + 2O_2 = S^{6+} + 4O^{2-} \tag{5}$$

$$S^{2-} + 4H_2O = S^{6+} + 4O^{2-} + 4H_2 \tag{6}$$

Eq. (5) demonstrates that oxygen plays the role of the electron acceptor during the oxidation of  $S^{2-}$  to  $S^{6+}$ , and Eq. (6) incorporates the water breakdown reaction in this process. The form of the equilibrium constant expression of Eq. (5) defines the functional shape of the sulfide-sulfate transition curve (i.e., the width of the transition). Assuming that the activities of  $S^{6+}$  and  $S^{2-}$  can be described by their concentrations (*c*), the equilibrium constant expression for Eq. (5) can be described by:

$$log(cS^{6+}/cS^{2-}) = 2logfO_2 + logK \tag{7}$$

From Eq. (7), the sulfide-sulfate transition is characterized by a slope of 2 in log  $fO_2$  space and an intercept that is a function of the equilibrium constant (e.g., Wallace and Carmichael, 1994; Jugo et al., 2010; Klimm et al. 2012). The discrepancy between the  $fO_2$  range of the sulfidesulfate transition predicted theoretically vs. experimentally in this study (2 log units  $fO_2$  vs. 1.12 log unit  $fO_2$ , respectively) is most likely due to the relatively large uncertainties in  $fO_2$  of the experiments. Fixing the slope parameter to the theoretical value of two for both Eq. (3) and (4) is a step towards reconciling the thermodynamic predictions with the experimental observations of this study, but we stress that more data is needed to rigorously confirm the width of the sulfide-sulfate transition.

Next, we compare the predictions of a recently published SCAS model (Zajacz and Tsay, 2019) and a SCSS model (Fortin et al., 2015) to test how accurately they predict the SCSS and SCAS observed in the experiments of the current study. Zajacz and Tsay (2019) developed a model to predict the SCAS in silicate melts as a function of temperature, pressure, and melt composition. Those authors primarily used data from previous studies and also conducted experiments to fill gaps in the existing dataset.

Fortin et al. (2015) determined the effect of H<sub>2</sub>O on the SCSS for a range of silicate melt compositions by performing experiments at 1250 °C, 1 GPa, and  $\sim \Delta FMQ$ -1.85 on basaltic to rhyolitic melt compositions and further calibrated their model using previous studies on the SCSS. The model is applicable at temperatures from 1050 °C to 1800 °C, which is significantly higher than the temperatures of most intermediate to evolved silicate melt experiments. We use the Fortin et al. (2015) SCSS model here even though the Li and Ripley (2009) SCSS model was calibrated to lower temperatures because the Fortin et al. (2015) model was more accurate than the Li and Ripley (2009) model when applied to these data. Despite the large range of melt compositions included in the calibration of Fortin et al. (2015), the model developed by those authors is heavily weighted towards mafic melt compositions, and those authors acknowledge that additional experiments are necessary to more accurately model the SCSS in intermediate and felsic silicate melts. Both the Zajacz and Tsay (2019) and Fortin et al. (2015) models are empirical. They include parameters to account for melt composition, pressure, and temperature and assume the presence of one oxidation state of S dissolved in the silicate melt: sulfate in the Zajacz and Tsay (2019) SCAS model and sulfide in the Fortin et al. (2015) SCSS model. Fortin et al. (2015) also derived a second SCSS model that included an  $fO_2$  term but found it had a lower R-squared value for the measured vs. modeled SCSS of the calibration dataset when compared to the model that did not include an  $fO_2$  parameter. The Fortin et al. (2015) SCSS model used here follows the approach without the  $fO_2$  term recommended by those authors; the other model that contains an  $fO_2$  term was tested on these data and gave a worse fit on our dataset.

