Revision 1

Title

Effect of alkalinity on sulfur concentration at sulfide saturation in hydrous basaltic andesite to shoshonite melts at 1270 °C and 1 GPa.

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1. Abstract

We have measured the effect of alkalis on S concentration at sulfide saturation (SCSS) in an underexplored compositional space of natural hydrous arc melts (basaltic andesite to shoshonite) at 1270°C and 1 GPa. At an oxygen fugacity approximately 2.5 log units below the fayalite-magnetite-quartz (FMQ) buffer, SCSS increases with Na₂O (562 ppm S/wt.% Na₂O), K₂O (98 ppm S/wt.% K₂O) and total alkalis (88 ppm S/wt.% Na₂O+K₂O) over the compositional range we have studied (1.6 – 3.1 wt.% Na₂O; 0 – 6.5 wt.% K₂O; 1.9 – 6.3 wt.% FeO⁶⁺). Experiments with ~1.3 wt.% H₂O show approximately two-fold less increase in SCSS with alkalinity compared to those with ~ 3.0 wt.% H₂O. Our results show a possible limit to the increase in SCSS solely by increasing alkali concentration at ~7.5 wt.% total alkali concentration. Using our results and published data, we retrained earlier SCSS models to provide a better fit to test data. We also developed a new empirical model using theoretical optical basicity as a compositional parameter that predicts SCSS in the overall dataset with slightly better accuracy compared to previous models:
\[ \ln(\text{SCSS}_{\text{ppm}}) = 16.34 - \frac{5784}{T} - 339.4 \frac{P}{T} + 10.85 \ln(\Lambda) + 3.750 X_{\text{FeO}} + 6.703 X_{H_2O} \]

with temperature (T) in Kelvin, pressure (P) in GPa, the optical basicity (\(\Lambda\)) and mole fractions (X) of FeO (calculated from Kress and Carmichael, 1991) and H2O in the melt. The discrepancies between observed and predicted SCSS for our experiments of varying alkalinity reflects the heavy bias toward anhydrous, alkali-poor basalt compositions in the underlying data sets on which most models are developed.

2. Introduction

Sulfur plays an important role in the geosphere by the formation of sulfide minerals or immiscible sulfide melts (e.g. Naldrett, 1969) which partition chalcophile elements (e.g. Cu, Pb, Zn) between silicate melts and sulfide phases, thereby controlling the movement of these elements between the mantle and crust, or in ore deposit generation (e.g. Sillitoe, 2010). The release of S into the atmosphere by degassing magmas is also important due to its impact on global climate (e.g. Scaillet and Macdonald, 2006; McLinden et al., 2016). Sulfur is also used in industrial processes as sulfate in glass refining and as sulfide in glass colouring (e.g. Falcone et al., 2011).

The geochemical behaviour of S in melts has a long history of study starting with Fineham and Richardson (1954) who used simple systems at 100 kPa to show that at \(\log f_{O2} < -5.5\), \(S^2^-\) displaces \(O^{2^-}\) anions in silicate and aluminate melts by the reaction:

\[ S^{2-}_{(\text{silicate melt})} + \frac{1}{2}O_2_{(\text{gas})} = O^{2-}_{(\text{silicate melt})} + \frac{1}{2}S_2_{(\text{gas})} \]  \[1\]

Haughton et al. (1974) discovered that S Concentration at Sulfide Saturation (SCSS) is strongly correlated with Fe concentration and temperature in natural melts, described by Mavrogenes and O’Neill (1999) with the reaction:

\[ \text{FeS}_{(\text{sulfide})} + 0.5O_2 = 0.5S_2 + 2\text{FeO}_{(\text{melt})} \]  \[2\]
Several other experimental studies also show that SCSS increases with increasing temperature and decreasing pressure and is also sensitive to $f_{O_2}$ and melt composition (e.g. Shima and Naldrett, 1975; Danckwerth et al., 1979; Wendlandt, 1982; Bradbury, 1983; Buchanan et al. 1983; Carroll and Rutherford, 1985, 1987, 1988; Mavrogenes and O’Neill, 1999; Holzheid and Grove, 2002; O’Neill and Mavrogenes, 2002; Clemente et al., 2004; Jugo et al., 2005a; Scaillet and Pichavant, 2005; Tsujimura and Kitakaze, 2005; Scaillet and Macdonald, 2006; Liu et al., 2007; Jugo, 2009; Jugo et al., 2010; Ariskin et al., 2013; Fortin et al., 2015). In particular, SCSS is negatively correlated with SiO$_2$ (e.g. Holzheid and Grove, 2002) and shows a U-shaped dependance on melt FeO content with a minimum between ~1 and 8 wt.% FeO (O’Neill and Mavrogenes, 2002; Tsujimura and Kitakaze, 2005; Wykes et al., 2015) where SCSS has little dependance on melt FeO. SCSS is also positively correlated with H$_2$O in the melt (Fortin et al., 2015).

Dissolution of S in silicate melts can occur by the substitution of S$^2-$ for non-bridging oxygen (NBO) in the melt via reaction [1]. It therefore follows that increasing the proportion of network-modifying cations (Fe$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and K$^+$), thus increasing NBO/T - the amount of NBO relative to tetrahedral oxygen (T) - at constant temperature, pressure and melt FeO, should also increase the SCSS of a melt. The alkali elements Na and K form network modifying cations of particular interest as they are known to affect several physical and chemical properties of melts, such as viscosity (Isard, 1969; Day, 1976) and NBO/T (Isard, 1969; Mysen et al., 1985). The latter effect can increase the concentration of S$^2-$ in a melt through reaction [1], although SCSS in melts is generally small enough that NBO are unlikely to be a limiting factor in S dissolution. Melt alkalinity is also known to increase the Fe$^{3+}$/Fe$^{2+}$ of a melt at a given $f_{O_2}$ (e.g. Paul and Douglas, 1965; Gwinn and Hess, 1989; Cicconi et al., 2015), which can increase the S$^{6+}$/S$^2-$ of a melt (Jenner et al., 2010) due to the stoichiometry of the equilibrium between Fe$^{2+}$ – Fe$^{3+}$ and S$^2-$ – S$^{6+}$ redox couples in the melt:

$$\text{SO}_4^{2-} + 8\text{Fe}^{2+} = \text{S}^{2-} + 8\text{Fe}^{3+}\text{O}_{1.5} \quad [3]$$
Because S^{6+} can be up to 10 times higher concentration in a melt than S^{2-} (e.g. Carroll and Rutherford, 1985, 1987; Jugo et al., 2005b), the higher Fe^{3+}/Fe^{2+} of an alkalic melt may increase SCSS by increasing S^{6+}/S^{2-}. The results of Klimm et al. (2012) show that the S^{6+}/S^{2-} transition at 0.2 GPa is indeed shifted to lower fO2 by ~1.5 log units in alkalic melts compared to basalts.

Alkali-rich magma series are found in all tectonic settings (e.g. Gupta, 2015) and, in arcs, are found with increasing distance from the trench (i.e. increasing height above the subducting plate (Dickinson, 1985). Alkali-rich rocks like shoshonites are an overall minor constituent of volcanic arcs, but can be associated with porphyry Cu deposits of economic interest (e.g. Müller and Groves, 1993; McInnes and Cameron, 1994; Lang et al., 1995; Sillitoe, 2010; Logan and Mihalynuk, 2014), suggesting a possible link between alkalinity and the transport of S and chalcophile elements in arc magmatic systems. A compilation of volcanic rocks (n > 42,000; Sarbas and Nohl, 2008) from arcs worldwide reveals extensive variation total alkali concentration as low as 1.5 wt.% and up to 10 wt.% in basaltic andesites to tephriphonolites from the low-K to shoshonite series (Figure 1). There are positive correlations of S and alkalinity in arc melt inclusions (Duca et al., 1994), with up to 0.3 wt.% S in the oxidized alkalic melt inclusions of the Roman Province (Metrich and Clocchiatti, 1996), though these results may be due to changes in fO2. Scaillet and Macdonald (2006) showed a strong positive correlation of SCSS with alkalinity in hydrous rhyolite melts, however, no work has yet tested whether the effect of alkalinity in less evolved magmas.