Fig. 3 shows how the predicted maximum S content of each anhydrite- and sulfide-saturated experiment compares to the actual S content measured. When applied to the anhydrite-saturated experiments, the Zajacz and Tsay (2019) model slightly underestimates the SCAS in experiment QD2-5 at  $\Delta$ FMQ+3.3, predicting a SCAS of 0.1046 wt% compared with the actual SCAS of 0.1138 wt% measured here. The Zajacz and Tsay (2019) SCAS model therefore is in good agreement with our single anhydritesaturated experiment. The Fortin et al. (2015) model overestimates the SCSS of all sulfide-saturated dacitic melts from  $\Delta$ FMQ-0.7 to  $\Delta$ FMQ+1.48 reported here, but underestimates the sulfide-saturated experiment at  $\Delta$ FMQ+1.54. Those authors quoted a relative error of 20%, however, the SCSS is overestimated by 85-118%, or by a factor of two for the experiments conducted at and below  $\Delta FMQ+1.48$ except the one at  $\Delta FMQ + 1$  (Fig. 3). The experiment at  $\Delta FMQ+1.54$  that the Fortin et al. (2015) SCSS model underestimates is positioned right at the beginning of the sulfide-sulfate transition.

To further test if either the Fortin et al. (2015) SCSS or the Zajacz and Tsay (2019) SCAS model can be applied to intermediate redox conditions for more evolved melt compositions in particular, we assessed the success of both models by plotting the measured vs. modeled SCSS and



Fig. 3. Same as Fig. 2, but only showing the sulfide- and sulfate-saturated experiments and the new black curve (Eqs. (3) and (4)). Open symbols represent the predictions of the SCSS model of Fortin et al. (2015; F-15) under the 'SCSS model' arrows on the left and the SCAS model of Zajacz and Tsay (2019; Z&T-19) under the 'SCAS model' arrows on the right. Vertical dashed lines connect the predicted SCSS and SCAS values with the measured S contents of experiments; numbers indicate the value of the difference between the model predictions and experimentally observed S contents in wt%.

SCAS values according to  $fO_2$  from a variety of studies in Fig. 4. The experiments plotted in Fig. 4 were all conducted using H<sub>2</sub>O-saturated dacitic to rhyolitic melt compositions and cover a larger range of temperature and pressure than those included in Figs. 2–3 (776–1100 °C; 35–398 MPa). The fit of each model is illustrated using the root mean square error (RMSE), which indicates the absolute fit of the models to the observations by measuring the distance from each point to the 1:1 line in Fig. 4 and is calculated using Eq. (8):

$$RMSE = \frac{\sqrt{\sum (S_{predicted} - S_{measured})^2}}{n}$$
(8)

The assessment shows that no systematic relationship exists between the accuracy of either model and fO2, indicating that  $fO_2$  is accounted for accurately in both models and not responsible for any scatter or deviations in the dataset of dacitic silicate melts compared here. The significant scatter and higher RMSE value in Fig. 4a relative to Fig. 4b shows that the Fortin et al. (2015) SCSS model is relatively less accurate for more evolved melts compared to the Zajacz and Tsay (2019) SCAS model, although both models capture the data relatively well with no outliers. Potential reasons for this, in addition to the Fortin et al. (2015) SCSS model lacking a robust number of data points from more evolved compositions and being based on a calibration for experiments conducted at > 1050 °C, relates to the H<sub>2</sub>O contents of the Fortin et al. (2015) experiments versus those compared in Fig. 4. Although the effect of water on the SCSS was investigated, none of the experiments performed by Fortin et al. (2015) were  $H_2O$ -saturated, whereas all experiments compared in Fig. 4 are  $H_2O$ -saturated. This is significant as it has been shown experimentally that basaltic and basaltic andesitic melts that are  $H_2O$ -undersaturated have a lower SCSS than the same melts that are  $H_2O$ -saturated (Moune et al., 2009). Whether or not this is the case for more evolved (e.g., polymerized) melts remains to be tested. Nonetheless, these data show that the Fortin et al. (2015) SCSS model works relatively well for more evolved melt compositions at significantly lower temperatures (down to 776 °C) than originally presented based on their calibration.