The objective of the present study is to systematically study the effect of alkali concentration on SCSS in arc-like hydrous basaltic andesite to shoshonite compositions, ultimately to assess the potential role of alkali-rich magmas in transporting S in the arc setting. Because SiO2 is the chief network former in natural magmas and is known to strongly impact SCSS, we restricted our study to compositions with ~51 wt.% SiO2 where there is a relative paucity of experimentation on SCSS at high alkali concentration (Figure 1). Similarly, we restrict our study to starting materials with intermediate...
FeO$^{\text{tot}}$ (6 – 8 wt.%), near the broad minimum in the U-shaped dependence of SCSS on FeO$^{\text{tot}}$ (O’Neill and Mavrogenes, 2002) to avoid changes in SCSS due to melt FeO$^{\text{tot}}$.

3. Methods

3.1 Starting materials

To examine the effect of alkalinity on SCSS in hydrous arc-like melts, we synthesized five starting materials with ~51 wt.% SiO$_2$; 6 – 8 wt.% FeO$^{\text{tot}}$ and with varying total alkali concentration (Figure 1, Table 1). The concentration of Na$_2$O and K$_2$O in the starting materials varies from 1.5 – 3.1 wt.% and 0 – 6.2 wt.%, respectively, to capture the range of alkali concentrations in natural arc basaltic andesites to shoshonites (Figure 1). Other major element concentrations in our starting materials are similarly within the range of natural arc volcanic rocks containing ~51 wt.% SiO$_2$ (Table 1). To synthesize each starting material, reagent grade oxides (SiO$_2$, TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ and MgO) and carbonates (CaCO$_3$, Na$_2$CO$_3$ and K$_2$CO$_3$) were weighed out, mixed by shaking for 15 minutes, loaded into platinum crucibles, de carbonated and then fused at 1400°C for 12 hours, quenched to a glass, extracted and ground to a powder with an agate pestle and mortar. The glass powder was then fused for a further 12 hours, optically examined to ensure complete vitrification and homogeneity and then re-ground to a powder. Gibbsite, Al(OH)$_3$, and FeSO$_4$ were added to the glass powder, with further grinding for 5 minutes under ethanol in an agate mortar and pestle, to add 3.5 and 1 wt.% H$_2$O and S, respectively. The addition of Al(OH)$_3$ and FeSO$_4$ also introduces Al and Fe to the starting materials, and the final concentrations of all the oxides are listed in Table 1. The powders were then stored at 80°C before use.

For three experiments (noted in Table 2), we reduced the H$_2$O content in the starting material by heating for 2 hours at 400°C to convert gibbsite (Al(OH)$_3$ – 35 wt.% H$_2$O) to boehmite (AlOOH – 15 wt.% H$_2$O; Zhu et al., 2010) prior to loading into capsules.

3.2 Experimental procedure
Because S is highly reactive, the choice of capsule material is critical. The conditions of the experiments (1 GPa, 1270°C) precluded the use of Au (Akella and Kennedy, 1971). Platinum is unsatisfactory due to severe Fe loss from the silicate melt to the capsule material, thus changing the melt composition and affecting SCSS. We found that Au$_{75}$Pd$_{25}$ capsules failed in experiments longer than four hours due to the formation of PdS alloy, which melts at 600°C thereby rupturing the capsule, and shorter duration experiments did not saturate in sulfide or sulfate. We therefore used 5 mm long graphite capsules, with a cylindrical cavity 2 mm in diameter and 3 mm in length, loaded with approximately 6 mg of starting material and sealed with snugly fitting graphite lids. The graphite capsules were placed into 3 mm (outer diameter) Pt capsules and sealed by welding. The overall length of the sealed Pt capsule was 6 mm. At 1270°C, the size of the thermal gradient is not significant issue in our experiments as measurements in our apparatus have shown that the thermal gradient at 1400°C is less than 20°C/mm, and this decreases with temperature, in agreement with other studies (e.g. Watson et al., 2002).

The sealed Pt capsules were held in the centre of a 30 mm long graphite furnace on MgO spacers. The junction of a WR$_{25}$-WR$_{25}$ (’Type C’) thermocouple was positioned 3 mm from the centre of the graphite furnace, separated from the Pt capsule by a 0.5 mm thick MgO disc, with the thermocouple wires otherwise protected by four-bore tubing made of high purity alumina. The capsule and graphite heater were placed within a 12.7 mm (outer diameter) BaCO$_3$ pressure assembly, wrapped in thin Pb foil to reduce friction with the pressure vessel. Experiments were performed at 1270°C and 1 GPa in an end-loaded piston cylinder apparatus with temperature controlled by a programmable Eurotherm PID controller which maintained experiment temperature to within 2°C. Pressure was manually controlled to within 0.02 GPa over the duration of each experiment. Friction correction for the BaCO$_3$ cells was determined to be less than 2% based on the melting point of Au at 1 GPa (Akella and Kennedy, 1971).

A small 150 µm thick Pt wire was placed with the starting materials in two experiments (P479 and P480) to estimate the $\dot{z}_{22}$ using the solubility of Fe in Pt (Médard et al., 2008).
For each experiment, the sample was pressurized to 0.5 GPa at ambient temperature and left for one hour. Temperature was then raised to 600°C at 40°C/min and held for 6 minutes at 0.5 GPa, after which the temperature was raised to 1270°C at 120°C/min. Pressure was gradually increased during the second temperature ramp, reaching 1 GPa less than one minute after reaching experimental run temperature. Experiments were quenched by shutting off power to the furnace, causing cooling at an initial rate of ~2500°C/minute and coming to room temperature in approximately 90 seconds. Capsules were extracted from the pressure assembly, mounted in 2.5 cm epoxy mounts and polished to expose the capsule and its contents in longitudinal section.

3.3 Electron Probe Micro-Analysis

Chemical compositions of the experimental run products (Table 3) were determined by Electron Probe Micro-Analysis (EPMA) at the University of British Columbia (UBC; Cameca SX-50) and the University of Alberta (UA; Cameca SX-100). At UBC, major elements in glass were analyzed using a beam diameter of 10 μm, beam current of 20 nA, accelerating voltage of 15 kV, with peak and background count times of 20 and 10 seconds, respectively. The S concentration in glass was determined with the same conditions but using 100 nA beam current with peak and background counting times of 240 and 120 seconds, respectively. The following standards were used: albite, Na (measured first); spinel, Al; diopside, Mg, Ca and Si; orthoclase, K; rutile, Ti; synthetic fayalite, Fe; pyrite, S. On the UA instrument, major elements and S in glass were analyzed using a beam diameter of 10 μm, beam current of 70 nA, accelerating voltage of 15 kV, with peak and background count times of 30 seconds (120 seconds for S). The UA instrument used the following standards: albite, Na; labradorite, Al; diopside, Mg, Ca and Si; sanidine, K; rutile, Ti; marcasite, Fe and S. For each instrument, 10 – 15 points were selected on each glass, away from sulfide droplets. Sulfide droplets were not analyzed as they were often too small (< 5 μm). To ensure internal consistency, three glasses were analyzed with both the UBC and UA instruments. These duplicate analyses (listed in Table 3) are
within error of each other for major elements and S, except for P476, where there is a ~7% discrepancy 
between the UA and UBC analyses which we consider to be minor. Multiple analyses of the VG-2 Juan 
de Fuca MORB glass standard (Smithsonian microbeam standard NMNH 111240-52) over several 
sessions gives an average of 1521 ± 82 ppm, within the range of recommended values for this material 
(1397 ± 172 ppm; Table 3), demonstrating the accuracy of the S analyses. Platinum wires were 
analyzed in experiments P479 and P480 (Table A-1) at UBC using a beam diameter of 5 µm, a beam 
current of 100 nA, accelerating voltage of 15 kV with peak count times of 60 seconds for Fe and 30 
seconds for Pt, with background count time of half the peak count time for these elements. The 
following standards were used for the metal analyses: pyrite, Fe; elemental metal, Pt.

3.4 Estimating alkali loss during EPMA

Exposure to a high current, small diameter electron beam during EPMA of hydrous silica-rich glasses 
can lead to significant under-reporting of the alkali elements, particularly Na, due to their migration 
away from the beam (Morgan and London, 1996, 2005). This phenomenon results in artificially low 
alkali concentration and correspondingly low analytical totals and it is important to assess the extent to 
which our analyses are affected by alkali migration during beam exposure. Time dependent intensity 
(TDI) corrections for Na, K, Si, Al and S were carried out for analyses done at UA using the Probe for 
EPMA Xtreme Edition software (Table A-2). TDI corrected concentrations of these elements are within 
error of the uncorrected values for all experiments except for Na₂O in P476. The difference between the 
TDI corrected and uncorrected Na₂O concentration of P476 is ~7% and is considered minor (Morgan 
and London 2005). Although TDI correction was not carried out at the UBC lab, the good agreement in 
analytical results from glasses analyzed at UA and UBC indicates that alkali loss is also not significant 
in the UBC analyses. In the discussion that follows, we use only the uncorrected alkali concentrations 
from the UA and UBC instruments.
3.5 H₂O measurement by Raman spectroscopy

Water content in experimental glasses may be estimated in a few different ways. Although H₂O content cannot be directly measured by EPMA, the difference of the sum of analyzed elements from 100 may be taken an indirect measure of the H₂O content of a glass. This ‘by difference’ method, however, is prone to errors associated with alkali loss during beam exposure, particularly for glasses with > 70 wt.% SiO₂ (Morgan and London, 1996, 2005). As discussed above, applying TDI corrections to our analyses shows little to no difference from uncorrected results indicating that the analyses are not affected by alkali loss. Nevertheless, the ‘by difference’ method is still not ideal as it is only an indirect measure of H₂O.

Micro-FTIR spectroscopy is a direct means of measuring H₂O in glass but cannot be used in our experiments due to the presence of sulfide droplets throughout the glass. A recently developed means of directly measuring H₂O in glasses relates the area of the OH stretching band at ~3550 cm⁻¹ (Aₜₜ) in the Raman spectra to the glass H₂O content (Behrens et al., 2006). Le Losq et al. (2012) show that normalizing Aₜₜ to the area of the Raman peaks relating to the glass silicate structure, from 100 – 1200 cm⁻¹ (Aₚ), obviates compositionally dependent modification of the OH stretching band, thereby negating the need for compositionally matched calibration standards (e.g. Behrens et al., 2006). The relationship between Aₜₜ/Aₚ and glass H₂O concentration demonstrated by Le Losq et al. (2012) is highly linear (to within 0.2 wt.%; 2σ). This method of H₂O measurement, calibrated for instrument differences (e.g. spectrometer CCD, grating etc.), was used by Fortin et al. (2015) in determining the H₂O concentration of glasses in their SCSS experiments.

We obtained Raman spectra of our glasses using a Renishaw InVia confocal Raman microscope at the University of Victoria using a 532 nm laser, 1200 line/mm grating and its 50x objective lens. At the start of each analytical session the spectrometer was calibrated on the ~520 cm⁻¹ peak of a Si wafer. The position of the atmospheric N₂ Raman peak (~2330 cm⁻¹) served as another indicator of spectrometer calibration over the course of each analytical session. Spectra were obtained from 100 to
4000 cm\(^{-1}\) with an acquisition time of 60 seconds. The laser was focused on the sample surface and set to 10% power to avoid damaging the glasses. Three acquisitions were accumulated for each glass to maximize the signal-to-noise ratio in the resulting spectrum. The raw Raman spectra were corrected for temperature and frequency-dependent scattering as per Long (1977) and to improve baseline correction prior to peak fitting (Behrens et al., 2006; Le Losq et al., 2012). A linear baseline from ~3000 cm\(^{-1}\) to ~3800 cm\(^{-1}\) was subtracted from the spectra and four Gaussian peaks were fit to the OH band at ~3550 cm\(^{-1}\) for each glass. In 100 – 1200 cm\(^{-1}\) region, the baseline subtracted was defined as a cubic spline anchored on the spectrum at ~200 cm\(^{-1}\), ~640 cm\(^{-1}\), ~800 cm\(^{-1}\) and ~1220 cm\(^{-1}\) as per Le Losq et al. (2012), and Gaussian peaks were fit to the resulting baseline-corrected spectra (Figure A-1). Baseline subtraction, peak fitting and area calculation were done using fityk (version 1.3.1). Because we did not have a range of glasses with independently known H\(_2\)O content with which to calibrate the slope of the \(A_{\text{w}}/A_4\) vs. H\(_2\)O relationship for the instrument we used, we initially applied the Le Losq et al. (2012) calibration. Measured in this way, the H\(_2\)O content of a MORB glass with known H\(_2\)O content (ALV1833-1, 2.14 ± 0.26 wt.% H\(_2\)O determined by FTIR; Stolper and Newman, 1994) is 3.6 ± 0.2 wt.% H\(_2\)O. This overestimate of 59% relative to the known H\(_2\)O content of ALV1833-1 is unsurprising as the Le Losq et al. (2012) calibration is specific to the Raman instrument those authors used. We therefore corrected H\(_2\)O concentrations obtained from the Le Losq et al. (2012) calibration by a factor of 0.59 and tested the accuracy of this correction by measuring an andesite glass with H\(_2\)O content known (Run 84, 3.80 ± 0.32 wt.% H\(_2\)O measured by FTIR; Mandeville et al., 2002). The corrected analysis of the Run 84 glass is 4.59 ± 0.62 wt% H\(_2\)O, within error of the H\(_2\)O concentration determined by FTIR, indicating that this correction method is appropriate. Because the \(A_{\text{w}}/A_4\) relationship with H\(_2\)O content is independent of bulk composition (Le Losq et al., 2012), the use of a MORB glass to determine the correction factor for the Le Losq et al. (2012) calibration for the instrument we used does not pose a problem for the varying alkali content of basaltic andesite glasses that we measure in this study.
The H$_2$O concentrations for the glasses in this study are listed in Table 3. As an indicator of precision, the glass in experiment P470 was measured in multiple sessions, giving an average $A_w/A_g$ of $5.7 \pm 0.6$, and H$_2$O concentration of $2.43 \pm 0.32$ wt.%. The H$_2$O concentrations determined by Raman spectroscopy are within 0.5 wt.% of the 'by difference' method (Figure 2). The H$_2$O in the glasses of experiments P479 and P480 could not be determined by Raman due to excessive fluorescence.

Although not ideal, we use the 'by difference' method as an estimate of H$_2$O content of the glass in the two latter experiments.

4. Results

Experimental run products consisted of glass and < 5 µm spherical sulfide droplets (Figure A-2). No bubbles are observed. Some experiments with RD0K starting material show a few pyroxene crystals (visually estimated to be < 1 % by mode) in addition to glass and sulfide droplets (Table 2). Experiments on the RD6K starting material of 1 and 4 hours duration (P466 and P474, respectively) have similar S contents within error (Table 3), implying that 1 hour is sufficient time for complete equilibration of S within the melt. The majority of sulfide-saturated experiments in the present study were of four hours duration (Table 2) which produced glasses with larger sulfide-free portions and thus easier to analyze by electron probe without beam overlap with disseminated sulfide droplets. Sulfur concentration in each glass varies by < 15%, relative (2σ ; Table 3) indicating homogenous S concentration throughout the melt over the duration of the experiments.