# 4.2. Applications to natural systems

The mass balance of S among silicate melt, minerals, and a magmatic volatile phase(s) has direct consequences for the atmospheric S yield of volcanic eruptions that impact short-term global climate and the amount of S available to form economic metal sulfide deposits in magmatichydrothermal ore deposits (Wallace, 2001; Candela and Piccoli, 2005; Shinohara, 2008; Halevy et al., 2010; Evans and Tomkins, 2011; Oppenheimer et al., 2011; Richards, 2015; Su et al., 2016; Simon et al., 2018). Quantifying how  $fO_2$  affects the S content of dacitic melts is relevant to understanding the quantity of S available to partition into mineral and volatile phases. The shift over 1.12 log units  $fO_2$  in the maximum S content capable of dissolving in a dacitic melt as the dominant oxidation state transitions from sulfide to sulfate demonstrates that  $fO_2$  greatly impacts the S mass balance during magmatic evolution. Assuming the results from the current study are applicable to dacitic melts under a range of mid- to upper-crustal pressure-temperature conditions, for a dacitic melt around



Fig. 4. Measured vs. modeled values of the SCSS (a) and the SCAS (b) of H<sub>2</sub>O-saturated dacitic to rhyolitic melts from this study and previous studies. a) Fortin et al. (2015) SCSS model applied to sulfide-saturated melts conducted at log fO2 values spanning  $\Delta$ FMQ-0.92 to  $\Delta$ FMQ+2.49; b) Zajacz and Tsay (2019) SCAS model applied to anhydrite-saturated melts conducted at  $\log fO_2$ values spanning  $\Delta$ FMO+1.66 to  $\Delta$ FMO+5. Note the difference in  $\Delta$ FMQ scale between (a) and (b). Solid black line shows 1:1 correspondence of modeled and measured values. The root mean square errors (RMSE) are listed in the bottom right corner of each plot. Dashed lines indicate  $\pm$  2.5x the RMSE (e.g., 2.5× the average model error) and is a measure of goodness of fit - any points that lie outside the dashed lines are considered outliers. Symbols are the same for (a) and (b) and abbreviations are as follows: B-04 = Botcharnikov et al. (2004); C&R-85 = Carroll and Rutherford (1985); C&R-87 = Carroll and Rutherford (1987); C-04 = Clemente et al. (2004); K-17 = Konecke et al. (2017); M&K-15 = Masotta and Keppler (2015); S-98 = Scaillet et al. (1998); This work = experiments from this study; Z&T-19 = Zajacz and Tsay (2019).

 $\Delta$ FMQ+1.5 an increase of ~1 log unit  $fO_2$  will result in about a factor of five increase in the dissolved S capacity of the silicate melt. The increase in S content of the melt would likely be accompanied by the destabilization of sulfide phases and an order of magnitude decrease in the

amount of S that partitions into the fluid phase (Keppler, 1999; Webster and Botcharnikov, 2011 and references therein; Zajacz et al., 2012; Jégo and Dasgupta, 2013; Reyes-Luna, 2015; Binder et al., 2018). For example, Zajacz et al. (2012) report that the vapor/melt partition coefficient for S in an andesitic system decreases from  $\sim$ 170 to  $\sim$ 25 as the oxidation state of S in andesitic melt transitions from  $S^{2-}$  to  $S^{6+}$ . It has been demonstrated that a magma can be oxidized by  $\sim 1 \log \text{ unit } fO_2$  relatively easily during degassing and/or auto-oxidation. For example, H and Fe<sup>2+</sup> are preferentially partitioned into the fluid phase and removed during open system degassing and the crystallization of Fe<sup>2+</sup>-bearing mineral phases (e.g., Fe<sup>2+</sup>rich pyroxene) increases the  $Fe^{3+}/\Sigma Fe$  ratio in the residual melt (Mathez, 1984; Candela, 1986; Burgisser et al., 2008; Halevy et al., 2010; Bell and Simon, 2011; Kelley and Cottrell, 2012; Evans 2012; Humphreys et al., 2015; Richards 2015). Conversely, if the same dacitic melt was originally oxidized around  $\Delta FMQ+2$  and then reduced to  $\Delta$ FMQ+1, the initially high melt S content would drop from  $\sim 0.1100$  wt% S to < 0.0250 wt% S, inducing sulfide saturation and causing an order of magnitude more S to partition into the fluid phase. Assimilation of reduced country rocks, mixing with a reduced basaltic magma at depth, degassing of S-rich fluid during differentiation, and crystallization of magnetite have been proposed as mechanisms capable of reducing a silicate melt (Kress, 1997; Ripley et al., 1999; Jenner et al., 2010; Kelley and Cottrell, 2012). These processes are particularly significant for arc magmatic systems, which are generally interpreted to be relatively oxidized, or already close to the sulfide-sulfate transition, and may therefore experience significant, drastic changes in S behavior and mobility during their evolution as assimilation of country rocks, crystallization, magma mixing, and/or degassing alter the  $fO_2$  of the system.