The $f_{O_2}$ of two experiments in graphite capsules (P479, P480) was estimated using the solubility of Fe in Pt wire loops loaded in the charges. We measured the Fe content of the Pt wire along three lines from the centre of the wire to ~3 – 5 µm from the edge, using up to six spots per line (Table A-1). In each profile, the concentration of Fe in the Pt wire varies from near zero at the centre to ~9 – 10 wt.% near the edge, indicating that the wire is not completely homogenized in these experiments. We extrapolated the Fe content of the wire to the edge with melt to estimate the $f_{O_2}$ using the oxybarometer.
of Médard *et al.* (2008). For P480, the projected Fe concentration at the Pt wire-melt interface (11.84
wt.% Fe) corresponds to log $f_{O_2} = -9.5$ (i.e. $\Delta FMQ = -2.7; \Delta CCO = -0.8$). For P479, the projected Fe
concentration at the Pt wire-melt interface (11.7 wt% Fe) corresponds to log $f_{O_2} = -9.2$ (i.e. $\Delta FMQ =$ -
2.4, $\Delta CCO = -0.5$). Although these two experiments contained H$_2$O (3.3 – 3.5 wt.%), the $f_{O_2}$ estimates
are within error of the lowest possible for anhydrous experiments in graphite-lined Pt capsules (i.e.
$\Delta CCO = -0.8 \pm 0.3$; Médard *et al.*, 2008). We therefore infer that any oxidizing effect of H$_2$O on the $f_{O_2}$
of our experiments (e.g. Botcharnikov *et al.*, 2005), including those that were partially dehydrated, is
negligible. In the calculations that follow, we take the average of the $f_{O_2}$ determinations for P480 and
P479 (log $f_{O_2} = -9.35, \Delta FMQ = -2.55, \Delta CCO = -0.65$) as the $f_{O_2}$ of all our experiments (Table 2).
The major element composition of the glasses (Table 3) is within 10% of the nominal composition of
the starting materials as given in Table 1, except for FeO$^{tot}$. Two glasses (P479 and P480, marked in
Figures 3, 4) have ~2 wt.% FeO$^{tot}$, reflect Fe loss from the melt into the Pt wire placed in these charges
to monitor $f_{O_2}$. In the remaining experiments, the glasses show FeO$^{tot}$ concentrations of 4 – 6 wt.%
(Figure 3a), which is ~1.8 wt.% less FeO$^{tot}$ compared to the nominal composition of the starting
materials (Table 1) and is attributable to partition of Fe into coexisting sulphide. Other than differences
in FeO$^{tot}$, the similarity between the nominal starting material compositions and the measured glasses
indicates that there was little loss of alkali elements by volatilization during fusion.
The major element concentration of the glasses varies chiefly in the concentration of FeO$^{tot}$, Al$_2$O$_3$,
Na$_2$O and K$_2$O (Table 3). There is a weak, negative correlation between FeO$^{tot}$ and SCSS in our
experiments ($R^2 = 0.06$ and 0.27 for unmodified and partially dehydrated experiments, respectively;
Figure 3a). The weakness of this correlation is expected given the broad, relatively flat inflection of the
U-shaped FeO$^{tot}$ vs. SCSS relationship between 1 and 8 wt.% FeO$^{tot}$ (O'Neill and Mavrogenes, 2001;
Wykes *et al.*, 2015).
Our results show SCSS negatively correlated with Al$_2$O$_3$, decreasing from 1540 ppm at 15.6 wt.%
Al$_2$O$_3$ to 700 ppm at 19.5 wt.% Al$_2$O$_3$ ($R^2 = 0.68$; Figure 3b) for undehydrated experiments. The three
experiments that were partially dehydrated show little separation in $\text{Al}_2\text{O}_3$ content and no correlation is observed with SCSS.

Alkali concentrations, individually and in total, are positively correlated with SCSS (Figure 3c-e). The strongest correlation is between $\text{Na}_2\text{O}$ and SCSS for unmodified and partially dehydrated experiments, respectively (Figure 3c). The slope of the $\text{Na}_2\text{O}$-SCSS relationship is 562 ppm S/wt.%. $\text{Na}_2\text{O}$ and 260 ppm S/wt.% $\text{Na}_2\text{O}$ for both fully hydrous and partially dehydrated experiments. The effect of $\text{K}_2\text{O}$ on SCSS is over five times less than that of $\text{Na}_2\text{O}$ or total alkali concentration in experiments using unmodified starting materials (98 ppm S/wt.% $\text{K}_2\text{O}$, 88 S/wt.% $\text{Na}_2\text{O}$+$\text{K}_2\text{O}$ (Fig. 3d). We use alkalinity, defined here as the molar ratio (Na+K)/Al to account for the co-variation of $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$ and $\text{Al}_2\text{O}_3$ and find that it is positively related to SCSS (Figure 3f). Similar to the individual and total alkali concentrations, the slope of the alkalinity-SCSS relationship for the experiments using unmodified starting materials is approximately twice that of the partially dehydrated starting materials (Fig. 3ef).

The concentration of $\text{H}_2\text{O}$ in glasses from experiments for which starting materials were fully hydrated are similar within error (2.4 – 3.1 wt.%; Table 3), except for P468 which shows 1.2 wt.% $\text{H}_2\text{O}$, likely due to water loss during welding of the Pt capsule. Experiments for which the starting materials were partially dehydrated all have $\text{H}_2\text{O}$ concentrations of ~1.3 wt.%. Experiments with 2.4 – 3.1 wt.% $\text{H}_2\text{O}$ (P474, P466, P476, P470) show higher SCSS than their partially dehydrated counterparts with ~1.3 wt.% $\text{H}_2\text{O}$ (P472, P478, P471) despite otherwise similar major element composition (Table 3). This effect in melts with lower $\text{H}_2\text{O}$ results in an approximate decrease in the slope of the SCSS vs. alcalis and alkalinity relationship by a factor of two (Figure 3c - f). Our results also show that SCSS increases by ~250 ppm S/wt.% $\text{H}_2\text{O}$ between the partially dehydrated and unmodified experiments of moderate and high alkalinity (RD6K and RD4K; Figure 4). The lowest alkalinity experiments (RD0K) on the other hand show a slope that is ten times lower (23 ppm S/wt.% $\text{H}_2\text{O}$) although the correlation is poor. ($R^2 = 0.14$).
5. Discussion

5.1 Effect of alkalinity on SCSS

Our results indicate that SCSS increases with alkalinity and that the effect of Na$_2$O is approximately five times greater than that of K$_2$O in hydrous compositions (Figure 3c, d). No previous work has directly examined changes in SCSS with increasing alkalinity. Previously published SCSS results at similar SiO$_2$ concentration to our experiments (~52 – 56 wt.% SiO$_2$) vary up to ~9 wt.% total alkalis and ~4 wt.% K$_2$O (Figure 1). The only published SCSS results with comparable SiO$_2$ and FeO$^{tot}$ as our data are from Peach et al. (1994). The range of Na$_2$O 2.2 to 2.7 wt.% in their experiments is relatively small, but correlates with SCSS ($R^2 = 0.81$). The increase in SCSS with Na$_2$O in the Peach et al. (1994) experiments is twice that of our experiments (1059 vs. 562 ppm S/wt.% Na$_2$O, respectively), though this may be attributed to the considerably higher temperature of those experiments (1450°C) compared to this study. We found no experiments in the literature of published SCSS results to allow us to compare our results on the effect of variable K$_2$O on SCSS.

The increase in SCSS that we observe in our experiments may be attributed to increased Fe$^{3+}$/Fe$^{2+}$ according to reaction [3] given that ferric iron is increasingly stabilized by high alkali element concentrations at a given fO$_2$ in silicate melts (Paul and Douglas, 1965; Gwinn and Hess, 1989, Cicconi et al., 2015). We have calculated Fe$_2$O$_3$/FeO using the Kress and Carmichael (1991) model, in which the coefficients for the alkali elements require Fe$_2$O$_3$/FeO increases with alkalinity when all other factors are constant. Contrary to Cicconi et al. (2015) we find that Na/(Na+K) is inversely correlated Fe$_2$O$_3$/FeO (Table 3), which is unsurprising as our experiments examine low K to shoshonite melt compositions in which K$_2$O varies far greater than Na$_2$O (Table 1).

Reaction [3] above indicates that increasing Fe$^{3+}$/Fe$^{2+}$ will strongly increase the S$^{6+}$/S$^2$ of a melt. As S$^{6+}$ is more soluble in melts (e.g. Jugo et al., 2005b), small changes in S$^{6+}$/S$^2$ due to changes in Fe$^{3+}$/Fe$^{2+}$ caused by increasing alkalinity will increase concentration of SCSS. This interpretation
requires the presence of S\textsuperscript{6+} even at the reduced f\textsubscript{O2} of our experiments, implying that increasing
alkalinity shifts the S\textsuperscript{2} – S\textsuperscript{6+} transition to lower f\textsubscript{O2} than in basalts. However, f\textsubscript{O2} estimates for our
experiments (FMQ-2.7) are ~1 log units lower than the onset of the S\textsuperscript{2} – S\textsuperscript{6+} transition in Fe-free,
alkaline glasses or in basalt (~FMQ-1 to FMQ- Klimm et al., 2012; Jugo et al., 2010) indicating that S
is likely predominantly present as S\textsuperscript{2-} and any increase in SCSS due to stabilization of S\textsuperscript{6+} may only be
minimal.

Given the strong dependence of SCSS on FeO\textsuperscript{tot} (O'Neill and Mavrogenes, 2002; Wykes et al., 2015),
it may be argued that the increase in SCSS that we observe is due to small changes in FeO\textsuperscript{tot} of our
melts (1.9 – 6.3 wt.%) and not due to alkalinity. Our data, however, do not show any relationship
between FeO\textsuperscript{tot} and SCSS (Figure 3a). Furthermore, the range of FeO\textsuperscript{tot} in our experiments is within the
relatively flat and wide inflection of the U-shaped SCSS relationship with FeO\textsuperscript{tot} between ~1 and 8
wt.% FeO\textsuperscript{tot}, as observed by Mavrogenes and O'Neill (2002) and Wykes et al. (2015). Thus, the
variation in FeO\textsuperscript{tot} in our experiments is not expected to greatly impact SCSS.

Our data shows an apparent peak in SCSS with increasing alkalinity (Figure 3e) with the highest
alkalinity experiments showing lower SCSS than moderate alkalinity ones. We observe this apparent
peak in SCSS in experiments using both fully hydrated and partially dehydrated starting materials.

Experiment P476 (7.3 wt.% total alkalis) shows 200 – 300 ppm more S than the highest alkalinity
experiments P466 and P474 (8.5 – 9.3 wt.% total alkalis) and experiment P478 (7.4 wt.% total alkalis)
shows 180 ppm more S than P472 (9.0 wt.% total alkalis). This observation implies that there may be a
limit to the increase in SCSS solely as a function of alkalinity.

5.2 Previous SCSS models and alkalinity

Modelling of SCSS as a function of temperature, pressure and melt composition has been a goal of
many studies. Mavrogenes and O’Neill (1999) used regression analysis to derive an empirical SCSS
model equation rooted in the thermodynamics of S\textsuperscript{2-} dissolution in silicate melts. Although those
authors recognized the importance of melt composition on SCSS, their work in a restricted
compositional space consideration only P and T. O’Neill and Mavrogenes (2002) conducted a large
number of experiments at 1400°C and 1 bar to determine the effect of composition on SCSS in the
CMAS ± Fe ± Ti system and found that SCSS was strongly inversely correlated with FeO\(^{\text{tot}}\) at < ~1
FeO\(^{\text{tot}}\) but increased with increasing FeO\(^{\text{tot}}\) above ~8 wt.% FeO\(^{\text{tot}}\) (i.e. an asymmetric U-shaped
relationship). Holzheid and Grove (2002) noted that the degree of melt polymerization strongly
controlled the SCSS and used the NBO/T ratio, to account for this in their model, based on data from
anhydrous experiments. Scaillet and Pichavant (2005) presented a model for melt S content, that
included a term for H\(_2\)O and six terms to account for T, P, f\(_{\text{SiO}}\), f\(_{\text{O}}\) and a single compositional term
embracing 10 oxide species terms. Liu et al. (2007) used a model of the form presented by
Mavrogenes and O’Neill (1999), but used ‘MFM’ to parameterize the melt composition. The MFM
parameter correlates positively with NBO/T and is modified from the M and FM parameters initially
used to predict zircon and rutile saturation, respectively (Watson and Harrison, 1983; Ryerson and
Watson, 1987). The MFM value for a melt is calculated as:

\[
\text{MFM} = \frac{N\text{a} + K + 2(Ca + Mg + Fe^{2+})}{Si(Al + Fe^{3+})} \quad [4]
\]

using the mole fractions of each element and calculating Fe\(^{2+}\) and Fe\(^{3+}\) by the method of Kress and
Carmichael (1991). The negative dependence of SCSS on melt FeO content (at low FeO) was included
in the empirical model Li and Ripley (2005) developed for anhydrous compositions, although those
authors removed this term in an updated model (Li and Ripley, 2009) that also accounted for H\(_2\)O.
The effect of H\(_2\)O on SCSS was explicitly tested and parameterized by Fortin et al. (2015) who
present two empirical SCSS models that account for H\(_2\)O: one, an update of the Liu et al. (2007) MFM
model, and a second model based on linear regression of oxide species present in the melt. Finally, we
note that Ni or Cu in sulphide melt has an impact on SCSS (Ariskin et al. (2013); Smythe et al, 2017).
The relatively low concentration of Ni compared to Fe in natural melts implies that, though the
formation of Fe-Ni-Cu complexes will shift SCSS, the effect will be relatively minor compared to other
variables such as FeC\textsuperscript{tot} (Smythe et al, 2017). Indeed, Fortin \textit{et al.} (2015) found that their oxide species
model predicted SCSS in Ni-bearing melts to within 5%, thus avoiding the need to separately
parameterize the Fe-Ni-S solution mechanism. In what follows, we refer to the models of Liu \textit{et al.}
(2007), Li and Ripley (2009) and Fortin \textit{et al.} (2015) as these are recent SCSS models that are based
on, and their predictions compare well against, larger and more comprehensive datasets than older
models.

In general, no single MFM-based model is consistently better than any other in predicting the SCSS
of our experiments (Figure 5a). The Liu \textit{et al.} (2007) model consistently deviates from the measured
SCSS by > 30% from measured SCSS. The Fortin \textit{et al.} (2015) MFM model best predicts the SCSS in
melts with high alkali concentration (alkalinity > 0.6), deviating by < 15% from the measured SCSS.
The Fortin \textit{et al.} (2015) MFM model deviates by -30 – +70% at alkalinity < 0.4. Comparing the oxide
species models that we consider (Figure 5b), the Fortin \textit{et al.} (2015) model is generally more successful
at predicting the SCSS of our experiments, deviating by 25 – 45% at low alkalinity to ~40% at high
alkalinity. The Li and Ripley (2009) model performs best for low alkalinity glasses, underestimating
SCSS by < 25%, however this model underestimates the observed SCSS by up to 70% in higher
alkalinity experiments. Both sets of models, MFM-based and oxide-based, show discrepancies between
predictions and observations that have an approximately parabolic, concave-up geometry with
increasing alkalinity, with minima at (Na+K)/Al = 0.4 – 0.5 for the MFM model.

Part of the reason these models inconsistently predict the effects of alkalinity on SCSS is due to the
heavy bias toward anhydrous MORB-like compositions in the data sets on which those models are
calibrated (Figure 1). As discussed above, the effect of alkalinity on SCSS has not been systematically
studied, resulting in sparse coverage of the high alkali compositional space relative to other
compositions (Figure 1), particularly for 52 – 56 wt.% SiO\textsubscript{2} melts of this study, resulting in very large
bias in the models. Although our experiments are on the outer limits of the compositional space of
previous SCSS experiments, they are within the realm of high-K or shoshonite series magmas in arcs (Figure 1b). Therefore, to increase the calibrated range of SCSS models, we have used our new experimental results to retrain the two models presented by Fortin et al. (2015), as these are the most recent, and present a model of our own in the following sections.