#### 5. CONCLUSION

Experiments were conducted to investigate the effect of  $fO_2$  on the sulfur content at sulfide saturation (SCSS) and the sulfur content at anhydrite saturation (SCAS) in a H<sub>2</sub>O-saturated dacitic melts at 1000 °C, 300 MPa, and across the  $fO_2$  range of the sulfide-sulfate transition  $(\Delta FMQ-0.7, \Delta FMQ+0, \Delta FMQ+0.5, \Delta FMQ+1, \Delta FMQ)$ +1.48, ΔFMQ+1.54, ΔFMQ+1.75, ΔFMQ+2.08, and  $\Delta$ FMQ+3.3). Results are consistent with previous studies and demonstrate that oxidized dacitic melts ( $\geq \Delta FMQ+2$ ) can dissolve about a factor of five more S than the same melt under reducing conditions ( $\leq \Delta FMQ+1$ ), and fill an important gap at intermediate  $fO_2$  ( $\Delta FMQ+1$  to  $\Delta FMQ$ +2). We tested the Jugo (2009) and Jugo et al. (2010) SCSS-SCAS model using a dacitic melt and demonstrated that a model derived from basaltic experiments does not accurately describe the S content measured in the sulfidesulfate transition region of dacitic melts. A modified version of the Jugo (2009) and Jugo et al. (2010) SCSS-SCAS model is presented for estimating the S content of dacitic melts as a function of fO2. The SCSS-SCAS<sub>dacitic</sub> model predicts

that the transition from a sulfide- to a sulfate-dominated melt occurs over 1.12 log units  $fO_2$  at  $\Delta FMQ+1.81 \pm 0.5$ 6 in dacitic melts, compared to  $\sim 2 \log \text{ units } fO_2$  centered at  $\Delta$ FMQ+1.5 predicted using the basaltic-derived SCSS-SCAS model ( $\sim \Delta FMQ + 0.6$  to  $\sim \Delta FMQ + 2.5$ ). We also evaluated the Fortin et al. (2015) SCSS model and the Zajacz and Tsay (2019) SCAS model on our dataset and show that while both models do well at predicting the SCSS and SCAS, respectively, even in the range of the sulfidesulfate transition, the Zajacz and Tsay (2019) SCAS model more accurately predicts the SCAS of our dacitic melt. This study highlights the need for more experiments at shallower temperature/pressure conditions to better constrain the mass balance of S during magmatic evolution in arc settings and demonstrates that a dacitic melt can experience drastic changes in S behavior and mobility as the dominant oxidation state of S in the melt transitions from sulfide to sulfate. Specifically, the  $fO_2$  range of  $\Delta FMQ+1$  to  $\Delta FMQ+2$  is where the SCSS and the SCAS in dacitic silicate melts changes rapidly, therefore processes such as assimilation, magma mixing, degassing, or crystallization can trigger important changes in the dominant oxidation state and mass balance of S during evolution.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# ACKNOWLEDGEMENT

We thank Dr. Owen Neill and Dr. Eric Hetland at the University of Michigan for expertise and assistance using the EPMA and fruitful conversations about modeling the SCSS and SCAS, respectively; Sarah Haselbach, Stefan Linsler, and Harald Behrens at Leibniz Universität for experimental support. The authors thank Dr. Matteo Masotta, Dr. Pedro Jugo, and three anonymous reviewers for their careful reading and comments to make the study and manuscript better. Discussions with Dr. Jugo in particular were key to understanding the results. We are also incredibly grateful for the handling and comments from AE Dr. Zoltan Zajacz and his insistence on improving key aspects of this manuscript.

#### FUNDING

Financial support in the form of an International Institute Grant, a Department of Earth and Environmental Sciences Turner Award, and Rackham Graduate Student Research Grant from the University of Michigan are gratefully acknowledged as well as a National Science Foundation Graduate Research Fellowship and Society of Economic Geologists Fellowship awarded to J.M.K. The experimental work was supported by DFG (German Science Foundation) project HO 1337/43 to F.H. A.C.S acknowledges support from NSF EAR 1524394.

## APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gca.2022.03.032.

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Associate editor: Zoltan Zajacz