5.3 Updates to previous models

As discussed above and by Fortin et al. (2015), H₂O has a significant control on SCSS. We therefore use the dataset compiled by Fortin et al. (2015), containing only data from the literature where the H₂O content of sulfide-bearing melts was directly measured, together with the results that we present in this study. The dataset comprises the 13 results from this study, 10 from sulfide-bearing experiments carried out in graphite-lined Pt capsules from Wykes et al. (2015), 18 of Fortin et al. (2015) and the 234 results compiled by those authors (Baker et al., 2001; Beermann et al., 2011; Brenan, 2008; Ding et al., 2014; Haughton et al., 1974; Holzheid and Grove, 2002; Jugo et al., 2005a, Liu et al., 2007; Mavrogenes and O’Neill, 1999; Moune et al., 2009; Peach and Mathez, 1993; Peach et al., 1994; Righter et al., 2009; Sattari et al., 2002). Although there are a great many SCSS measurements, we have not included all of them in our database primarily because they did not measure glass H₂O content directly or because they used very different bulk compositions (see Fortin et al. 2015 for details). The sulfide-bearing experiments done in Re capsules by Wykes et al. (2015) were not included in our data compilation as those authors were unable to constrain the lower f₀₂ limit of those experiments. The dataset was randomly split into a training subset (n= 209) including all the SCSS data from the present study, and a verification subset (n=66), a 3:1 split of the overall dataset.

We determined coefficients to the parameters of the MFM and oxide species models (Table 4) presented by Fortin et al. (2015), using linear regression and 10-fold cross-validation, repeated 10 times, with the R package ‘caret’ (R Core Team, 2017; Kuhn, 2017). The retrained MFM model is:
\[ \ln(\text{SCSS}_{\text{ppm}}) = 10.55 - \frac{5081}{T} - 366.7 \frac{P}{T} + 0.4653 \ln \text{MFM} \\
+ 0.3276 \ln X_{\text{FeO}} + 2.967 X_{\text{H}_2\text{O}} \]  

[5]

with \( T \) in Kelvin, \( P \) in GPa, and \( X_i \) being the mole fraction of oxide \( i \). The coefficients to equation [5] are within error of those presented by Fortin et al. (2015), but the updated MFM model provides a slightly reduced fit to the training dataset, with an \( R^2 = 0.791 \) and \( \chi^2 = 3.29 \) for the updated model compared to 0.807 and 3.71, respectively, for the old model. The updated MFM model, however, performs well on the randomly selected verification dataset (\( R^2 = 0.855 \), \( \chi^2 = 0.879 \)). The average squared residual in the training dataset for the updated MFM model is similar to that of the original model (0.11).

The updated oxide species model is:

\[ \ln(\text{SCSS}_{\text{ppm}}) = 36.05 - \frac{6115}{T} - 363.3 \frac{P}{T} - 21.01 X_{\text{H}_2\text{O}} - 26.68 X_{\text{SiO}_2} \\
-19.97 X_{\text{TiO}_2} - 27.34 X_{\text{Al}_2\text{O}_3} - 18.10 X_{\text{FeOtot}} - 23.71 X_{\text{MgO}} \\
-21.08 X_{\text{CaO}} - 23.51 X_{\text{Na}_2\text{O}} - 26.69 X_{\text{K}_2\text{O}} \]  

[6]

with \( T \), \( P \) and \( X_i \) as above. The coefficients to equation [6] are also within error of those presented by Fortin et al. (2015), and the updated and original oxide species models reproduce their training datasets similarly well: \( R^2 = 0.904 \) and \( \chi^2 = 1.49 \) for the updated model compared to 0.918 and 1.56, respectively, for the original model. The updated model also performs well in predicting SCSS of the verification dataset (\( R^2 = 0.929 \), \( \chi^2 = 0.432 \)). The average squared residual for the training dataset for the updated oxide model (0.05) is similar to the original model (0.04). The greatest difference between the oxide species model coefficients presented by Fortin et al. (2015) and our updated version are for \( \text{Na}_2\text{O} \) and \( \text{K}_2\text{O} \), though they are still within error.

The updated MFM model shows negligible improvement in predicting SCSS of our experiments (Figure 5a), with SCSS predictions that are consistently 10 – 15% lower than the Fortin et al. (2015). The updated MFM model shows smaller differences between predicted and observed SCSS at low alkalinity, but slightly greater difference at high alkalinity. The updated oxide species model is more
obviously improved compared to the original, giving SCSS predictions that are ~25% lower than
observed SCSS at high alkalinity (Figure 5b). The updated oxide species model fares as well as the
original Fortin et al. (2015) oxide model at low alkalinity, overestimating SCSS by up to ~50%.

5.4 Developing a new model

We chose to develop a new SCSS model based on the MFM model of Liu et al. (2007), updated by
Fortin et al. (2015). Models relying on universal melt descriptors depend on the linearity of the
relationship between observed SCSS and the chosen compositional parameter. The MFM parameter
(equation [4]) was chosen by Liu et al. (2007) on this basis and correlates positively with NBO/T. In
natural log space, MFM shows a linear relationship against observed SCSS for the experiments in the
Fortin et al. (2015) compilation (Figure 6a). However, although the experiments from the present study
show a strong linear trend with MFM, the separation in their MFM values accounts for only 6% of the
overall range of MFM in the database of previously publish SCSS results, even though our experiments
vary from basaltic andesite to shoshonitic compositions. This relative lack of variation for such a large
compositional shift may be why the MFM model performance with changing alkalinity is not greatly
increased between the updated MFM model we present above and that presented by Fortin et al.

In an effort to find a compositional parameter that better reflects the variation in alkalinity of our
experiments, we have assessed optical basicity (Λ, lambda), a universal melt descriptor used in material
sciences to quantify the polymerization of slags. Optical basicity is essentially the weighted average of
the negative charge borne by the cations in a melt (Mills, 1993). As per Mills (1993), Λ is calculated as:

\[ \Lambda = \frac{\sum X_i m_i \Lambda_{th,i}}{\sum X_i m_i} \]  \hspace{1cm} [7]

where \( X_i \) is the mole fraction of oxide \( i \), \( n \) is the number of \( O \) associated with \( i \), \( \Lambda_{th,i} \) is the theoretical \( \Lambda \)
of \( i \) and the summation is over the different oxide species present in the melt. In the present work, we
used values for $\Lambda_{\text{th}}$ for the oxide species (Table A-3) from Mills (1993) and Duffy (1996). The mole
fractions of Fe$_2$O$_3$ and FeO were calculated using the Kress and Carmichael (1991) model which is
calibrated on a dataset comprising an extremely wide range of SiO$_2$ and alkalinity, from oganite to
basalt and rhyolite, encompassing our experiment compositions. Botcharnikov et al. (2005) found that
H$_2$O has a negligible effect on the Fe$^{2+}$/Fe$^{3+}$ ratio of a melt, thus small variations in the H$_2$O content of
our glasses will not significantly affect the mole fractions of Fe$_2$O$_3$ and FeO calculated using the Kress
and Carmichael (1991) model. Similar to MFM, $\Lambda$ also has a linear relationship with observed SCSS.
However, because $\Lambda$ accounts for the identity of the cation species via $\Lambda_{\text{th}}$ in addition to their relative
abundance, the high alkalinity glasses from our study have higher $\Lambda$ compared to low alkalinity glasses
(Table 3, Figure 6b). The range of $\Lambda$ in our experiments accounts for ~13% of the variation in the
overall database of previously published SCSS results.
We used $\Lambda$ in an empirical SCSS model with the same form as the MFM model of Fortin et al.
(2015):

$$\ln SCSS_{ppm} = a + \frac{b}{T} + c \frac{P}{T} + d \ln \Lambda + e X_{FeO} + f X_{H_2O}$$  \[8\]

where T is temperature in Kelvin, P is pressure in GPa, $\Lambda$ is optical basicity calculated as above
(equation [7]), $X_{FeO}$ is the mole fraction of FeO calculated by the method of Kress and Carmichael
(1991), and $X_{H_2O}$ is the mole fraction of H$_2$O. Fortin et al. (2015) used $\ln X_{FeO}$, however, we found
that using $X_{FeO}$ gave an improved fit (see Section 5.6 for the implications of this). We determined the
coefficients to equation [8] (referred to hereafter as the OB model) by multiple linear regression with
the R package ‘caret’ (R Core Team, 2017; Kuhn, 2017), using 10-fold cross-validation repeated 10
times, applied to the same training and verification datasets as used above to update the Fortin et al.
(2015) models to include our new data. The resulting OB model is:

$$\ln SCSS_{ppm} = 16.44 - \frac{6.681}{T} - 379.8 \frac{P}{T} + 10.61 \ln \Lambda + 3.533 X_{FeO} + 6.601 X_{H_2O}$$  \[9\]
The digits presented for the coefficients and their standard errors in Table 5 are not intended to imply that level of precision but are presented to avoid rounding errors in implementation.

The OB model provides a good fit to the training dataset with $R^2$, $\chi^2$ and mean squared residual values of 0.865, 2.13 and 0.07, respectively, and for the verification data set ($R^2 = 0.903$, $\chi^2 = 0.615$, mean squared residual = 0.06). The OB model predicts SCSS in the training and verification datasets to within 5 – 10% of the measured value in natural log space for all but one result at low SCSS (Figure 7a). This is equivalent to differences between predicted and observed SCSS of -50 – +125% over the full range of observed SCSS (Figure 7b), though in most cases the OB model overestimates SCSS by < 70% and underestimates it by < 35%.

The OB model reduces the spread of predicted SCSS for our experiments to within -10 – +60% of the observed SCSS, compared to -30 – +60% for the updated MFM model (Figure 8) and -25 – +60% for the Fortin et al. (2015) MFM model (Figure 7a). In detail, the Fortin et al. (2015) MFM model performs better at high alkalinity, predicting SCSS to within ±15%, compared to OB model predictions which deviate by -10 – +30% from the observed SCSS. In the lowest alkalinity glasses, the OB model fares better than either the Fortin et al. (2015) MFM model or our updated version of that model (equation [5]), with predictions ~ 5 – 20% closer to the actual SCSS than either of those models.

The difference between the observed and predicted SCSS is larger for the highest and lowest alkalinity experiments for the OB model but is within 10% of the observed SCSS at moderate alkalinity $(Na+K)/Al = 0.4$ to 0.6; Figure 8). The same approximately parabolic geometry of discrepancy between predicted and observed SCSS with increasing alkalinity is seen in the MFM and oxide species models as well (Figure 6, 8), except vertically offset. A possible reason for the discrepancy may be gleaned from considering the range of compositions for which SCSS experiments have been carried out. Figure 1 shows that the silica and alkalinity range of published SCSS experiments is quite small when considering experiments for which H$_2$O concentrations have been directly measured. At low alkalinity, the majority of experiments are anhydrous and basaltic compared to the hydrous, basaltic
andesite compositions studied here. Further, there is almost no previous work in the compositional
vicinity of our highest alkalinity experiments. Thus, our experiments at the extremes of alkalinity are
on the edge of the compositional space in which the models presented have been calibrated and it is to
be expected that model performance will be degraded at these extremes (Figures 6, 8). On the other
hand, our experiments at moderate to high alkalinity (i.e. (Na+K)/Al = 0.4 to 0.6) occupy a region of
compositional space where the database of experiments shows the greatest co-variation of alcalis and
SiO₂ (Figure 1). The OB model accordingly performs well at moderate alkalinity, predicting SCSS to
within 10% of the observed value (Figure 8).

Lastly, it is also possible that the approximately parabolic shape of the misfit between observations
and SCSS model predictions (Figures 5a, 8) is partly due to the form of the models used, thereby
indicating a fundamental shortcoming in the models. However, we cannot conclusively determine
whether sample bias in the datasets underlying the models or shortcomings of the model forms
themselves plays a greater role in producing the observed misfit between observed and predicted
SCSS with increasing alkalinity.

5.5 SCSS models and low FeO systems

Although the present work is focused on examining the effect of alkalinity on SCSS to update
empirical models, we briefly comment on the models discussed here when applied to systems with low
FeOᵣ (i.e. < 1 wt.%). Mavrogenes and O’Neill (2002) show that melt FeOᵣ is a dominant
compositional control on SCSS at > ~ 8 and < ~ 1 wt.% FeOᵣ. Wykes et al. (2015) showed that the
MFM model and, by extension its variants (Liu et al. 2007; Fortin et al. 2015) are fundamentally
unable to predict the increasing SCSS of low FeOᵣ silicate melts as these models have a positive
coefficient to the lnX₂O₅ term. We attempted to include the effect of low FeOᵣ on SCSS in the OB
model by including the SCSS experiments from O’Neill and Mavrogenes (2002) and Wykes et al.
(2015) in the training datasets and by using a variety of terms to account for the ascending and
descending limbs of the SCSS vs FeO\textsuperscript{tot} relationship. The fit of our and other MFM models to the
training and verification datasets were severely reduced (typical R\textsuperscript{2} values of ~0.5) likely due to the
very different compositions studied by O’Neill and Mavrogenes (2002) compared to the experiments
used here. Additionally, inclusion of the more than 200 experiments from O’Neill and Mavrogenes
(2002) skews the overall dataset to low pressure (100 kPa) and relatively high temperatures (1673 K),
thus biasing the models away from higher pressures and lower temperatures. Therefore, we have not
further considered the strong negative dependence of SCSS on FeO\textsuperscript{tot} in the present work, although we
recognize that the effect of low FeO on SCSS is undoubtedly important in granitic and rhyolitic
systems, for example.

6. Conclusions and future work

We have investigated the effect of alkali concentration on the SCSS of basaltic andesite to shoshonite
melts. Our results show an approximately two-fold increase in SCSS for melts with high alkalinity
(\~1500 ppm S at (Na+K)/Al \approx 0.6) compared to low alkalinity (\~700 ppm S at (Na+K)/Al \approx 0.15),
when other compositional parameters (i.e. SiO\textsubscript{2}, FeO\textsuperscript{tot}, H\textsubscript{2}O) are relatively unchanged. The effect of
Na\textsubscript{2}O on SCSS is five times greater than that of K\textsubscript{2}O in the investigated compositional range. An
apparent peak in SCSS with increasing alkalinity at a total alkali content of \~7.5 wt.% (i.e. (Na+K)/Al
\approx 0.6), if due to changes in the melt environment that disfavour the dissolution of S as S\textsuperscript{6+}, is testable
by more experiments and detailed examination of the regions where S bonds are observed in Raman
spectra (200 – 1200 cm\textsuperscript{-1} and \~2600 cm\textsuperscript{-1}; e.g. Klimm et al., 2012).

We used our new results to examine the performance of published empirical SCSS models. The
MFM model of Fortin et al. (2015) overestimate SCSS at low alkalinity by 40 – 70%, but performs
well with \~15% deviation from observed SCSS at high alkalinity. The Fortin et al. (2015) oxide species
model underestimates SCSS by \~40% at high alkalinity. Models trained on earlier datasets cannot fully
capture the variation in SCSS with alkalinity. Our new model, built on the work of Fortin et al. (2015),
employs theoretical optical basicity (OB) to account for the different identities of network modifiers
and network formers and not only their mole fractions. Compared with earlier models, the OB model
reduces the spread of SCSS predictions with changing alkalinity and also provides a slightly better fit
to the overall database of SCSS experiments for which H$_2$O concentration is directly measured.

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Figure captions

Figure 1: a) Total Alkali-Silica diagram (LeMaitre, 2002) and b) Potassium classification diagram (LeBas et al., 1986) showing the starting materials from the present study and the distribution of SCSS experiments from the literature that we used in this study (see text for details) in the context of arc lavas from around the world. Arc data from GEOROC (http://georoc.mpch-mainz.gwdg.de/georoc/; Sarbas and Nohl, 2008). Experimental data (see text for details) are from Haughton et al. (1974), Peach and Mathez (1993), Peach et al. (1994), Mavrogenes and O’Neill (1999), Baker et al. (2001), Holzheid and Grove (2002), Sattari et al. (2002), Jugo et al. (2005a), Liu et al. (2007), Brenan (2008), Moune et al. (2009), Righter et al. (2009), Beermann et al. (2011), Ding et al. (2014), Fortin et al. (2015) and Wykes et al. (2015).

Figure 2: Comparison of H₂O measured directly by Raman spectroscopy and indirectly by EPMA (by difference method). Experiment P468 shows low H₂O content most likely due to H₂O loss during Pt capsule welding. Error bars are 2σ.

Figure 3: Bivariate diagrams showing S concentration in sulfide saturated glasses plotted against the concentration of a) Al₂O₃; b) Na₂O; c) K₂O; d) molar Na + K / Al. Experiments that contained Pt wire are marked with a small black square (see text for details). The solid lines are regressed through the experiments using fully hydrated starting materials (equations near the top of each panel) whereas the dashed lines are through partially dehydrated starting materials (equations near the bottom of each panel). Error bars are 2σ and where they are not seen, the error bars are smaller than the symbols.

Figure 4: Variation of SCSS as a function of H₂O in experiments where the starting materials were run unmodified and after partial dehydration. Linear regression of the data are as follows (S in ppm, H₂O in wt.%): RD0K, S = 643.7 + 22.83·H₂O (R² = 0.14); RD4K, S = 517.9 + 250.1·H₂O (R² = 0.99); RD6K,
$S = 708.1 + 247.6 \cdot H_2O \ (R^2 = 0.96)$, Experiments P479 and P480 are not shown as there were no experiments performed using those starting materials after partial dehydration.

Figure 5: Percent difference between predicted and measured SCSS in our experiments plotted against molar (Na + K)/Al for a) MFM parameterized models (Liu et al., 2007; Fortin et al., 2015, Model A) and b) oxide species models (Li and Ripley, 2009; Fortin et al., 2015, Model B). Also shown are the results of the updated models using data from the present study. The light grey and dark grey regions are 25% and 10% error envelopes, respectively.

Figure 6: SCSS in experimental glasses from this and previous work (see text and caption of Figure 1 for references) plotted as a function of a) MFM and b) optical basicity calculated using the formula presented by Mills (1993) with the optical basicity values given by Mills (1993) and Duffy (1996). The arrow point in the direction of increasing alkalinity of the glasses from the present study.

Figure 7: a) Predicted SCSS plotted against measured SCSS using the OB model for the training and verification datasets. The solid line shows a 1:1 relationship (0% error) and the dashed and dotted lines are 5% and 10% error envelopes respectively. b) The percent difference between modelled and measured SCSS in training and verification datasets plotted against measured SCSS.

Figure 8: Percent difference between predicted and measured SCSS in our experiments plotted against molar (Na + K)/Al for the OB model from the present study. Also shown are the results of the updated MFM and oxide species models presented in this study. The light grey and dark grey regions are 25% and 10% error envelopes, respectively.
Figure A-1: Representative examples of the Raman spectra that we obtained to quantify H₂O using the method as described in the text. The spectra are corrected and baseline subtracted. Although some structure is visible in the low wavenumber regions corresponding to the silicate structure, we are unable to determine from this data the relative intensities of peaks known to be related to S bonds (i.e. sulfate at 990 cm⁻¹, sulfide at 372 and 2574 cm⁻¹; Klimm et al., 2012). We note the increase in intensity of a peak at 1080 cm⁻¹ with increasing alkalinity.

Figure A-2: Back-scattered electron images of glasses from experiments a) P470 (RD0K), and b) P474 (RD6K), showing the different sizes and generally circular shape of sulfide droplets typical of the run products from this study. The white scale bar in both images represents 100 μm.
This study

- partially dehydrated
- unmodified
- contains Pt wire

Previous studies

- Peach et al. (1994)
MFM based models

oxide based models

- updated model (this study)
- Fortin et al. (2015)
- Liu et al. (2007)
- Li and Ripley (2009)
+ partially dehydrated starting material

A

B

Na + K / Al

S_model - S_meas

S_meas
Table 1. Starting material compositions

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<th></th>
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<th>RD1K*</th>
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<th>RD6K</th>
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* RD1K is a 4:1 mixture (by weight) of RD0K and RD6K
** RD3K is a 1:1 mixture (by weight) of RD0K and RD6K
a example of natural basaltic andesite, Guam (Regan et al., 2008)
b example of natural shoshonite (Gomez-Tuena et al., 2011)
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Abbreviations: liq = liquid; sulf = sulfide droplet; px = pyroxene.
*starting material partially dehydrated prior to use
Table 3

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Values in parentheses are 2σ error
*starting material partially dehydrated prior to use
**measured by Raman
<sup>a</sup> calculated as per Kress and Carmichael (1991)
<sup>b</sup> calculated as per Mills (1993) and Duffy (1996); see text and Supplementary table
<sup>c</sup> Smithsonian microbeam standard NMNH 111240-52 recommended values; S con
Table 3
Composition of glasses determined by EPMA (wt.% except S, ppm)

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*3 for details

centration is the average of all reported analyses
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<th>Coefficient**</th>
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<td></td>
<td>X_{CaO}</td>
<td>-21.08 (10.85)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>X_{Na2O}</td>
<td>-23.51 (11.50)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>X_{H2O}</td>
<td>-26.69 (10.34)</td>
</tr>
</tbody>
</table>

| R^2_{training} | 0.791 | 0.807 | R^2_{training} | 0.904 |
| X^2_{training}  | 3.29  | 3.71  | X^2_{training} | 1.49  |
| R^2_{validation} | 0.855 |     | R^2_{validation} | 0.929 |
| X^2_{validation} | 0.879 |     | X^2_{validation} | 0.432 |

* this study  
** Fortin et al. (2015)

coefficients and standard error provided to greater-than-significant digits to avoid round
Table 4

<table>
<thead>
<tr>
<th>Coefficient**</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>34.784 (7.089)</td>
<td></td>
</tr>
<tr>
<td>-5772.3 (407.85)</td>
<td></td>
</tr>
<tr>
<td>-346.54 (37.39)</td>
<td></td>
</tr>
<tr>
<td>-20.393 (7.109)</td>
<td></td>
</tr>
<tr>
<td>-25.499 (7.068)</td>
<td></td>
</tr>
<tr>
<td>-18.344 (7.331)</td>
<td></td>
</tr>
<tr>
<td>-27.381 (6.683)</td>
<td></td>
</tr>
<tr>
<td>-17.275 (7.159)</td>
<td></td>
</tr>
<tr>
<td>-22.398 (7.003)</td>
<td></td>
</tr>
<tr>
<td>-20.378 (7.242)</td>
<td></td>
</tr>
<tr>
<td>-18.954 (7.445)</td>
<td></td>
</tr>
<tr>
<td>-32.194 (7.556)</td>
<td></td>
</tr>
<tr>
<td>0.918</td>
<td></td>
</tr>
<tr>
<td>1.46</td>
<td></td>
</tr>
</tbody>
</table>

I-off errors.
Table 5: OB model parameters

<table>
<thead>
<tr>
<th>Parameter (label)*</th>
<th>Coefficient</th>
<th>Std. Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept (a)</td>
<td>16.44</td>
<td>0.41</td>
</tr>
<tr>
<td>1/T (b)</td>
<td>-6081</td>
<td>446</td>
</tr>
<tr>
<td>P/T (c)</td>
<td>-379.8</td>
<td>45.8</td>
</tr>
<tr>
<td>ln[M] (d)</td>
<td>10.61</td>
<td>0.67</td>
</tr>
<tr>
<td>X_{FeO} (e)</td>
<td>3.533</td>
<td>0.563</td>
</tr>
<tr>
<td>X_{H2O} (f)</td>
<td>6.601</td>
<td>0.472</td>
</tr>
</tbody>
</table>

R^2_{training} = 0.865
|X^2_{training} = 2.13
R^2_{verification} = 0.903
|X^2_{verification} = 0.615

* labels refer to equation [8] in text